รายงานวิจัยฉบับสมบูรณ์

เรื่อง

การหาองค์ประกอบทางเคมีและการค้นหาสารออกฤทธิ์ทางชีวภาพจากต้นติ้วขน (*Cratoxylum formosum* ssp. *pruniflorum*) ต้นกำจาย (*Caesalpinia digyna*) และ ต้นโพทะเล (*Thespesia populnea*)

Chemical Constituents and Bioactive compounds from *Cratoxylumformosum* ssp. *pruniflorum*, *Caesalpinia digyna* and *Thespesia populnea*

สุชาดา จันทร์พรหมมา และคณะ

กันยายน 2553

สัญญาเลขที่ DBG 4880019

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1. รองศาสตราจารย์ ดร. สุชาดา จันทร์พรหมมา มหาวิทยาลัยสงขลานครินทร์
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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

ทุนวิจัยพื้นฐานแบบกำหนดทิศทางเคมีทางยา

กิตติกรรมประกาศ

คณะผู้วิจัยขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) ที่ได้สนับสนุนทุนวิจัย และขอขอบคุณมหาวิทยาลัยสงขลานครินทร์ ที่ได้ให้สนับสนุนทุนวิจัยสมทบจากเงินรายได้มหาวิทยาลัย ทำให้สามารถดำเนินงานวิจัยได้สำเร็จตามความมุ่งหมาย

คณะผู้วิจัยขอขอบคุณ Professor Dr. Hoong-Kun Fun, X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, Penang, Malaysia ที่ได้ให้ความช่วยเหลือในการเก็บข้อมูลการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยวและคำแนะนำต่าง ๆ

คณะผู้วิจัยขอขอบคุณ คุณณวงศ์ บุนนาค และ คุณสมพงศ์ บุญศรี ผู้ช่วยวิจัย และขอขอบคุณ คุณธีรศักดิ์ อนันตพงศ์ ภาควิชาเทคโนโลยีชีวภาพ คณะอุตสาหกรรมเกษตร มหาวิทยาลัยสงขลานครินทร์ ในการทดสอบฤทธิ์ทางชีวภาพ ขอขอบคุณผู้บริหาร และเจ้าหน้าที่ของ สกว. และ มหาวิทยาลัยสงขลานครินทร์ ทุกท่าน ที่มีส่วนช่วยในการสนับสนุน อำนวยความสะดวก และช่วยเหลือทำให้งานวิจัยดำเนินไปได้ด้วยดี

สุชาดา จันทร์พรหมมา และ คณะ

บทคัดย่อ

Project Code: DBG4880019

Project Title: การหาองค์ประกอบทางเคมีและการค้นหาสารออกฤทธิ์ทางชีวภาพจากต้นติ้วขน (*Cratoxylum formosum* ssp. *pruniflorum*) ต้นกำจาย (*Caesalpinia digyna*) และต้นโพทะเล (*Thespesia populnea*)

Investigators: Principle investigator: สุชาดา จันทร์พรหมมา

Co-investigators: ฉัตรชนก กะราลัย และ อัครวิทย์ กาญจณโอภาส

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Objectives:

1. เพื่อหาองค์ประกอบทางเคมีจากต้นติ้วขน ต้นกำจาย และต้นโพทะเล
2. เพื่อหาสารออกฤทธิ์ทางชีวภาพจากต้นติ้วขน ต้นกำจาย และต้นโพทะเล
3. เพื่อหาโครงสร้างผลึกของสารผลิตภัณฑ์ธรรมชาติบริสุทธิ์ที่สามารถแยกและตกผลึกจากพืชทั้งสามชนิดนี้

Methodology: สกัดแยก หาโครงสร้าง และทดสอบฤทธิ์ทางชีวภาพของสารที่แยกได้ คือ ฤทธิ์ต้านเชื้อแบคทีเรีย และฤทธิ์การยับยั้งการเจริญเติบโตของเซลล์มะเร็ง ตกผลึก และหาโครงสร้างผลึกของสารด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยว

Results: จากการสกัดและแยกองค์ประกอบทางเคมีจากส่วนสกัดหยาบ CH_2Cl_2 และ acetone จากรากและกิ่งต้นติ้วขน ต้นกำจาย และแก่นต้นโพทะเล ด้วยวิธีทางโครมาโทกราฟี สามารถแยกสารประกอบประเภท xanthones และ anthraquinones จากต้นติ้วขนได้ 37 สาร และทำการหาโครงสร้างโดยใช้ข้อมูลทางสเปกโทรสโกปี นอกจากนี้ได้ทำการแยกองค์ประกอบทางเคมีจากส่วนสกัดหยาบ dichloromethane จาก ต้นกำจาย สามารถแยกสารประกอบประเภท flavonoids ได้จำนวน 4 สาร และจากแก่นต้นโพทะเล สามารถแยกสารประกอบประเภท flavonoids ได้จำนวน 19 สาร และได้ทำการหาโครงสร้างด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยวของสารที่ตกผลึกได้ และทำการทดสอบการออกฤทธิ์ทางชีวภาพ คือ ฤทธิ์การยับยั้งเชื้อแบคทีเรียและฤทธิ์การยับยั้งการเจริญเติบโตของเซลล์มะเร็งของสารที่แยกได้ พบสารออกฤทธิ์ทางชีวภาพที่น่าสนใจหลายสาร

Discussion and Conclusion: จากการศึกษาองค์ประกอบทางเคมีและการทดสอบฤทธิ์ทางชีวภาพของสารที่แยกได้จากพืชดังกล่าวพบว่าได้สารชนิดใหม่หลายชนิดและสารที่แยกได้หลายตัวมีฤทธิ์ทางชีวภาพที่น่าสนใจและสารบางตัวมีฤทธิ์ยับยั้งแบบจำเพาะเจาะจงต่อเชื้อแบคทีเรีย

คำหลัก Natural Products, *Cratoxylum formosum* ssp. *pruniflorum*, *Caesalpinia digyna*, *Thespesia populnea*, crystal structure, antibacterial activity, Cytotoxicity และ Bioactivity

ABSTRACT

Project Code: DBG4880019

Project Title: Chemical Constituents and Bioactive compounds from *Cratoxylum formosum* ssp. *pruniflorum*, *Caesalpinia digyna* and *Thespesia populnea*

Investigators: Principle investigator: Suchada Chantrapromma

Co-investigators: Chatchanok Karalai, Akkharawit Kanjana-Opas

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Objectives: 1. To investigate chemical constituents from the roots and barks of *Cratoxylum formosum* ssp. *pruniflorum*; the twigs and stems of *Caesalpinia digyna* and the heartwood and wood of *Thespesia populnea.*

2. To search for bioactive compounds the roots and barks of *Cratoxylum formosum* ssp. *pruniflorum*; the twigs and stems of *Caesalpinia digyna* and the heartwood and wood of *Thespesia populnea*.

3. To study the crystal structures of the isolated compounds which can be crystallized.

Methodology: Extraction, isolation and characterization, and evaluation of antibacterial and cytotoxic activities of the isolated compounds. Crystallization and determination of the crystal structures by single crystal x-ray structure determination.

Results: The CH_2Cl_2 and acetone extracts of the roots and barks of *Cratoxylum formosum* ssp. *pruniflorum*; CH_2Cl_2 extract of the twigs and stems of *Caesalpinia digyna* and the CH_2Cl_2 extract of the heartwood and wood of *Thespesia populnea* were subjected to column chromatography. Thirty seven xanthones and anthraquinones from *Cratoxylum formosum* ssp. *pruniflorum*; four flavonoids from *Caesalpinia digyna* and nineteen flavonoids from *Thespesia populnea* were isolated. Their structures were evaluated by spectroscopic methods. In addition, the structures of the compounds that can be crystallized out were also confirmed by single crystal X-ray diffraction. Antibacterial and cytotoxic activities of the isolates were evaluated.

Discussion and Conclusion: From the studies of chemical constituents and their biological activities from these three plants, several new compounds have been isolated. Several compounds possess interesting biological activities and some of them show specific antibacterial activity.

Keywords: Natural Products, *Cratoxylum formosum* ssp. *pruniflorum*, *Caesalpinia digyna*, *Thespesia populnea*, crystal structure, antibacterial activity, Cytotoxicity and Bioactivity

สารบัญ

บทนำ

จากรายงานการวิจัยของพืชสกุล *Cratoxylum* และ *Caesalpinia* พบว่าพืชในสกุลทั้งสองนี้เป็นพืชที่น่าสนใจเนื่องจากมีรายงานการออกฤทธิ์ทางชีวภาพหลายชนิด เช่น antibacterial antitumor antifungal และ antioxidant เป็นต้น ซึ่งจากข้อมูลการศึกษาองค์ประกอบทางเคมีและการออกฤทธิ์ทางชีวภาพของพืชทั้งสองสกุลนี้ พบว่าพืชในวงศ์ Leguminosae อนุวงศ์ Caesalpinioideae สกุล *Caesalpinia* มีสารออกฤทธิ์ทางชีวภาพที่น่าสนใจมากมาย เช่น anticancer, antitumor, antibacterial, antifungal, antioxidant และ antitubercular ซึ่งต้นกำจาย (*Caesalpinia digyna*) เป็นพืชในวงศ์ Leguminosae อนุวงศ์ Caesalpinioideae สกุล *Caesalpinia* เป็นพืชที่น่าสนใจและคาดว่าน่าจะมีสารออกฤทธิ์ทางชีวภาพที่น่าสนใจเช่นพืชในสกุลเดียวกันและจากฐานข้อมูลมีการรายงานการวิจัยเกี่ยวกับต้นกำจายน้อยมาก จึงมีความน่าสนใจที่ในการหาองค์ประกอบทางเคมีจากต้นไม้ชนิดนี้และเพื่อค้นหาสารออกฤทธิ์ทางชีวภาพ

ส่วนพืชในวงศ์ Guttiferae สกุล *Cratoxylum* มีรายงานสารออกฤทธิ์ทางชีวภาพ ได้แก่ antibacterial (Munekazu et al., 1996) cytotoxicity activity (Seo et al., 2002; Pattanaprateeb et al., 2005) immunomodulatory activity (Pinto et al., 1997) และต้นติ้วขน (*Cratoxylum formosum* subsp. *pruniflorum*) เป็นต้นไม้ชนิดหนึ่งซึ่งอยู่ในวงศ์ Guttiferae สกุล *Cratoxylum* ถูกใช้เป็นยาพื้นบ้านในการรักษาโรค เช่น แก้โรคท้องร่วง ขับลม แก้ไข้ ยาบำรุงกำลัง เป็นต้น มีรายงานการวิจัยเกี่ยวกับองค์ประกอบทางเคมีอยู่บ้างแต่มีการรายงานการทดสอบฤทธิ์ทางชีวภาพน้อยมาก จึงคาดว่าน่าจะพบองค์ประกอบทางเคมีใหม่ ๆ อีก พร้อมพบสารออกฤทธิ์ทางชีวภาพที่น่าสนใจจากพืชทั้งสองชนิดนี้ หรือเพื่อเป็นสารตั้งต้นในการพัฒนาเพื่อเป็นสารที่ออกฤทธิ์อีกต่อไป

นอกจากพืชสองชนิดนี้แล้วได้ทำการวิจัยเพิ่มเติมในส่วนของต้นโพทะเล (*Thespesia populnea*) อีกด้วย

1. ต้นติ้วขน

ชื่อวิทยาศาสตร์ *Cratoxylum formosum* ssp. *pruniflorum*
ชื่อวงศ์ GUTTIFERAE
ชื่อพื้นเมือง กุ่ยฉ่องเช้า (กะเหรี่ยงลำปาง) กวยโชง (กะเหรี่ยงกาญจนบุรี) ตาว (สตูล) ติ้วแดง ติ้วยาง ติ้วเลือด (พายัพ) ติ้วส้ม (นครราชสีมา) ติ้วเหลือง แต้ว **ติ้วขน** (ไทย) เตา (เลย) เน็คเคร่แย (ละว้าเชียงใหม่) ราเง้ง (เขมรสุรินทร์) มูโต๊ะ (นราธิวาส มาเลเซีย) ขี้ติ้ว ตาว (สตูล)

ลักษณะทางพฤกษศาสตร์

ต้น เป็นไม้ต้นขนาดเล็กถึงขนาดใหญ่ ผลัดใบ สูง 8 - 15 ม. เรือนยอด เป็นพุ่มกลม โปร่ง กิ่งอ่อนมีขนนุ่มทั่วไป กิ่งเล็กตามลำต้นและกิ่งใหญ่มักลายสภาพเป็นหนามแข็ง ๆ เปลือกนอก สีน้ำตาลปนดำ แตกเป็นสะเก็ดเล็ก ๆ ห้อยย้อยลง เปลือกใน สีน้ำตาลแกมเหลือง และมีน้ำยางสีเหลืองปนแดงซึมออกมา เมื่อตัดใหม่ ๆ กระพี้ขาวแยกจากแก่นเห็นได้ชัด

ใบ ใบเดี่ยว ติดตรงข้ามกันเป็นคู่ ๆ ทรงใบรูปรแกมรูปไข่กลับและรูปขอบขนาน ขนาด 2 - 5 X 3 - 13 ซม. โคนสอบเรียว ส่วนที่ค่อนไปทางปลายใบโตออก ปลายสุดสอบเข้า เนื้อบางมีต่อมใส ๆ กระจายเต็มไปหมด หลังใบมีขนสาก ท้องใบมีขนนุ่มหนาแน่น ใบอ่อนออกสีชมพูเรื่อ ๆ ส่วนใบแก่ก่อนผลัดใบจะมีสีแดงหรือแดงอิฐ ขอบใบเรียบ ก้านใบยาวไม่เกิน 1 ซม. เส้นแขนงใบ 7 - 13 คู่ เส้นโค้งและปลายเส้นจะโค้งจรดกับเส้นถัดไปก่อนถึงขอบใบ

ดอก ออกเป็นกลุ่ม ก้านช่อสั้นออกตามง่ามใบ ดอกสีขาวหรือชมพูอ่อน ๆ กลิ่นหอมอ่อน ๆ กลีบดอกยาวเป็นสองเท่าของกลีบรองกลีบดอก กลีบรองฐานดอกและกลีบดอกมี 5 กลีบ แต่ละกลีบเป็นอิสระแก่กัน กลีบรองกลีบดอกมีขนประปราย ส่วนกลีบดอกเกลี้ยง เกสรผู้จำนวนมากสีเหลืองอ่อน แบ่งออกเป็นสามกลุ่ม รังไข่ รูปรี ๆ เกลี้ยง ภายในแบ่งเป็น 3 ช่อง แต่ละช่องมีไข่อ่อนมาก หลอดรังไข่มี 3 หลอด

ผล ผลแห้ง รูปรี ๆ ยาวประมาณ 2 ซม. หรือย่อมกว่าเล็กน้อย แข็ง มีคราบสีนวล ติดตามผิว แก่จัดแตกอ้าออกตามรอยประสานเป็น 3 แฉก เผยให้เห็นเมล็ดรูปขอบขนานเล็ก ๆ ที่มีปีกโค้ง ๆ เรียงอัดอยู่แน่น กลีบขั้วจุก ผลจะหุ้มติดผลประมาณ 1/4 ของความยาวผล แหล่งที่พบ ป่าเต็งรัง

ระยะเวลาในการออกดอกและเป็นผล ออกดอกระหว่างเดือน มกราคม-เมษายน และเป็นผลระหว่าง เดือนกุมภาพันธ์-พฤษภาคม ก่อนออกดอกจะทิ้งใบหมด ดอกจะเริ่มออกพร้อมกับการผลิใบใหม่ จึงมักมีทั้งดอกและผลติดอยู่ในเวลาเดียวกัน

ด้านสมุนไพร ใบอ่อนและยอดอ่อนรับประทานสดช่วยระบายท้อง รากและใบใช้ต้มกินแก้ปวดท้อง เปลือกและใบตำผสมกับน้ำมันมะพร้าวทาแก้โรคผิวหนัง น้ำยางจากลำต้นใช้รักษาบาดแผลและทาแก้ฝ่าเท้าแตก

ด้านเป็นพืชอาหาร ยอดอ่อน ใบอ่อนและดอก ใช้รับประทานเป็นผัก กับอาหารประเภทส้มตำ ลาบ น้ำตก และอาหารประเภทยำต่าง ๆ หรือใส่ต้มยำต่าง ๆ เพื่อปรุงให้มีรสเปรี้ยวแทนมะนาว แต่นิยมรับประทานน้อยกว่าติ้วขาว เพาะติ้วขนมีรสชาติขมหรือฝาดกว่าติ้วขาว

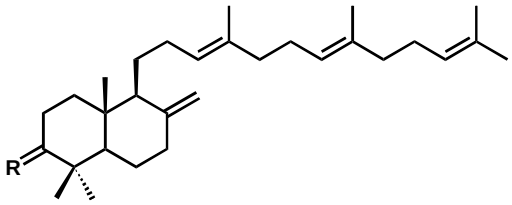
การสืบค้นและทบทวนวรรณกรรม

พืชในสกุล *Cratoxylum* จัดอยู่ในวงศ์ Guttiferae มีรายงานสารออกฤทธิ์ทางชีวภาพ ได้แก่ antibacterial (Munekazu et al., 1996 [**1**]) cytotoxicity activity (Seo et al., 2002; [**2**] Pattanaprateeb et al., 2005 [**3**]) immunomodulatory activity (Pinto et al., 1997 [**4**]) และต้นติ้ว

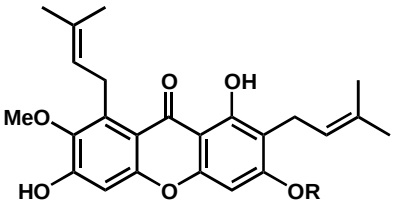
ขน (*Cratoxylum formosum* ssp. *pruniflorum*) เป็นต้นไม้ชนิดหนึ่งซึ่งอยู่ในวงศ์ Guttiferae สกุล *Cratoxylum* ถูกใช้เป็นยาพื้นบ้านในการรักษาโรค เช่น แก้โรคท้องร่วง ขับลม แก้ไข้ ยาบำรุงกำลัง เป็นต้น มีรายงานการวิจัยเกี่ยวกับองค์ประกอบทางเคมีอยู่บ้างแต่มีการรายงานการทดสอบฤทธิ์ทางชีวภาพน้อยมาก กลุ่มผู้วิจัยจึงคาดว่าน่าจะพบองค์ประกอบทางเคมีใหม่ ๆ อีก พร้อมพบสารออกฤทธิ์ทางชีวภาพที่น่าสนใจจากพืชทั้งสองชนิดนี้ หรือเพื่อเป็นสารตั้งต้นในการพัฒนาเพื่อเป็นสารที่ออกฤทธิ์อีกต่อไป และขณะนี้กลุ่มผู้วิจัยได้ทำการวิจัยเบื้องต้น และสามารถแยกสารบริสุทธิ์และทดสอบฤทธิ์ทางชีวภาพของส่วนสกัดหยาบและสารบริสุทธิ์ของพืชทั้งสองชนิดนี้พบว่าสารบางตัวที่มีฤทธิ์ที่น่าสนใจ

จากการสำรวจเอกสารการวิจัยของต้นติ้วขน (*Cratoxylum formosum* ssp. *pruniflorum*) มีรายงานการวิจัยดังนี้

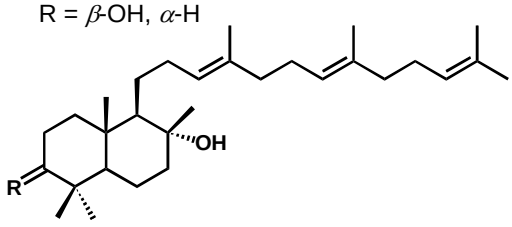
ในปี 1993 Bennett [**5**] และคณะ ได้ทำการศึกษาในส่วนเปลือกของ *C. cochinchinense* สามารถแยกสารในกลุ่มของ bicyclic triterpenoids และ xanthones ได้ดังนี้



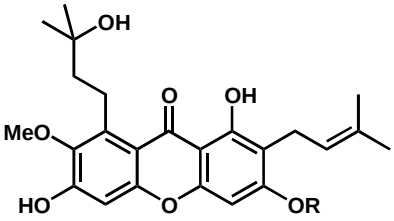
R = H_2
R = β-OH, α-H



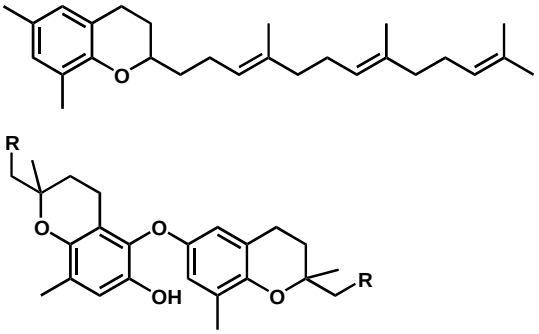
R = H
R = Me



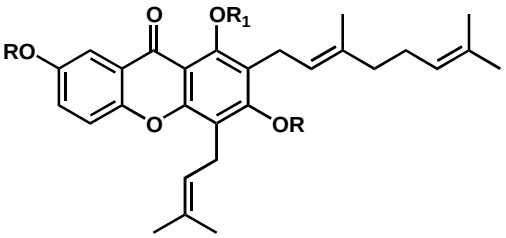
R = O
R = β-OH, α-H



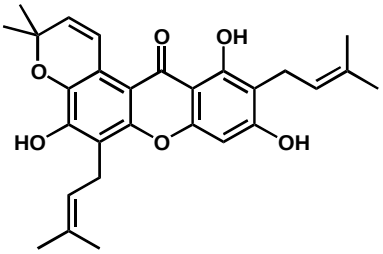
R = H
R = Me

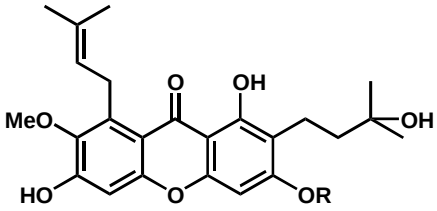


R = Farmesyl

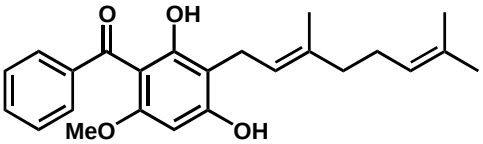


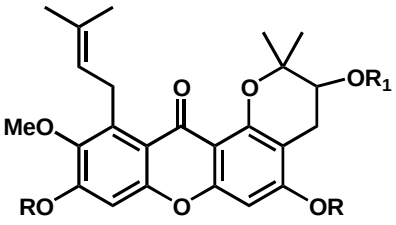
R = H, Me, Me
R_1 = H, H, Me



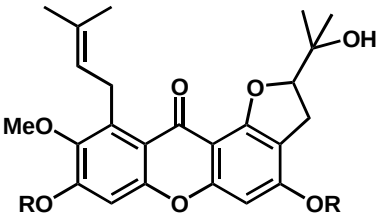


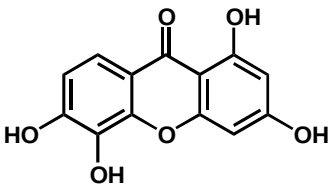
R = H
R = Me

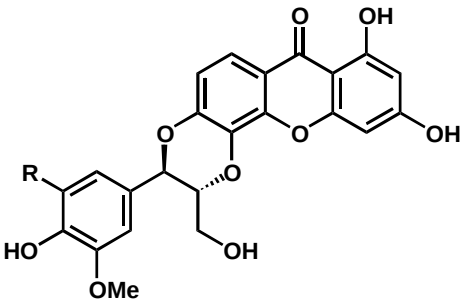




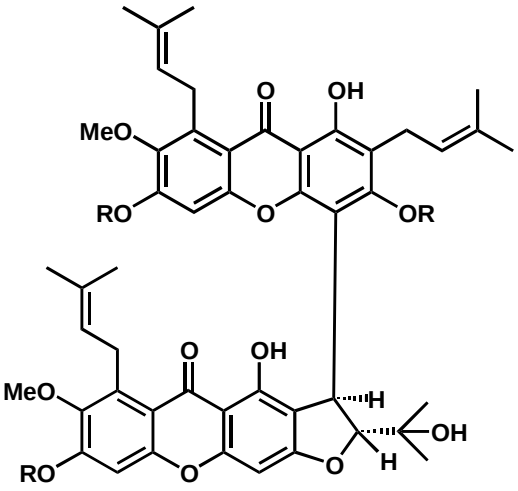
R = H, Me, Me
R_1 = H, H, Ac





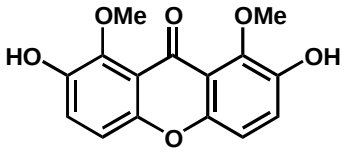


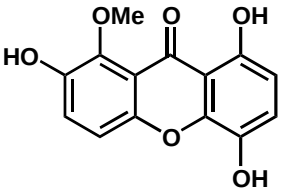
ในปี 1995 Sia [**6**] และคณะ ได้ทำการศึกษาในส่วนเปลือกของ *C. cochinchinense* สามารถแยกสารในกลุ่มของ xanthones และ bis-xanthones ได้ดังนี้

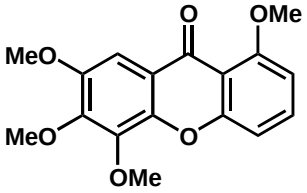


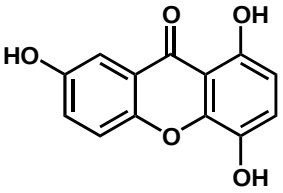
R = Me
R = H

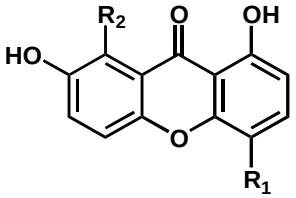
ในปี 1996 Linuma [**7**] และคณะ ได้ทำการศึกษาในส่วนเปลือกของ *C. formosum* สามารถแยกสารในกลุ่มของ xanthones และ flavonoids ได้ดังนี้



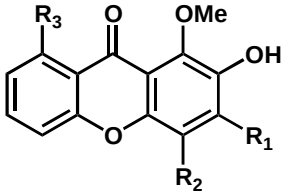




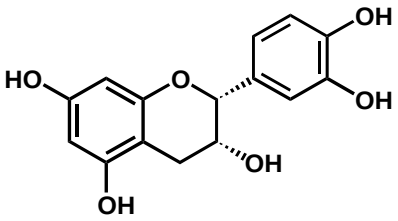


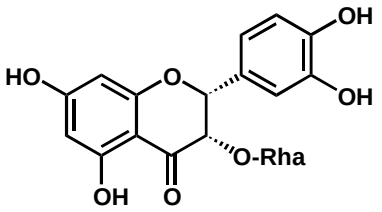


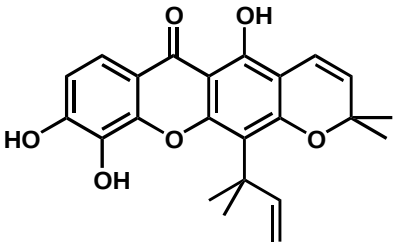
R_1 = OMe, H, H
R_2 = H, H, OMe

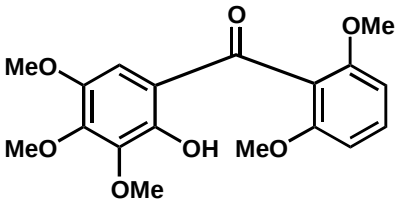


R_1 = OMe, OH, OMe
R_2 = OMe, OH, OMe
R_3 = OMe, H, H

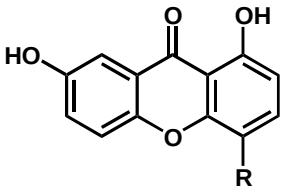




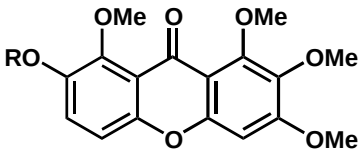




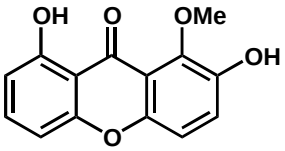
ในปี 1998 Kijjoa [**8**] และคณะ ได้ทำการศึกษาในส่วนเนื้อไม้ของ *C. maingayi* สามารถแยกสารในกลุ่มของ xanthones ได้ดังนี้



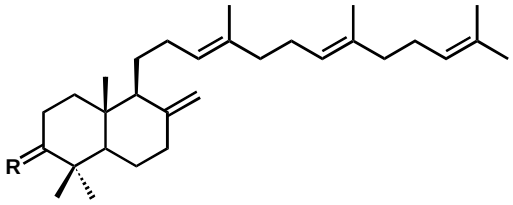
R = H
R = OMe



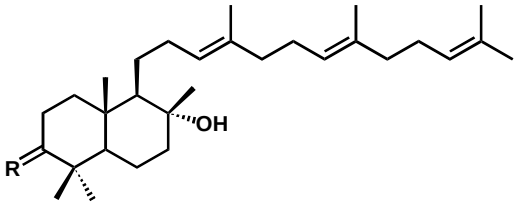
R = H
R = Ac



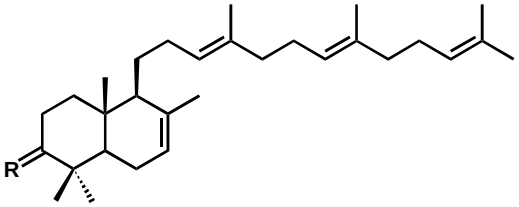
ในปี 1998 Nguyen [**9**] และคณะ ได้ทำการศึกษาในส่วนเนื้อไม้ของ *C. cochinchinense* สามารถแยกสารในกลุ่มของ bicyclic triterpenoids, xanthones และ anthraquinone ได้ดังนี้



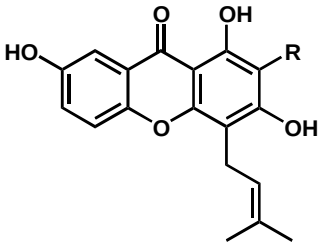
R = α–H, β–OH
R = H_2



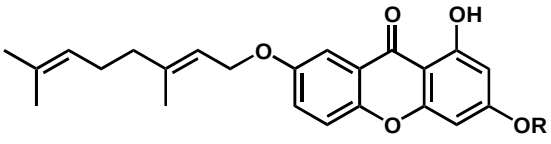
R = H_2
R = O
R = α-H, β-H



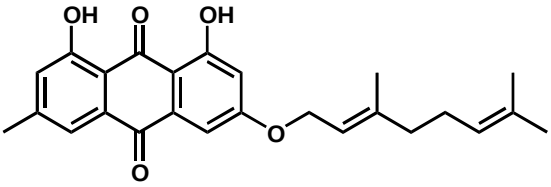
R = α–H, β–H
R = H_2
R = α–H, β–H
R = O



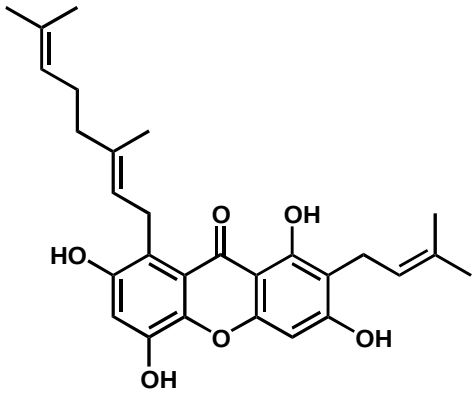
R = geranyl
R = prenyl

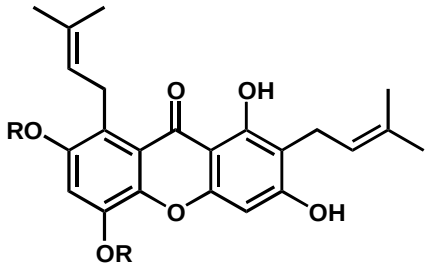


R = H
R = Me

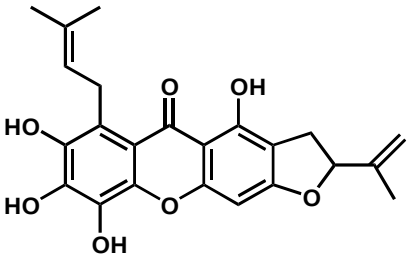
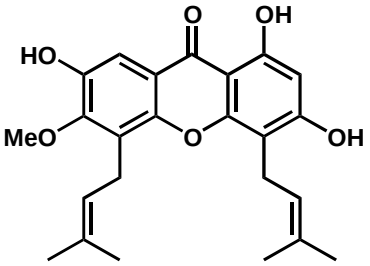
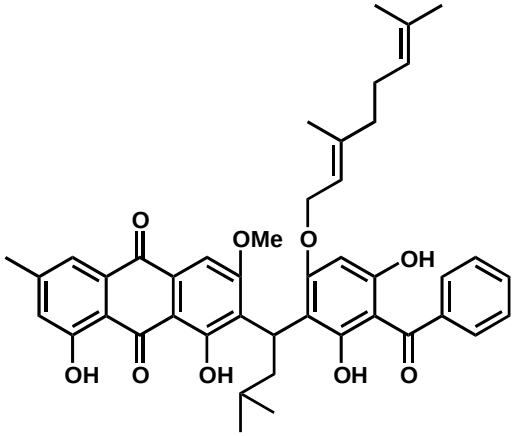
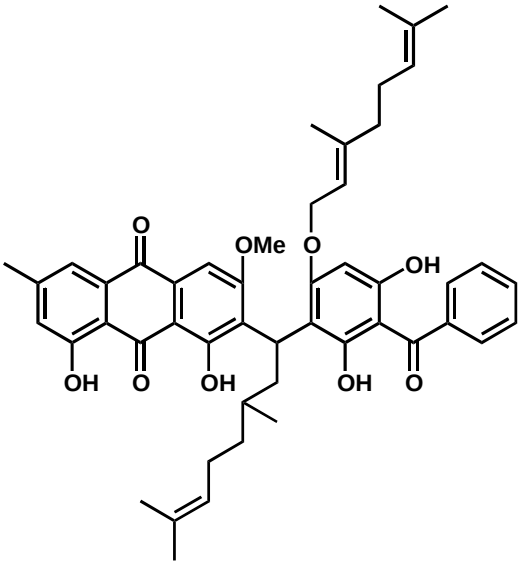
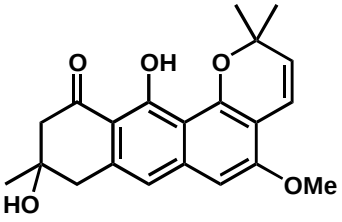
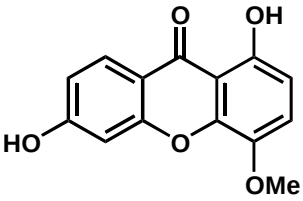


ในปี 2002 Seo [**2**] และคณะ ได้ทำการศึกษาในส่วนเนื้อไม้ของ *C. sumatranum* สามารถแยกสารในกลุ่มของ anthraquinobenzophenones และ xanthones ได้ดังนี้

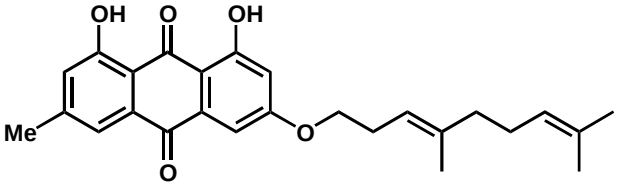
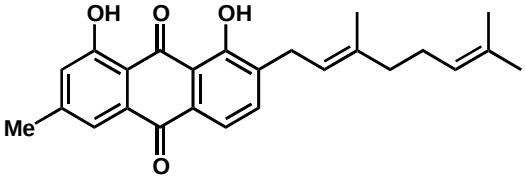
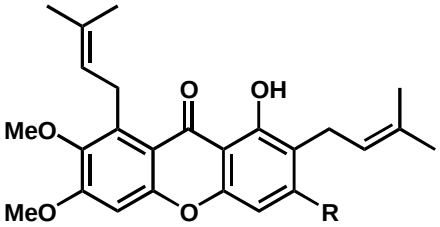
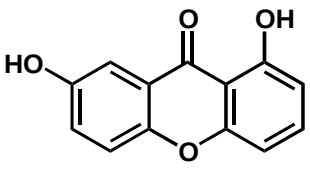




R = H
R = Me

ในปี 2005 Pattanaprateeb [**3**] และคณะ ได้ทำการศึกษาในส่วนเปลือกของ *C. aborecens* สามารถแยกสารในกลุ่มของ anthraquinones และ xanthones ได้ดังนี้

R = OH
R = OMe

แต่อย่างไรก็ดีมีการรายงานการศึกษาฤทธิ์ทางชีวภาพของสารบริสุทธิ์ที่แยกได้น้อยมาก

2. ต้นกำจาย

ชื่อวิทยาศาสตร์ *Caesalpinia digyna*

ชื่อวงศ์ LEGUMINOSAE-CAESALPINIOIDEAE

ชื่อพื้นเมือง : กำจาย กระจาย ขี้คาก (แพร่), ขี้แรด (ภาคกลาง), งาย (ปัตตานี), ตาฉู่แม สื่อกีพอ (กะเหรี่ยง-แม่ฮ่องสอน), มะหนามจาย มะนามจาย (ตาก), มะเบ่น(ไทยใหญ่-ภาคเหนือ), หนามแดง (ตราด), หนามหัน (จันทบุรี), ฮาย ฮายปูน (ภาคใต้)

ลักษณะทางพฤกษศาสตร์

ไม้พุ่มเลื้อย ลำต้นและก้านใบมีหนามแหลมแข็งโค้งลงคล้ายหนามกุหลาบ

ใบ ประกอบแบบขนนกสองชั้น เรียงสลับ หูใบเรียวแคบ ร่วงง่าย ใบย่อย 8-12 คู่ เรียงตรงข้ามกัน

ช่อดอก แบบช่อกระจะ ออกตามง่ามใบและปลายกิ่ง กลีบเลี้ยง 5 กลีบ ขนาดไม่เท่ากัน โคนติดกัน เป็นรูปถ้วยตื้นๆ กลีบดอก 5 กลีบ สีเหลือง ขนาดไม่เท่ากัน เกสรเพศผู้ 10 อัน

ฝัก ไม่แตก รูปขอบขนาน ตรงกลางป่องเล็กน้อย มี 2-3 เมล็ด

เมล็ด สีน้ำตาลคล้ำค่อนข้างกลม

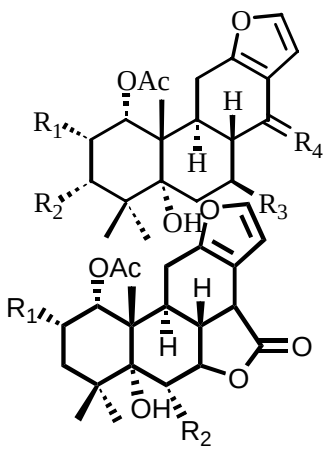
ด้านสมุนไพร ชำระล้างบาดแผล ห้ามโลหิต สมานแผล ปรุงเป็นยากินแก้ท้องร่วง รากใช้ปรุงเป็นยาแก้ไข้

ด้านการใช้ประโยชน์ ฝักให้น้ำฝาดใช้ย้อมผ้า หนัง แห อวน

การสืบค้นและทบทวนวรรณกรรม

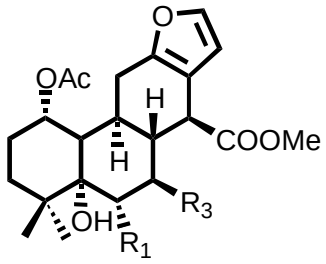
สำหรับการสำรวจเอกสารการวิจัยที่เกี่ยวข้องกับองค์ประกอบทางเคมีและการออกฤทธิ์ไม่ปรากฏการรายงานของต้นกำจาย (*Caesalpinia digyna*) แต่มีรายงานสารที่พบใน Caesalpinia Genus ส่วนใหญ่เป็นสารประกอบพวก cassane และ norcassane diterpenes จากการสำรวจเอกสารพืชใน genus นี้ มีการรายงานสารที่พบและการออกฤทธิ์ดังนี้

ปี 2005 Linn [**1**] และคณะ ได้รายงานสารที่แยกได้จากต้น *Caesalpinia crista* (เทพี) และรายงานการออกฤทธิ์ Antimalarial activity โดย cassane- และ norcassane-type diterpenes ที่พบคือ

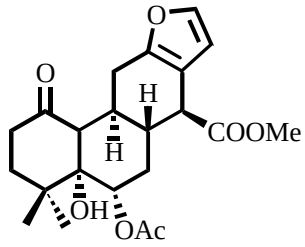


	R1	R2	R3	R4
1	H	OAc	H	CH2
2	OAc	OAc	H	O
3	H	H	OH	O
4	OAc	H	H	O
5	H	OAc	H	O
6	OAc	OAc	H	CH2

	R_1	R_2	
7	H	OAc	(0.80)
8	H	H	(0.80)



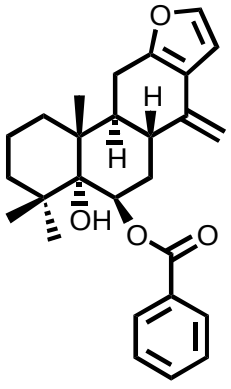
	R_1	R_2	
9	OAc	H	(6.50)
10	H	OAc	(0.60)



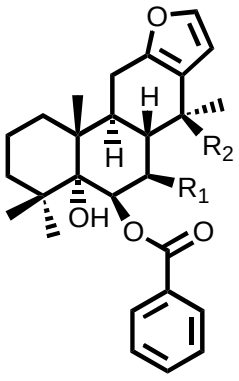
12

Linn, *et al*., *J. Nat. Prod*. **2005**, 68, 706-710. [**1**]

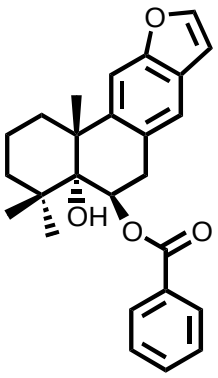
ปี 2002 Ragasa [**2**] และคณะ ได้รายงานสารที่แยกได้จากต้น *Caesalpinia pulcherrima* (หางนกยูงไทย) และรายงานการออกฤทธิ์ต้านเชื้อแบคทีเรีย Antimicrobial activity (*S. aureus*, *E. coli*, *P. aeruginosa* และ *B. subtilis*) และต้านเชื้อฟังกัล (*C. albicans* และ *T. mentagrophytes*) สารที่พบคือ



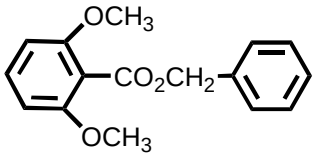
1



2 : R_1 = H, R_2 = OH
3 : R_1 = OH, R_2 = H



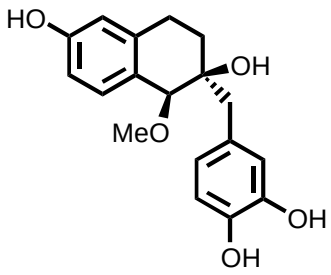
4



5

Ragasa, *et al*., 2002, *J. Nat. Prod*. **2002**, 65, 1107-1110. [**2**]

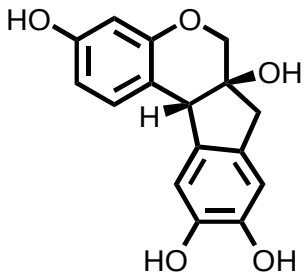
ปี 2003 Reddy [**3**] และคณะ ได้รายงานสารที่แยกได้จากต้น *Caesalpinia sappan* (ฝาง) และรายงานการออกฤทธิ์ต้านเชื้อรา *Beauveria bassiana* ของสารประกอบ 4-*O*-methylsappanol



4-*O*-methylsappanol

Reddy, *et al*., Fitoterapia **2003**, 74, 600-602. [**3**]

ปี 2004 Hong-xi [**4**] และคณะ ได้รายงานสารที่แยกได้จากต้น *Caesalpinia sappan* (ฝาง) และรายงานการออกฤทธิ์ต้านเชื้อแบคทีเรีย ของสารประกอบ brazilin



brasilin

Hong-Xi, *et al*., Phytotherapy Research **2004**, 18(8), 647-651. [**4**]

ปี 1977 Hiroshi [**5**] และคณะ ได้รายงานสารที่แยกได้จากต้น *Caesalpinia sappan* (ฝาง) และรายงานการออกฤทธิ์ต้านการอักเสบ Anti-inflammatory.

3. ต้นโพทะเล

ชื่อวิทยาศาสตร์ ***Thespesia populneoides***
ชื่อวงศ์ **Malvaceae**
ชื่อพื้นเมือง โพทะเล (กลาง) ปอกะหมัดไพร (ราชบุรี), ปอมัดไซ (เพชรบุรี), บากู (ปัตตานี, มลายู)

ลักษณะทางพฤกษศาสตร์

ไม้พุ่มเลื้อย จัดอยู่ใน เป็นไม้ยืนต้น ขนาดเล็กสูง 8-12 เมตร ลำต้นโค้ง แตกกิ่งในระดับต่ำ เรือนยอดแผ่กว้าง ค่อนข้างหนาทึบ เปลือกเรียบสีเทาอ่อนหรือขรุขระมี รอยแตกตามยาวเป็นร่องลึก

ใบ เดี่ยว เรียงสลับ รูปคล้ายหัวใจ โคนใบเว้าตื้น ความกว้างและความยาวของใบเท่า ๆ กัน

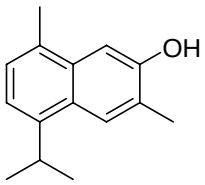
ดอก ออกตามง่ามใบเป็นดอกเดี่ยวหรือเป็นคู่ ก้านดอกยาวประมาณ 5-12 ซม.โนเอียงหรือห้อยลง ไม่มีใบประดับ วงกลีบเลี้ยงรูปถ้วยไม่มีแฉก คล้ายแผ่นหนังไม่หลุดร่วง กลีบดอกสีเหลืองรูปไข่ โคนกลีบติดกันรูประฆัง มีจุดสีแดงเข้มอมน้ำตาลแต้มที่โคนกลีบดอกด้านใน ดอกบานเต็มที่ภายในวันเดียว แล้วจะเปลี่ยนสีเป็นชมพูแกมม่วงอ่อน เหี่ยวบนต้น ก่อนร่วงหล่นในวันถัดมา หลอดเกสรตัวผู้สีเหลืองจาง ๆ มีอับเรณูติดอยู่ตลอดความยาวของหลอด ออกดอกประมาณเดือนกันยายน-ตุลาคม

ผล เป็นผลค่อนข้างกลมเปลือกแข็ง มีวงกลีบเลี้ยงรูปคล้ายจานอยู่ที่ขั้วผล ผลแก่เต็มที่มีเปลือกแยกออก ได้เป็น 3 ชั้น เปลือกชั้นนอกเรียบ เปลือกชั้นกลางหนา กว่าเปลือกชั้นในแข็ง โดยเปลือกชั้นนอกจะแตกออกเป็น 5 แฉก ประมาณครึ่งผลทางด้านปลายผล เมล็ดมีขนสั้นสีทองปกคลุม พบมากในที่ดอนหรือชายฝั่งทะเลและริมแม่น้ำที่ดิน เป็นดินร่วนปนทราย

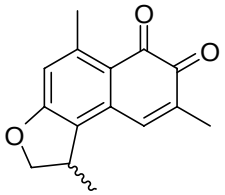
สรรพคุณ ใบใช้ทำผงยาใส่แผลเรื้อรัง และใช้เป็นยาระบายอ่อน ดอก ใช้ต้มกับน้ำนมหยอดหูรักษาอาการเจ็บหู เปลือก เป็นยาทำให้อาเจียน ส่วนเมือกที่ได้จากการนำเปลือกสดมาแช่น้ำ ใช้รักษาโรคที่เกี่ยวกับทางเดินอาหาร ราก ใช้รักษาอาการไข้ เป็นยาระบายและขับปัสสาวะ

การสืบค้นและทบทวนวรรณกรรม

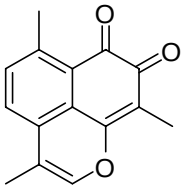
จากการตรวจเอกสารจากฐานข้อมูล SciFinder Scholar พบว่า ยังไม่มีรายงานการวิจัยที่ศึกษาด้านองค์ประกอบทางเคมีจากต้นโพทะเลได้มีการศึกษาและรายงานไปแล้วนั้นพบว่าองค์ประกอบหลักที่แยกได้คือสารกลุ่ม cadinane sesquiterpene [**1**, **2**, **3**] ดังแสดง



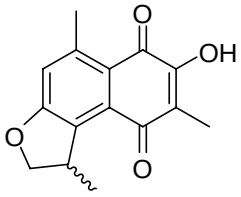
7-Hydroxycadalene



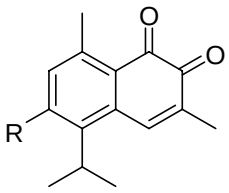
Mansonone D



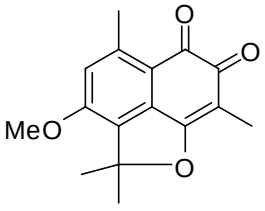
Mansonone F



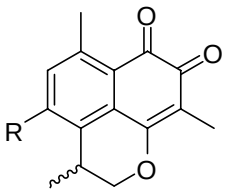
Thespesone



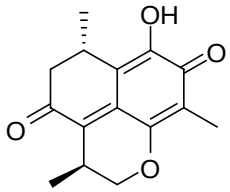
Mansonone C : R = H
Mansonone G : R = OH



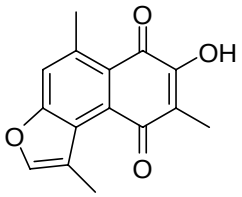
Dehydrooxoperizinone-6-methyl ether



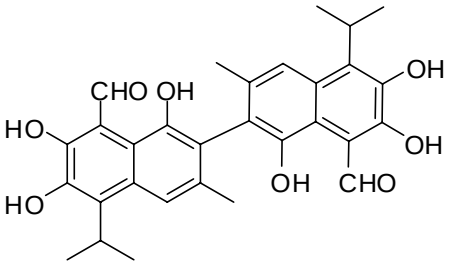
Mansonone E : R = H
Mansonone H : R = OH
Mansonone M : R = OMe



7-Hydroxy-2,3,5,6-tetrahydro-3,6,9-trimethyl-naphtho[1,8-*b,c*] pyran-4,8-dione



Thespesenone



Gossypol

ผลการวิจัยและอภิปรายผล

1. การสกัดและแยกสารจากต้นติ้วขน

การทดลอง

1.1. General experimental procedures

Melting points were determined on the Fisher-John melting point apparatus. Optical rotations were measured on a JASCO P-1020 digital polarimeter. UV and IR spectra were recorded on SPECORD S 100 (Analytikjena) and Perkin-Elmer FTS FT-IR spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz Varian UNITY INOVA and/or 300 MHz Bruker FTNMR Ultra Shield^{TM} spectrometers in $CDCl_3$ or CD_3OD with TMS as the internal standard. Chemical shifts are reported in δ (ppm) and coupling constants (*J*) are expressed in hertz. EI and HREI mass spectra were measured on a Kratos MS 25 RFA spectrometer. Quick column chromatography (QCC) and column chromatography (CC) were carried out on silica gel 60 F_{254} (Merck) and silica gel 100 (Merck), respectively.

1.2. Plant material

Barks and roots of *C. formosum* ssp. *pruniflorum* were collected in May 2004 from Nong Khai Province, northeastern part of Thailand. Identification was made by Prof. Puangpen Sirirugsa, Department of Biology, Faculty of Science, Prince of Songkla University and a specimen (No. 0012677) was deposited at Prince of Songkla University Herbarium.

1.3. Extraction and Isolation

1.3.1. Extraction and Isolation of the crude CH_2Cl_2 of the roots of *C. formosum* ssp. *pruniflorum*

Air-dried roots (5.30 kg) were extracted with CH_2Cl_2 (2 × 20 L, for 5 days) at room temperature. The crude CH_2Cl_2 extracts were evaporated under reduced pressure to afford a brownish crude (30.04 g) extract. The crude extract was subjected to QCC on silica gel using hexane as the first eluent and then increasing polarity with EtOAc and acetone, respectively, to give 8 fractions (FR1-FR8). Fraction FR2 was separated

by CC eluting with CH_2Cl_2—hexane (4:1, v/v) to afford 4 subfractions (FR2A-FR2D). Subfraction FR2A was further purified by CC with EtOAc—hexane

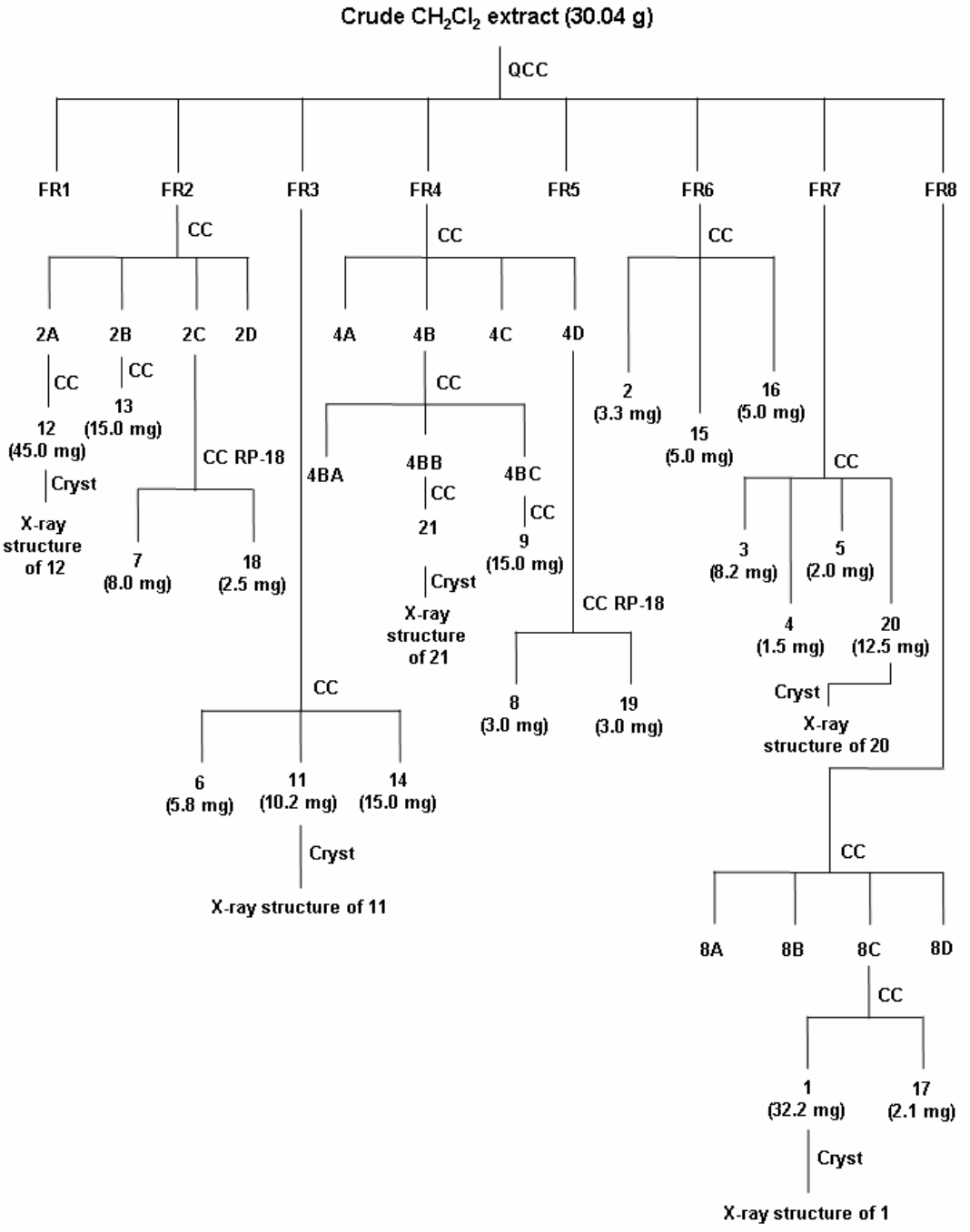


Fig 1.3.1. The separation scheme of crude CH_2Cl_2 extract from the roots of *C. formosum* ssp. *pruniflorum*

(3:7, v/v) to give **12** (45.0 mg). Subfraction FR2B was further purified by CC eluting with acetone-hexane (1:9, v/v) to give **13** (15.0 mg). Subfraction FR2C was further purified by CC on reversed-phase silica gel C-18 with MeOH to give **7** (8.0 mg) and **18** (2.5 mg). Fraction FR3 (2.56 g) was separated by CC with acetone—hexane (3:17, v/v) to give **14** (15.0 mg), **6** (5.8 mg) and **11** (10.2 mg), which was further recrystallized in $CHCl_3$—MeOH (4:1, v/v) to yield yellow needle single crystals. Fraction FR4 was subjected to CC with acetone—hexane (1:4, v/v) to afford 5 subfractions (FR4A-FR4E). Subfraction FR4B was separated by CC with acetone—hexane to give 3 fractions (FR4BA-FR4BC). Subfraction FR4B was further purified by CC eluted with a gradient of acetone—hexane to give **21** (15.0 mg). Subfraction FR4BC was further purified by CC on reversed-phase silica gel C-18 with MeOH to give **9** (15.0 mg). Subfraction FR4D was further purified by CC on reversed-phase silica gel C-18 with MeOH to give **8** (3.0 mg) and **19** (3.0 mg). Fraction FR6 was purified by CC with acetone—hexane (1:4, v/v) to give **2** (3.3 mg)**, 15** (5.0 mg) and **16** (5.0 mg). Fraction FR7 was further purified by CC with EtOAc—hexane (2:3, v/v) to give **3** (8.2 mg), **4** (1.5 mg), **5** (2.0 mg) and **20** (12.5 mg). Fraction FR8 was separated by CC with a gradient of acetone—hexane to give 4 fractions (FR8A-FR8D). Subfraction FR8C was further purified by CC with a gradient of acetone—hexane to give **17** (2.1 mg) and **1** (32.2 mg), which was further recrystallized from $CHCl_3$—MeOH (4:1, v/v) to yield pale yellow single crystals.

1.3.2. Extraction and Isolation of the crude CH_2Cl_2 of the barks of *C. formosum* ssp. *pruniflorum*

Ground-dried barks (4.00 kg) were extracted with CH_2Cl_2 and acetone (each 2 × 20 L, for 5 days) at room temperature, successively. The crude extracts were evaporated under reduced pressure to afford brownish crude CH_2Cl_2 (76.28 g) and acetone (21.74 g) extracts. The crude CH_2Cl_2 extract was subjected to QCC eluting with increasing polarities of EtOAc and acetone in hexane to afford 10 fractions (F1-F10). Fraction F1 (2.01 g) was separated by CC with acetone—hexane (1:19, v/v) to afford 3 subfractions (F1A-F1C). Subfraction F1B was further purified by CC with EtOAc—hexane (1:9, v/v) to give **28** (3.3 mg) and **29** (5.6 mg). Fraction F2 (58.06 g) was further separated by CC using a gradient of hexane with EtOAc to afford 8

subfractions (F2A-F2H) and **33** (150.0 mg). Subfraction F2C (120.02 g) was further purified by CC with EtOAc—hexane (1:4, v/v) to give **10** (5.2 mg) and **26** (68.2 mg). Subfraction F2D was purified by CC with CH_2Cl_2—hexane (3:2, v/v) to give 3 fractions (F2DA-F2DC). Subfraction F2DB was further purified by prep TLC with CH_2Cl_2—hexane (3:7, v/v) to give **32** (1.5 mg). Subfraction F2G was subjected to CC with acetone-hexane (1:9, v/v) to give **30** (5.0 mg) and **24** (30.20 mg). Subfraction F2H was subjected to CC eluted with a gradient of acetone-hexane to give **25** (35.50 mg). Fraction F3 was separated by CC with acetone-hexane (1:9, v/v) to afford 5 fractions (F3A-F3E). Subfraction F3D was further purified by CC with acetone-hexane (3:17, v/v) to give **35** (25.0 mg). Fraction F4 was separated by CC eluted with a gradient of acetone-hexane to afford 7 fractions (F4A-F4G). Subfraction F4E and 4F were further purified by preparative TLC and eluting with a gradient of acetone-hexane to give **22** (7.4 mg) and **23** (15.2 mg) respectively. Fraction F6 was separated by CC with acetone-hexane (3:17, v/v) to afford 7 subfractions (F6A-F6G). Subfraction F6B was further purified by CC with EtOAc—hexane (3:7, v/v) to give **28** (8.0 mg).

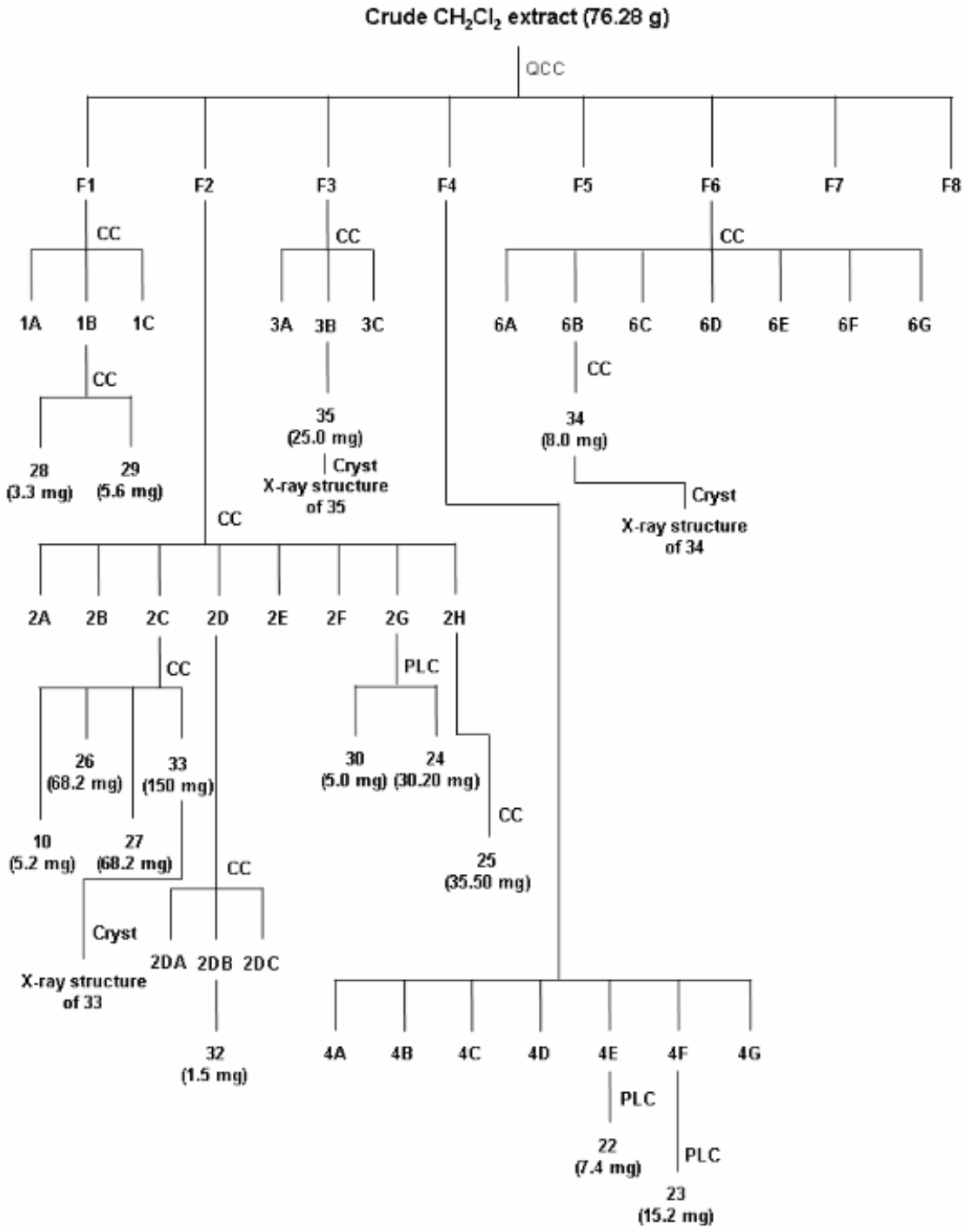


Fig 1.3.2. The separation scheme of crude CH_2Cl_2 extract from the barks of *C. formosum* ssp. *Pruniflorum*

1.3.3. Extraction and Isolation of the crude CH_2Cl_2 of the barks of *C. formosum* ssp. *pruniflorum*

The crude acetone was subjected to QCC eluting with a gradient of hexane—acetone to afford 12 fractions (FA1-FA12). Fraction FA2 (1.98 g) was further separated by CC with acetone—hexane (3:97, v/v) to give 6 subfractions (FA2A-FA2F). Subfraction FA2B (422.0 mg) was further purified by CC with acetone—hexane (1:19, v/v) to give **27** (3.0 mg). Fraction FA3 was further purified by CC with EtOAc—hexane (1:9, v/v) to give **36** (4.0 mg). Fraction FA7 was separated by CC with acetone—hexane (1:4, v/v) to give **31** (3.1 mg) and **37** (5.0 mg).

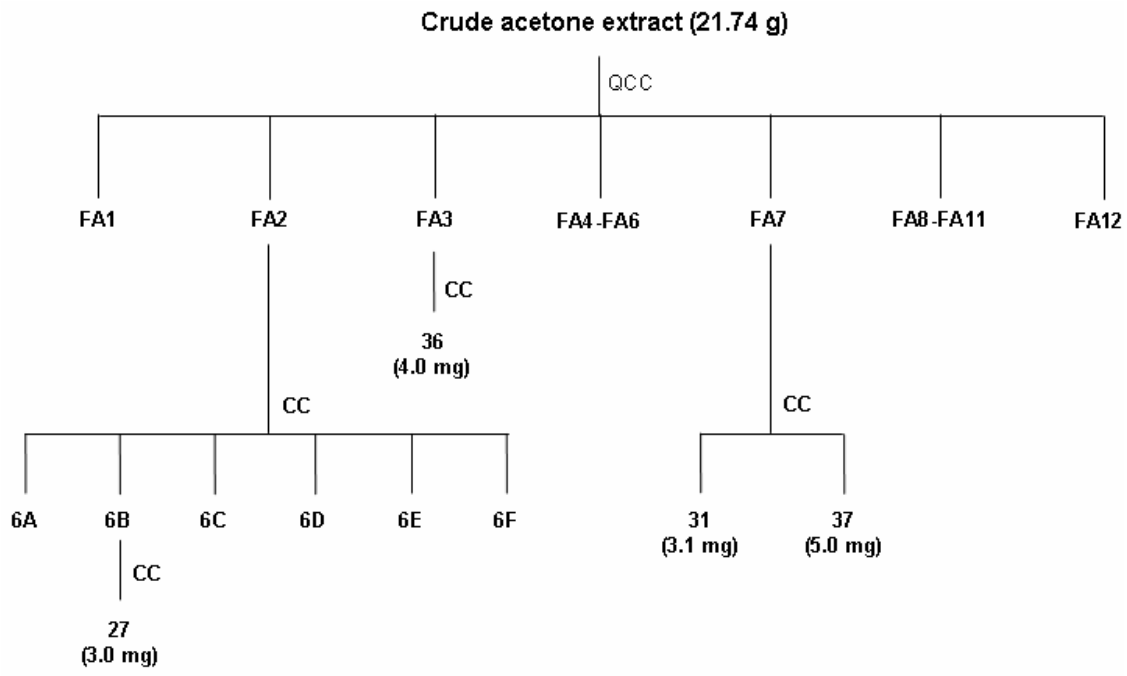
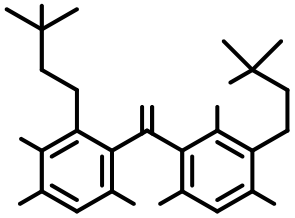


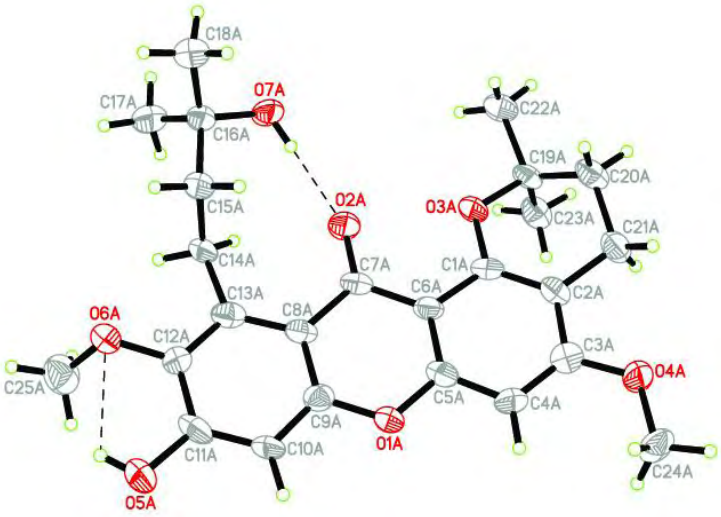
Fig 1.3.3. The separation scheme of crude acetone extract from the barks of *C. formosum* ssp. *pruniflorum*

1.4. Characterization of isolated compounds

1.4.1. Pruniflorone A (1, [10])



The structure of compound 1

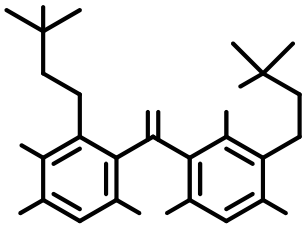


The X-ray structure of compound 1

Boonnak, N. *et al*., *Tetrahedron* **2006**, *62*, 8850–8859. [**10**]

1.4.1.1. Pruniflorone A (1). Pale yellow needle crystals, mp 259-260 ^{O}C; $[\alpha]_{D}^{26}$ -5.1 (*c* 0.430, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 247 (4.29), 261 (4.34), 314 (4.17), 355 (3.55) nm; IR (KBr) ν_{max} 3414, 1642, 1614 cm^{-1}; HREIMS *m/z* $[M]^+$ 442.1994 (calcd for $C_{25}H_{30}O_7$, 442.1992); ^{1}H NMR ($CDCl_3$, 300 MHz), see **Table 1**; ^{13}C NMR (CD_3OD/ $CDCl_3$, 75 MHz), see **Table 2**; HMBC data see **Table 3**; NOESY data see **Table 4**.

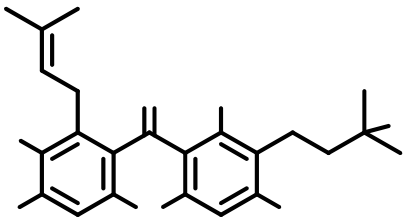
1.4.2. Pruniflorone B (2, [10])



The structure of compound 2

1.4.2.1. Pruniflorone B (2). Yellow powder, mp 215-217 ^{O}C, $[\alpha]_D^{26}$ -4.0 (*c* 0.165, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 246 (4.01), 299 (3.79), 334 (3.40) nm; IR (neat) ν_{max} 3177, 1639, 1611 cm^{-1}; HREIMS *m/z* $[M]^+$ 456.2116 (calcd for $C_{26}H_{32}O_7$, 456.2148); ^{1}H NMR ($CDCl_3$, 500 MHz), see **Table 1**; ^{13}C NMR ($CD_3OD/CDCl_3$, 125 MHz), see **Table 2**; HMBC data see **Table 3**; NOESY data see **Table 4**.

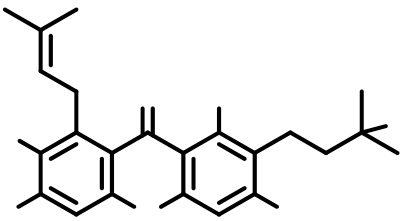
1.4.3. Pruniflorone C (3, [10])



The structure of compound 3

1.4.3.1. Pruniflorone C (3). Yellow solid, mp 134-136 ^{O}C; $[\alpha]_D^{27}$ -5.5 (*c* 0.145, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 245 (3.89), 259 (3.86), 313 (3.75), 353 (3.25) nm; IR (KBr) ν_{max} 3414, 1632, 1614 cm^{-1}; HREIMS *m/z* $[M]^+$ 442.1995 (calcd for $C_{25}H_{30}O_7$, 442.1992); ^{1}H NMR ($CD_3OD/CDCl_3$, 300 MHz), see **Table 1**; ^{13}C NMR ($CDCl_3/CD_3OD$, 125 MHz), see **Table 2**; HMBC data see **Table 3**; NOESY data see **Table 4**.

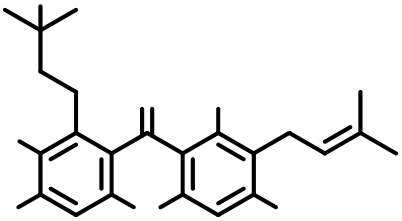
1.4.4. Pruniflorone D (4, [10])



The structure of compound 4

1.4.4.1. Pruniflorone D (4). Yellow viscous oil, $[\alpha]_D^{26}$ 17.5 (*c* 0.075, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 249 (5.00), 259 (4.98), 312 (4.92), 352 (4.35) nm; IR (neat) ν_{max} 3170, 1646, 1597 cm^{-1}; HREIMS *m/z* $[M]^+$ 456.2198 (calcd for $C_{26}H_{32}O_7$, 456.2148); ^1H NMR ($CD_3OD/CDCl_3$, 500 MHz), see **Table 1**; ^{13}C NMR ($CD_3OD/CDCl_3$, 125 MHz), see **Table 2**; HMBC data see **Table 3**; NOESY data see **Table 4**.

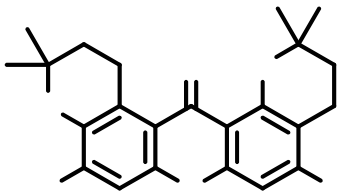
1.4.5. Pruniflorone E (5, [10])



The structure of compound 5

1.4.5.1. Pruniflorone E (5). Yellow gum, $[\alpha]_D^{27}$ -4.4 (*c* 0.130, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 245 (3.91), 260 (3.88), 312 (3.78), 353 (3.25) nm; IR (KBr) ν_{max} 3414, 1635, 1614 cm^{-1}; HREIMS *m/z* $[M]^+$ 442.2000 (calcd for $C_{25}H_{30}O_7$, 442.1992); ^1H NMR ($CD_3OD/CDCl_3$, 300 MHz), see **Table 1**; ^{13}C NMR ($CD_3OD/CDCl_3$, 125 MHz), see **Table 2**; HMBC data see **Table 3**; NOESY data see **Table 4**.

1.4.6. Pruniflorone F (6, [10])



The structure of compound 6

1.4.6.1. Pruniflorone F (6). Pale yellow powder, mp 235-236 ^{O}C; $[\alpha]_{D}^{26}$-9.2 (*c* 0.290, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 255 (3.94), 258 (3.99), 302 (3.77), 349 (3.40) nm; IR (KBr) v_{max} 3177, 1614 cm^{-1}; HREIMS *m/z* $[M]^+$ 410.1728 (calcd for $C_{24}H_{26}O_6$, 410.1729); ^{1}H NMR ($CDCl_3$, 300 MHz), see **Table 1**; ^{13}C NMR ($CDCl_3$, 75 MHz), see **Table 2**; HMBC data see **Table 3**; NOESY data see **Table 4**.

Table 1 ^{1}H-NMR spectral data of **1-6** (δ in ppm, multiplicities, *J* in Hz)

Position	**1**[a]	**2**[b]	**3**[c]	**4**[b]	**5**[c]	**6**[a]
4	6.29 s	6.33 s	6.32 s	6.34 s	6.38 s	6.35 s
5	6.72 s	6.76 s	6.75 s	6.82 s	6.78 s	6.74 s
1′	2.73 br t (7.5)	2.63 br t (7.0)	3.33 d (7.2)	3.36 d (7.5)	2.72 m	2.64 t (6.9)
2′	1.72 br t (7.5)	1.83 br t (7.0)	5.21 br t (7.2)	5.23 br t (7.5)	1.71 m	1.82 t (6.9)
4′	1.34 s	1.41 s	1.79 s	1.81 s	1.29 s	1.46 s
5′	1.34 s	1.41 s	1.68 s	1.69 s	1.29 s	1.46 s
1″	3.38 m	3.37 m	3.39 m	3.38 m	4.12 d (6.9)	3.58 t (6.9)
2″	1.78 m	1.79 m	1.77 m	1.77 m	5.26 m	1.84 t (6.9)
4″	1.30 s	1.31 s	1.32 s	1.30 s	1.85 s	1.36 s
5″	1.30 s	1.31 s	1.32 s	1.30 s	1.69 s	1.36 s
1-OH			d	13.60 s	d	
3-OMe	3.90 s	3.89 s	3.90 s	3.91 s	3.92 s	3.90 s
7-OMe	3.84 s	3.83 s	3.84 s	3.86 s	3.80 s	
3″-OMe		3.35 s		3.32 s		

[a] Recorded at 300 MHz in $CDCl_3$ [b] Recorded at 500 MHz in $CDCl_3$

[c] Recorded at 300 MHz in $CD_3OD/CDCl_3$ [d] exchangable with CD_3OD

Table 2 ^{13}C NMR (75 MHz) spectral data of **1-6** in $CD_3OD/CDCl_3$

Position	**1**	**2**[a]	**3**[a]	**4**[a,b]	**5**[a]	**6**[b]
1	155.2	155.3	159.1	159.8	159.8	155.6
2	105.6	105.4	111.3*	111.5	103.6	105.2
3	162.0	161.4	163.3	163.5	163.3	161.3
4	89.6	89.6	88.7	88.8	88.9	89.7
5	101.3	100.8	101.7	101.4	101.7	99.7
6	154.6	154.5	156.0	154.5	155.1	150.1
7	143.3	142.3	143.1	142.6	143.0	137.7
8	138.4	138.5	138.4	138.8	137.2	122.0
9	177.5	176.4	181.8	182.0	181.9	177.4
4a	157.1	156.9	155.1	155.2	155.4	157.2
4b	155.2	152.9	155.6	155.8	155.6	151.7
8a	113.8	115.5	111.2*	112.5	112.0	114.1
9a	107.2	107.9	103.5	103.8	111.9	107.8
1′	16.9	17.1	21.1	21.4	16.9	17.1
2′	31.3	31.4	122.1	122.3	42.1	31.5
3′	75.7	75.2*	131.6	131.7	71.1	75.2*
4′	26.1	26.5	17.5	17.8	28.9	26.6
5′	26.1	26.5	25.6	25.8	28.9	26.6
1′′	21.8	21.8	21.8	22.2	26.4	22.6
2′′	43.9	39.7	44.0	39.9	123.2	33.1
3′′	70.7	75.1*	70.8	74.9	131.9	75.3*
4′′	28.7	25.3	28.7	25.2	18.1	26.5
5′′	28.7	25.3	28.7	25.2	25.8	26.5
3-OMe	55.6	55.7	55.3	55.8	55.8	55.7
7-OMe	60.9	62.0	61.2	62.2	61.4	
3′′-OMe		49.2		49.2		

[a] Recorded at 125 MHz

[b] Recorded in $CDCl_3$ * May be interchangable

Table 3 HMBC (300 MHz) spectral data of **1**-**6** in $CDCl_3$

Position	**1**[a]	**2**[b]	**3**[a]	**4**[b]	**5**[a]	**6**
4	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-3, C-9, C-4a, C-9a
5	C-7, C-8, C-9, C-4b, C-8a	C-6, C-7, C-9, C-4b, C-8a	C-6, C-7, C-8, C-4b, C-8a, C-9	C-6, C-9, C-4b, C-8a,	C-6, C-7, C-9, C-4b, C-8a	C-6, C-7, C-9, C-4b, C-8a
1′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′	C-1, C-2, C-3, C-2′, C-3′
2′	C-2, C-1′, C-3′, C-4′, C-5′	C-2, C-1′, C-3′, C-4′, C-5′		C-2, C-4′, C-5′	C-3′, C-4′, C-5′	C-2, C-1′, C-3′, C-4′, C-5′
4′	C-1, C-1′, C-2′	C-2′, C-3′	C-2′, C-3′, C-5′	C-2′, C-3′	C-2′, C-3′	C-2′, C-3′
5′	C-1, C-1′, C-2′	C-2′, C-3′	C-2′,C-3′, C-4′	C-2′, C-3′	C-2′, C-3′	C-2′, C-3′
1″	C-7, C-8, C-8a, C-3″	C-7, C-8, C-8a, C-2″, C-3″,	C-7, C-8, C-8a, C-3″	C-7, C-8, C-8a, C-2″	C-8	C-7, C-8, C-8a, C-2″, C-3″
2″	C-8, C-3″, C-4″, C-5″	C-8, C-1″, C-3″, C-4″, C-5″	C-8, C-3″	C-1″, C-3″, C-4″, C-5″		C-8, C-1″, C-3″, C-4″, C-5″
4″	C-1″, C-2″, C-3″	C-2″, C-3″	C-1″, C-2″, C-3″	C-2″, C-3″	C-2″, C-3″, C-5″	C-2″, C-3″
5″	C-1″, C-2″, C-3″	C-2″, C-3″	C-1″, C-2″, C-	C-2″, C-3″	C-2″, C-3″, C-4″	C-2″, C-3″

			3′′			
1-OH				C-1, C-2, C-9a		
3-OMe	C-3	C-3	C-3	C-3	C-3	C-3
7-OMe	C-7	C-7	C-7	C-7	C-7	
3′′-OMe		C-3′′		C-3′′		

[a] Recorded in $CD_3OD/CDCl_3$

[b] Recorded at 500 MHz

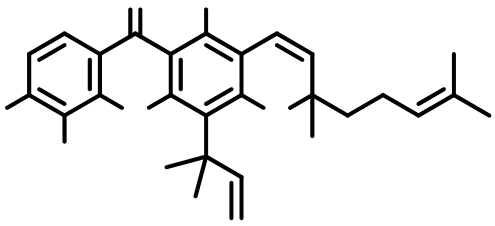
Table 4 NOESY (300 MHz) spectral data of **1**-**6** in $CDCl_3$

2′′	H-1′′, H-4′′, H-5′′	H-4′′, H-5′′, 3′′-OMe	H-1′′, H-4′′, H-5′′	H-1′′, H-4′′, H-5′′, 3′′-OMe	H-5′′	H-1′′, H-4′′, H-5′′
4′′	H-2′′	H-2′′	H-2′′	H-3′′		H-2′′
5′′	H-2′′	H-2′′	H-2′′	H-3′′	H-2′′	H-2′′
1-OH						
3-OMe	H-4	H-4	H-4	H-4		H-4
7-OMe						
3′′-OMe				H-4′′, H-5′′, 3′′-OMe		

[a] Recorded in $CD_3OD/CDCl_3$

[b] Recorded at 500 MHz

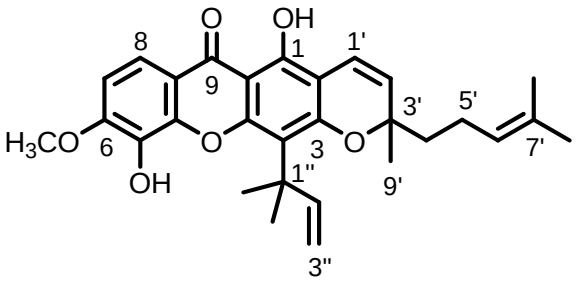
1.4.7. Pruniflorone G (7, [10])



The structure of compound 7

1.4.7.1. Pruniflorone G (7). Brown powder, mp 143.145 ^{O}C, $[\alpha]_D^{27}$ -7.4 (*c* 0.425, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 243 (4.56), 288 (4.81), 335 (4.53) nm; IR (KBr) ν_{max} 3414, 1646, 1628, 1580 cm^{-1}; EIMS *m/z* 462 (11) $[M]^{+}\cdot$, 447 (5), 379 (100); HREIMS *m/z* $[M]^{+}$ 462.2063 (calcd for $C_{28}H_{30}O_6$, 462.2042); ^{1}H and ^{13}C NMR data see **Table 5**; HMBC and NOESY data see **Table 6**.

1.4.8. Pruniflorone H (8, [10])



The structure of compound 8

1.4.8.1. Pruniflorone H (8). Yellow powder, mp 175-177 ^{O}C, $[\alpha]_D^{27}$ -56.5 (*c* 0.050, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 252 (4.06), 289 (4.22), 336 (4.01) nm; IR (KBr) ν_{max} 3400, 1632, 1597, 1573 cm^{-1}; EIMS *m/z* 476 (31) $[M]^{+}\cdot$, 461 (15), 393 (100), 279 (15), 167 (39), 149 (94), 97 (21), 85 (22), 83 (29); HREIMS *m/z* $[M]^{+}$ 476.2215 (calcd for $C_{29}H_{32}O_6$, 476.2199); ^{1}H and ^{13}C NMR data see **Table 5**; HMBC and NOESY data see **Table 6**.

Table 5 ^{1}H and ^{13}C NMR spectral data of **7** and **8** in $CDCl_3$

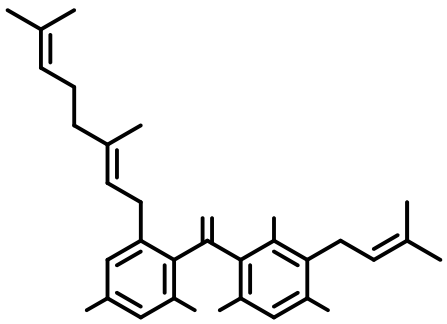
Position	**7**		**8**	
	^{1}H (J in Hz)[a]	^{13}C (δ)[b]	^{1}H (J in Hz)[a]	^{13}C (δ)[b]
1		156.8		156.6
2		105.2		104.9
3		159.2		159.3
4		112.7		113.0
5		131.0		133.4
6		149.0		151.4
7	6.96 d (9.0)	112.8	6.97 d (9.0)	108.2
8	7.69 d (9.0)	117.5	7.75 d (9.0)	116.8
9		180.7		181.0
4a		154.1		154.8
4b		144.5		144.3
8a		113.7		114.2
9a		102.9		103.0
1′	6.83 d (9.9)	116.7	6.81 d (9.9)	116.7
2′	5.58 d (9.9)	125.6	5.56 d (9.9)	125.6
3′		81.1		81.1
4′	1.91 m*	41.8	1.89 m*	41.7
	1.72 m*		1.70 m*	
5′	2.14 m	23.2	2.10 m	23.3
6′	5.13 br t (7.2)	123.7	5.12 br t (7.5)	123.7
7′		132.1		132.0
8′	1.60 s	17.6	1.59 s	17.6
9′	1.47 s	26.9	1.45 s	26.9
10′	1.69 s	25.7	1.68 s	25.6
1″		41.4		41.3
2″	6.75 dd (10.8, 17.7)	156.7	6.66 dd (10.5, 17.4)	154.9
3″	5.05 dd (1.2, 10.8)	103.3	5.04 dd (1.2, 10.5)	104.5
	5.23 dd (1.2, 17.7)		5.18 dd (1.2, 17.4)	
4″	1.66 s	28.0	1.66 s	28.4
5″	1.66 s	28.4	1.66 s	28.4
1-OH	13.50 s		13.50 s	
6-OMe			3.32 s	56.6

[a] Recorded at 300 MHz
[b] Recorded at 75 MHz
* Reduced from HMQC experiment

Table 6 HMBC and NOESY (300 MHz) spectral data of **7**-**8** in $CDCl_3$

Position	**7**		**8**	
	HMBC	NOESY	HMBC	NOESY
7		H-8	C-5, C-6, C-8a	H-8, 6-OMe
8	C-6, C-9	H-7	C-6, C-9	H-7
1′	C-1, C-2, C-3, C-3′	H-2′	C-1, C-2, C-3, C-3′	H-2′
2′	C-2, C-3, C-3′, C-4′, C-9′	H-1′, H-4′	C-2, C-3′	H-1′
4′	C-3′, C-5′	H-2′, H-6′	C-3′	
5′	C-3′, C-4′, C-6′, C-7′	H-6′	C-4′	
6′	C-5′, C-8′, C-10′	H-4′, H-5′	C-4′	
8′	C-6′, C-7′		C-6′, C-7′	
9′	C-2′,C-3′, C-4′		C-3′, C-4′	
10′	C-6′, C-7′		C-6′, C-7′	
2″	C-4, C-1″	H-3″	C-4, C-1″	H-3″
3″	C-1″, C-2″	H-2″	C-1″, C-2″, C-4″, C-5″	H-2″, H-4″, H-5″
4″	C-4, C-1″		C-4, C-1″, C-2″	H-3″
5″	C-4, C-1″		C-4, C-1″, C-2″	H-3″
1-OH	C-1, C-2, C-9a		C-1, C-2, C-9a	
6-OMe			C-6	H-7

1.4.9. Pruniflorone I (9, [10])



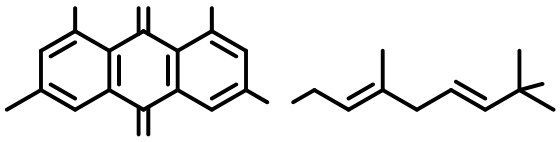
The structure of compound 9

1.4.9.1. Pruniflorone I (9). Brown viscous oil, $[\alpha]_D^{27}$ -11.3 (*c* 1.150, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 264 (4.70), 310 (4.45), 380 (3.94) nm; IR (neat) ν_{max} 3400, 1642, 1608 cm^{-1}; HREIMS *m/z* $[M]^+$ 448.2277 (calcd for $C_{28}H_{32}O_5$, 448.2250); NMR spectral data ($CDCl_3$, 300 MHz) see **Table 7**.

Table 7 NMR (300 MHz) spectral data of **9** in $CDCl_3$

Position	**9**			
	^1H (J in Hz)	^{13}C (δ)	HMBC	NOESY
1		160.7		
2		108.5		
3		162.1		
4	6.19 s	93.2	C-2, C-3, C-9, C-4a, C-9a	
5	7.17 s	116.7	C-6, C-9, C-4b, C-8a	
6		152.0		
7	7.18 s	123.7	C-6, C-8	
8		127.1		
9		183.4		
4a		155.3		
4b		151.3		
8a		118.4		
9a		104.1		
1′	3.35 d (6.9)	21.5	C-1, C-2, C-3, C-2′, C-3′	H-2′, H-4′
2′	5.19 br t (6.9)	121.4	C-4′	H-1′, H-5′
3′		135.5		
4′	1.66 s	25.8	C-2′, C-3′	H-1′
5′	1.74 s	17.9	C-2′, C-3′	H-2′
1″	4.20 d (6.6)	25.6	C-7, C-8, C-4a, C-8a, C-2′, C-3′	H-2″, H-9″
2″	5.16 br t (6.6)	121.5	C-8, C-4′, C-9′	H-1″, H-4″
3″		138.6		
4″	1.98 m	39.7	C-3′, C-9′	H-2″
5″	1.98 m	26.4	C-4′, C-6′, C-7′	H-6″
6″	4.94 m	123.8	C-4′, C-5′, C-8′	H-5″, H-8″
7″		132.0		
8″	1.55 s	25.8	C-6′, C-7′	H-6″
9″	1.77 s	16.4	C-2′, C-3′	H-1″
10″	1.48 s	17.7	C-6′, C-7′	
1-OH	13.54 s		C-1, C-2, C-9a	

1.4.10. Pruniflorone J (10, [10])



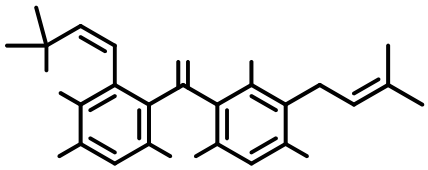
The structure of compound 10

1.4.10.1. Pruniflorone J (10). Orange viscous oil, $[\alpha]_D^{27}$ -98.4 (*c* 0.250, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 269 (4.33), 283 (4.32), 366 (3.37), 440 (3.86) nm; IR (neat) ν_{max} 3414, 1673, 1625 cm^{-1}; HREIMS *m/z* $[M]^+$ 422.1737 (calcd for $C_{25}H_{26}O_6$, 422.1729); NMR spectral data ($CDCl_3$, 500 MHz) see **Table 8**.

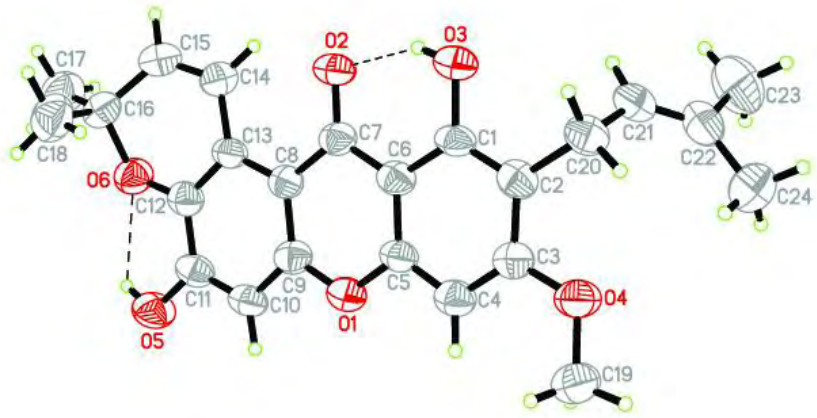
Table 8 NMR (500 MHz) spectral data of **10** in $CDCl_3$

Position	**10**			
	^{1}H (*J* in Hz)	^{13}C (δ)	HMBC	NOESY
1-OH	12.30 s	165.1	C-1, C-2, C-9a	
2	6.68 d (2.5)	107.6	C-1, C-4	H-1′
3		165.8		
4	7.37 d (2.5)	108.7	C-3, C-10, C-9a	H-1′
5	7.62 br s	121.3	C-7, C-10, C-8a, C-6(Me)	6-Me
6		148.4		
7	7.08 br s	124.5	C-5, C-8, C-8a, C-6(Me)	6-Me
8-OH	12.13 s	163.0	C-7, C-8, C-8a	
9		190.8		
10		182.0		
4a		135.2		
4b		133.2		
8a		113.7		
9a		110.1		
1′	4.68 d (6.5)	65.8	C-3, C-2′, C-3′	
2′	5.50 br t (6.5)	119.0	C-4′	
3′		141.5		
4′	2.79 d (6.5)	42.1	C-2′, C-3′, C-5′, C-6′, C-9′	
5′	5.62 dd (6.5, 15.5)	123.9	C-4′, C-7′	
6′	5.69 d (15.5)	140.5	C-4′, C-7′, C-8′, C-10′	
7′		70.8		
8′	1.33 s	29.8	C-6′, C-7′,	
9′	1.77 s	16.8	C-2′, C-3′, C-4′	
10′	1.33 s	29.8	C-6′, C-7′	
6-Me	2.45 s	22.2	C-5, C-6, C-7	H-5, H-7

1.4.11. Dulxisxanthone F (11, [11])



The structure of compound 11



The X-ray structure of compound 11

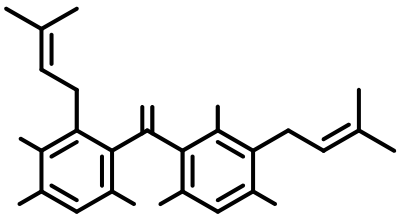
Boonnak, N. *et al*., *Tetrahedron* **2006**, *62*, 8850–8859. [**10**]

1.4.11.1. Dulxisxanthone F (11). Yellow needle-shaped single crystals were obtained from a $CHCl_3$-CH_3OH (9:1, v/v) solvent after several days. mp 232-233 ^{O}C; NMR spectral data ($CDCl_3$), see **Table 9**.

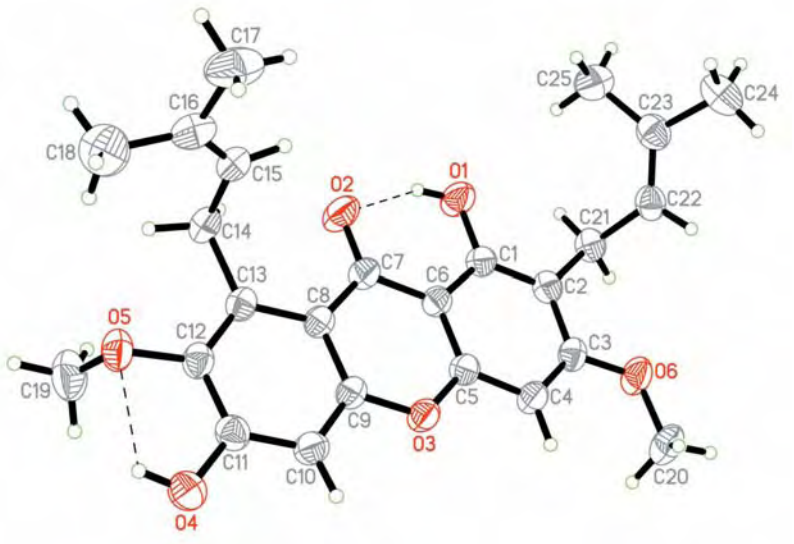
Table 9 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 11**

Position	**^{13}C**	**DEPT**	**HMQC**	**HMBC ($^{1}H \rightarrow {}^{13}C$)**
1-OH	159.6	C	13.35, *s*	1, 2, 9a
2	111.5	C		
3	163.6	C		
4	88.9	CH	6.36, *s*	2, 3, 9, 4a, 9a
5	102.2	CH	6.82, *s*	6, 7, 9, 4b, 8a
6	150.7	C		
7	137.5	C		
8	120.5	C		
9	182.4	C		
4a	155.3	C		
4b	153.3	C		
8a	109.0	C		
9a	104.6	C		
1′	21.4	CH_2	3.35, *d*, 6.9	1, 2, 3, 2′, 3′
2′	122.3	CH	5.23, *br t*, 6.9 Hz	-
3′	132.0	C		
4′	17.8	CH_3	1.80, *s*	2′, 3′
5′	25.8	CH_3	1.68, *s*	2′, 3′
1″	121.0	CH	8.04, *d*, 10.2 Hz	7, 8, 8a, 3″
2″	132.2	CH	5.82, *d*, 10.2 Hz	8, 3″, 4″, 5″
3″	77.2	C		
4″	27.4	CH_3	1.50, *s*	2″, 3″
5″	27.4	CH_3	1.50, *s*	2″, 3″
3-OMe	55.8	$-OCH_3$	3.91, *s*	3

1.4.12. β-mangostin (12, [12])



The structure of compound 12



The X-ray structure of compound 12

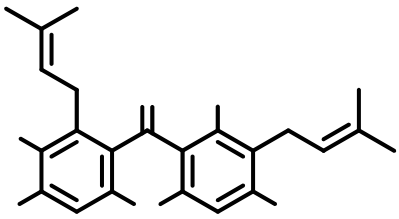
Chantrapromma, S. et al., *Acta Cryst*. **2006**, *E62*, o360–o362. [**13**]

1.4.12.1. β-mangostin (12). Yellow needle-shaped single crystals were obtained from a $CHCl_3$-CH_3OH (4:1, v/v) solvent after several days. m.p. 172-174 ^{O}C; NMR spectral data ($CDCl_3$), see **Table 10**.

Table 10 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 12**

Position	**^{13}C**	**DEPT**	**HMQC**	**HMBC ($^{1}H \rightarrow {}^{13}C$)**
1-OH	159.8	C	13.41, *s*	1, 2, 9a
2	111.5	C		
3	163.5	C		
4	88.8	CH	6.32, *s*	2, 3, 9, 4a, 9a
5	101.5	CH	6.82, *s*	6, 7, 9, 4b, 8a
6	154.4	C		
7	142.6	C		
8	137.0	C		
9	181.9	C		
4a	155.7	C		
4b	155.2	C		
8a	112.4	C		
9a	103.8	C		
1′	21.4	CH_2	3.35, *d*, 7.2	1, 2, 3, 2′, 3′, 5′
2′	122.4	CH	5.22, *m*	1′, 3′
3′	131.7	C		
4′	17.8	CH_3	1.80, *s*	2′, 3′
5′	25.8	CH_3	1.68, *s*	2′, 3′
1″	26.5	CH_2	4.09, *d*, 6.0	7, 8, 8a, 2″, 3″, 5″
2″	123.2	CH	5.26, *m*	1″, 3″
3″	132.0	C		
4″	18.2	CH_3	1.83, *s*	2″, 3″
5″	25.8	CH_3	1.68, *s*	2″, 3″
3-OMe	62.0	$-OCH_3$	3.90, *s*	3
7-OMe	55.8	$-OCH_3$	3.81, *s*	7

1.4.13. α-mangostin (13, [12])



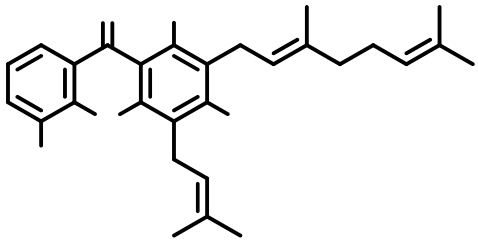
The structure of compound 13

1.4.13.1. α-mangostin (13). Deep red viscous oil. NMR spectral data ($CDCl_3$), see **Table 11**.

Table 11 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 13**

Position	**^{13}C**	**DEPT**	**HMQC**	**HMBC ($^{1}H \rightarrow {}^{13}C$)**
1-OH	160.2	C	13.77, *s*	1, 2, 9a
2	110.0	C		
3	161.7	C		
4	92.5	CH	6.29, *s*	2, 3, 9, 4a, 9a
5	101.7	CH	6.82, *s*	6, 7, 9, 4b, 8a
6	155.4	C		
7	143.0	C		
8	137.3	C		
9	181.9	C		
4a	154.8	C		
4b	155.5	C		
8a	111.6	C		
9a	103.7	C		
1′	21.3	CH_2	3.45, *d*, 7.2	1, 2, 3, 2′, 3′
2′	122.3	CH	5.29, *m*	-
3′	132.2	C		
4′	17.7	CH_3	1.84, *s*	2′, 3′
5′	25.7	CH_3	1.77, *s*	2′, 3′
1″	26.3	CH_2	4.09, *d*, 6.0	7, 8, 8a, 2″, 3″
2″	123.4	CH	5.26, *m*	-
3″	131.6	C		
4″	18.0	CH_3	1.84, *s*	2″, 3″
5″	25.6	CH_3	1.69, *s*	2″, 3″
7-OMe	61.2	$-OCH_3$	3.81, *s*	7

1.4.14. Formoxanthone A (14, [14])



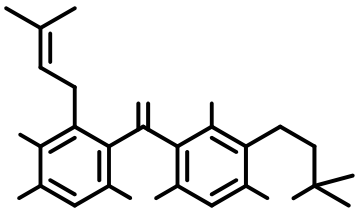
The structure of compound 14

1.4.14.1 Formoxanthone A (14). Yellow powder. m.p. = 112-114 C°; UV (CH_3OH) λ_{max} 245, 260, 319, 367 nm; IR (KBr) v_{max} 3370, 1650 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 12**.

Table 12 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 14**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1-OH	158.6	C	13.20, *s*	1, 2, 9a
2	109.0	C		
3-OH	161.0	C	6.57, *s*	2, 3, 4, 4a
4	105.7	C		
5-OH	144.5	C	5.86, *br s*	-
6	119.8	CH	7.29, *dd*, 7.8, 0.9	8, 4b
7	123.8	CH	7.22, *t*, 7.8	5, 8a
8	116.9	CH	7.75, *dd*, 7.8, 0.9	9, 4b
9	181.1	C		
4a	152.5	C		
4b	144.3	C		
8a	120.9	C		
9a	103.3	C		
1′	21.6	CH_2	3.50, *d*, 7.2	1, 2, 3, 2′, 3′
2′	121.1	CH	5.29, *br* t, 7.2	1′, 4′, 9′
3′	140.1	C		
4′	39.7	CH_2	2.11, *m*	2′, 3′, 6′
5′	26.3	CH_2	2.11, *m*	3′, 7′
6′	123.7	CH	5.06, *m*	-
7′	132.2	C		
8′	17.7	CH_3	1.60, *s*	6′, 7′
9′	16.3	CH_3	1.85, *s*	2′, 3′
10′	25.7	CH_3	1.68, *s*	6′, 7′
1″	22.0	CH_2	3.54, *d*, 6.9	3, 4, 4a, 2″, 3″
2″	122.4	CH	5.26, *br t*, 6.9	5″
3″	133.1	C		
4″	17.9	CH_3	1.86, *s*	2″, 3″
5″	25.6	CH_3	1.74, *s*	2″, 3″

1.4.15. 3-Isomagnostin (15, [12])



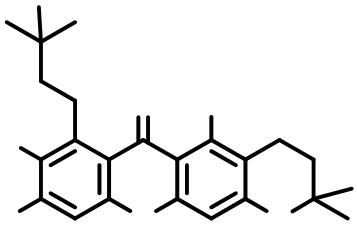
The structure of compound 15

1.4.15.1. 3-Isomagnostin (15). Yellow powder. m.p. = 112-114 C°; NMR spectral data ($CDCl_3$) see **Table 13**.

Table 13 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 15**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	160.6	C	13.73, *s*	1, 2, 9a
2	103.8	C		
3	160.7	C		
4	94.0	CH	6.23, *s*	3, 9, 4a, 9a
5	101.6	CH	6.82, *s*	6, 7, 9, 4b, 8a
6-OH	155.9	C	6.42, *br s*	-
7	142.4	C		
8	136.9	C		
9	182.0	C		
4a	152.5	C		
4b	154.7	C		
8a	112.1	C		
9a	102.9	C		
1′	16.1	CH_2	2.71, *t*, 6.6	1, 2, 3, 2′, 3′
2′	31.9	CH_2	1.83, *t*, 6.6	2, 1′, 3′
3′	76.0	C		
4′	26.7	CH_3	1.37, *s*	2′, 3′
5′	26.7	CH_3	1.37, *s*	2′, 3′
1″	26.5	CH_2	4.10, *d*, 6.3	7, 8, 8a, 2″, 3″
2″	123.3	CH	5.27, *br t*, 6.3	-
3″	132.3	C		
4″	18.2	CH_3	1.83, *s*	2″, 3″, 5″
5″	25.8	CH_3	1.69, *s*	2″, 3″, 4″
7-OCH_3	62.0	-OCH_3	3.80, *s*	7

1.4.16. 3,4-dihydro-5,9-dihydroxy-8-methoxy-7-(3-methoxy-3-methylbutyl)-2,2-dimethyl-2*H*,6*H*-pyrano-[3,-2-b]xanthen-6-one (16, [**15**])**.**



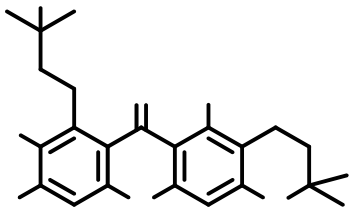
The structure of compound 16

1.4.16.1. 3,4-dihydro-5,9-dihydroxy-8-methoxy-7-(3-methoxy-3-methyl-butyl)-2,2-dimethyl-2*H*,6*H*-pyrano-[3,-2-b]xanthen-6-one (16). Yellow powder. NMR spectral data ($CDCl_3$) see **Table 14**.

Table 14 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 16**

Position	**^{13}C**	**DEPT**	**HMQC**	**HMBC ($^{1}H \rightarrow ^{13}C$)**
1-OH	160.7	C	13.90, *s*	-
2	103.7	C		
3	160.7	C		
4	94.0	CH	6.23, *s*	3, 4a, 9a
5	101.5	CH	6.81, *s*	6, 7, 4b, 8a
6	156.0	C		-
7	142.4	C		
8	138.7	C		
9	182.0	C		
4a	154.5	C		
4b	154.7	C		
8a	111.9	C		
9a	102.8	C		
1′	16.1	CH_2	2.71, *t*, 6.9	1, 2, 3, 2′, 3′
2′	31.9	CH_2	1.84, *t*, 6.9	2, 1′, 3′, 4′, 5′
3′	76.0	C		
4′	26.8	CH_3	1.37, *s*	3′
5′	26.8	CH_3	1.37, *s*	3′
1″	22.1	CH_2	3.39, *br t*, 8.1	7, 8, 8a, 2″
2″	39.8	CH	1.75, *br t*, 8.1	8, 1″, 3″, 4″, 5″
3″	74.9	C		
4″	25.2	CH_3	1.30, *s*	2″, 3″
5″	25.2	CH_3	1.30, *s*	2″, 3″
3″-OCH_3	49.2	-OCH_3	3.32, *s*	3″
7-OCH_3	62.1	-OCH_3	3.86, *s*	7

1.4.17. 3,4-dihydro-5,9-dihydroxy-7-(3-hydroxy-3-methylbutyl)-8-methoxy-2,2-dimethyl-2*H*,6*H*-pyrano[3,2-b]xanthen-6-one (17, [15])



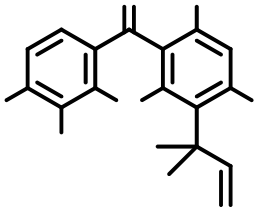
The structure of compound 17

1.4.17.1. 3,4-dihydro-5,9-dihydroxy-7-(3-hydroxy-3-methylbutyl)-8-methoxy-2,2-di-methyl-2*H*,6*H*-pyrano[3,2-b]xanthen-6-one (17). Yellow powder; NMR spectral data ($CDCl_3$) see **Table 15**.

Table 15 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 17**

Position	**^{13}C**	**DEPT**	**HMQC**	**HMBC ($^{1}H \rightarrow {}^{13}C$)**
1-OH	160.5	C	13.60, *s*	-
2	103.9	C		
3	160.9	C		
4	94.1	CH	6.22, *s*	3, 9, 4a
5	101.8	CH	6.83, *s*	6, 7, 9, 4b, 8a
6	154.7	C		-
7	142.5	C		
8	138.4	C		
9	182.0	C		
4a	154.8	C		
4b	156.1	C		
8a	111.8	C		
9a	102.8	C		
1′	16.1	CH_2	2.70, *t*, 6.9	1, 2, 3, 2′, 3′
2′	31.9	CH_2	1.83, *t*, 6.9	2, 3′, 4′, 5′
3′	76.1	C		
4′	26.8	CH_3	1.37, *s*	2′, 3′
5′	26.8	CH_3	1.37, *s*	2′, 3′
1″	22.1	CH_2	3.42, *br t*, 8.1	7, 8, 3″
2″	44.4	CH_2	1.79, *br t*, 8.1	8, 1″, 3″, 4″, 5″
3″	70.8	C		
4″	29.3	CH_3	1.33, *s*	2″, 3″
5″	29.3	CH_3	1.33, *s*	2″, 3″
7-OCH_3	62.2	-OCH_3	3.86, *s*	7

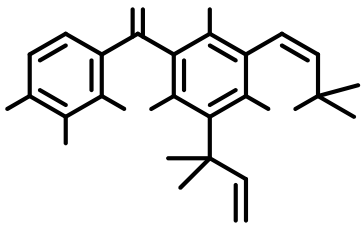
1.4.18. Isocudraniaxanthone B (18, [16])



The structure of compound 18

1.4.18.1. Isocudraniaxanthone B (18). Yellow powder. ^{1}H NMR spectral data (300, MHz, $CDCl_3$) ; 13.38 (*s*, 1-OH), 6.40 (*s*, H-2), 3.90 (*s*, 3-OCH_3), 6.94 (*d*, *J* = 8.4 Hz, H-7), 7.69 (*d*, *J* = 8.4 Hz, H-8), 7.73 (*dd*, *J* = 17.7, 10.8 Hz, H-2′), 5.21 (*br d*, *J* = 17.4 Hz, H-3′a), 5.04 (*br d*, *J* = 10.5 Hz, H-3′b), 1.58 (*s*, 4′-CH_3/ 5′-CH_3)

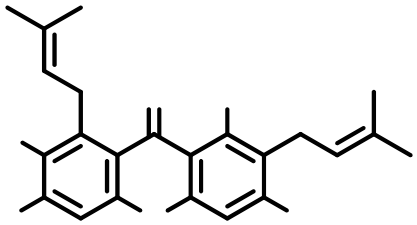
1.4.19. 10-*O*-methylmacluraxanthone (19, [17])



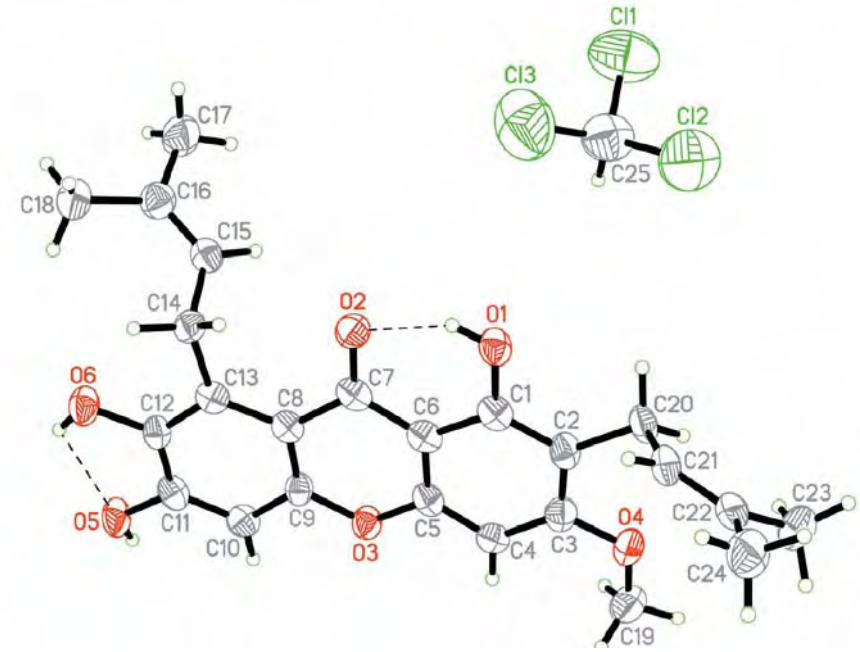
The structure of compound 19

1.4.19.1. 10-*O*-methylmacluraxanthone (19). Yellow powder. ^{1}H NMR spectral data (300, MHz, $CDCl_3$) ; 13.52 (*s*, 1-OH), 3.98 (*s*, 6-OCH_3), 6.97 (*d*, *J* = 8.7 Hz, H-7), 7.74 (*d*, *J* = 8.7 Hz, H-8), 6.77 (*d*, *J* = 9.9 Hz, H-1′), 5.61 (*d*, *J* = 9.9 Hz, H-2′), 1.51 (*s*, 4′-CH_3/5′-CH_3), 6.66 (*dd*, *J* = 17.7, 10.8 Hz, H-2′′), 5.18 (*br d*, *J* = 17.7 Hz, H-3′′a), 5.04 (*br d*, *J* = 10.8 Hz, H-3′′b), 1.66 (*s*, 4′′-CH_3/5′′-CH_3)

1.4.20. Dulxisxanthone B (20, [18])



The structure of compound 20

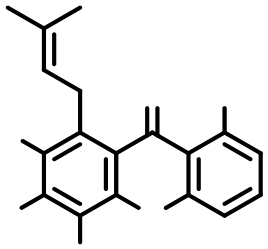


The X-ray structure of compound 20

Boonnak, N. *et al*., *Acta Cryst*. **2005**, *E61*, o4376–o4378. [**19**]

1.4.20.1. Dulxisxanthone B (20). Yellow needle-shaped single crystals were obtained from a $CHCl_3$-CH_3OH (7:3, v/v) solvent after several days. mp 122-124 ^{O}C; ^{1}H NMR spectral data (300, MHz, $CDCl_3$) ; 13.44 (*s*, 1-OH), 3.90 (*s*, 3-OCH_3), 6.81 (*s*, H-5), 6.32 (*s*, H-4), 3.35 (*d*, *J* = 7.2 Hz, H-1′), 5.23 (*br t*, *J* = 6.9 Hz, H-2′), 1.80 (*s*, 4′-CH_3), 1.68 (*s*, 5′-CH_3), 4.33 (*d*, *J* = 6.9 Hz, H-1′′), 5.31 (*br t*, *J* = 6.9 Hz, H-2′′), 1.89 (*s*, 4′′-CH_3), 1.79 (*s*, 5′′-CH_3)

1.4.21. 1,5-dihydroxy-6,-7-dimethoxy-8-isoprenylxanthone (21, [11])



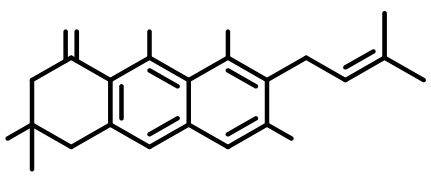
The structure of compound 21

1.4.21.1. 1,5-dihydroxy-6,-7-dimethoxy-8-isoprenylxanthone (21). Yellow needle-shaped single crystals were obtained from a $CHCl_3$-CH_3OH (9:1, v/v) solvent after several days. mp 232-233 ^{O}C; NMR spectral data ($CDCl_3$), see **Table 16**.

Table 16 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 21**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	162.1	C	13.08, *s*	1, 2, 9a
2	110.6	CH	6.76, *d*, 8.4	1, 4, 4a, 9a
3	136.1	CH	7.52, *t*, 8.4	1, 4, 4a
4	106.2	CH	6.92, *d*, 8.4	1, 2, 9, 4a, 9a
5-OH	135.9	C	5.98, *s*	5, 6, 4b
6	145.4	C		
7	147.3	C		
8	128.3	C		
9	183.6	C		
4a	155.2	C		
4b	143.4	C		
8a	114.5	C		
9a	109.2	C		
1′	25.4	CH_2	4.04, *d*, 6.6	7, 8, 8a, 2′, 3′
2′	123.5	CH	5.21, *br t*, 6.6	8
3′	131.6	C		
4′	18.1	CH_3	1.85, *s*	2′, 3′
5′	25.9	CH_3	1.70, *s*	2′, 3′
6-OMe	61.1	$-OCH_3$	4.07, *s*	6
7-OMe	61.1	$-OCH_3$	3.82, *s*	7

1.4.22. Vismone E (22, [20])



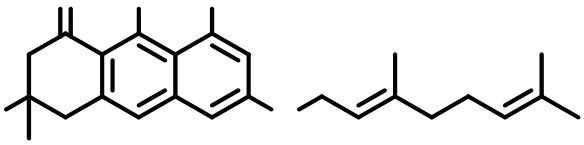
The structure of compound 22

1.4.22.1. Vismone E (22). Greenish brown viscous oil. NMR spectral data ($CDCl_3$) see **Table 17**.

Table 17 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 22**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	156.0	C	9.95, *s*	1, 2, 3, 9a
2	114.8	C		
3	163.9	C		
4	97.8	CH	6.54, *s*	2, 3, 9, 9a
5	43.4	CH_2	3.04, *br s*	6, 10, 4a, 6-Me
6	71.0	C		
7	51.1	CH_2	2.83, *br d*, 2.4 Hz	6, 8, 8a, 6-Me
8	201.6	C		
9-OH	167.1	C	16.14, *s*	
10	117.6	CH	6.86, *s*	4, 5, 4a, 5a
4a	134.1	C		
5a	138.9	C		
8a	108.5	C		
9a	108.5	C		
1′	22.0	CH_2	3.44, *d*, 6.9 Hz	1, 2, 3, 2′
2′	122.3	CH	5.24, *br t*, 6.9 Hz	
3′	131.7	C		
4′	17.8	CH_3	1.81, *s*	2′, 3′
5′	25.8	CH_3	1.68, *s*	2′, 3′
3-OMe	55.6	CH_3	3.92, *s*	3
6-Me	28.8	CH_3	1.44, *s*	5, 6, 7

1.4.23. Vismone D (23, [21])



The structure of compound 23

1.4.23.1. Vismone D (23). Greenish brown viscous oil. NMR spectral data ($CDCl_3$) see **Table 18**.

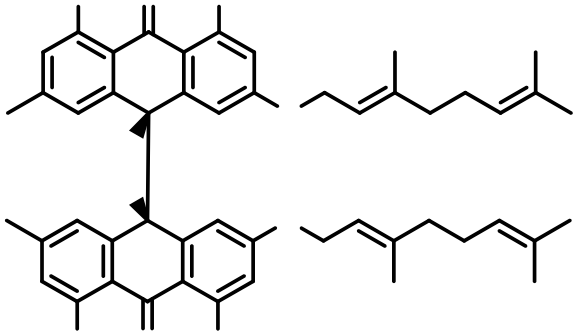
Table 18 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 23**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	156.0	C	9.95, *s*	1, 2, 3, 9a
2	114.8	C		
3	163.9	C		
4	97.8	CH	6.54, *s*	2, 3, 9, 9a
5	43.4	CH_2	3.04, *br s*	6, 10, 4a, 6-Me
6	71.0	C		
7	51.1	CH_2	2.83, *br d*, 2.4 Hz	6, 8, 8a, 6-Me
8	201.6	C		
9-OH	167.1	C	16.14, *s*	
10	117.6	CH	6.86, *s*	4, 5, 4a, 5a
4a	134.1	C		
5a	138.9	C		
8a	108.5	C		
9a	108.5	C		
1′	22.0	CH_2	3.44, *d*, 6.9 Hz	1, 2, 3, 2′
2′	122.3	CH	5.24, *br t*, 6.9 Hz	
3′	131.7	C		
4′	17.8	CH_3	1.81, *s*	2′, 3′
5′	25.8	CH_3	1.68, *s*	2′, 3′
3-OMe	55.6	CH_3	3.92, *s*	3
6-Me	28.8	CH_3	1.44, *s*	5, 6, 7

7

HO

1.4.24. Bianthrone A_1 (24, [22])



The structure of compound 24

1.4.24.1. Bianthrone A_1 (24). Yellow-green solid. EIMS 782 (calcd for *m/z* 782); NMR spectral data ($CDCl_3$) see **Table 19**.

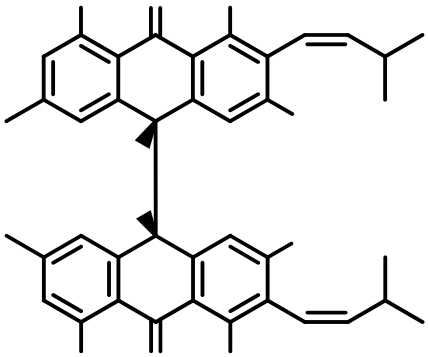
Table 19 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 24**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1-OH	164.6	C	12.20, *s*	1, 2, 9a
2	100.8	CH	6.40, *d*, 2.4 Hz	1, 2, 3, 9a
3	164.7	C		
4	108.2	CH	6.14, *d*, 2.4 Hz	3, 9, 9a
5	120.7	CH	6.11, *br s*	6, 7, 9, 8a, 6-Me
6	146.8	C		
7	117.0	CH	6.69, *br s*	5, 8a, 6-Me
8-OH	162.0	C	11.91, *s*	7, 8, 8a
9	190.3	C		
10	56.6	CH	4.33, *s*	4, 5, 4a, 5a, 8a, 9a
4a	142.8	C		
5a	139.9	C		
8a	114.3	C		
9a	111.0	C		
11	65.4	CH_2	4.58, *d*, 6.6 Hz	3, 12, 13
12	118.3	CH	5.49, *br t*, 6.6 Hz	11, 14
13	142.5	C		
14	39.6	CH_2	2.14, *m*	12, 13
15	26.3	CH_2	2.14, *m*	16
16	123.7	CH	5.12, *br t*, 6.6 Hz	14, 15, 18, 20
17	132.0	C		
18	25.7	CH_3	1.70, *s*	16, 17, 20
19	16.8	CH_3	1.79, *s*	12, 13
20	17.7	CH_3	1.63, *s*	16, 17, 18
6-Me	22.0	CH_3	2.30, *s*	5, 6, 7

Table 19 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 24** (continued)

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1′-OH	164.6	C	12.12, *s*	1′, 2′, 9a′
2′	100.7	CH	6.35, *d*, 2.4 Hz	1′, 2′, 3′
3′	164.7	C		
4′	108.4	CH	5.99, *d*, 2.4 Hz	3′, 9′, 9a′
5′	120.8	CH	5.97, *br s*	6′, 9′, 8a′, 6′-Me
6′	146.6	C		
7′	116.9	CH	6.69, *br s*	5′, 8a′, 6′-Me
8′-OH	162.0	C	11.81, *s*	7, 8, 8a′
9′	190.3	C		
10′	56.6	CH	4.32, *s*	5′, 4a′, 5a′, 8a′, 9a′
4a′	143.5	C		
5a′	140.2	C		
8a′	114.0	C		
9a′	110.7	C		
11′	65.3	CH_2	4.53, *d*, 6.6 Hz	3′, 12′, 13′
12′	118.3	CH	5.47, *br t*, 6.6 Hz	11′, 14′
13′	142.5	C		
14′	39.6	CH_2	2.14, *m*	12′, 13′
15′	26.3	CH_2	2.14, *m*	16′
16′	123.7	CH	5.12, *br t*, 6.6 Hz	14′, 15′, 18′, 20′
17′	132.0	C		
18′	25.7	CH_3	1.70, *s*	16′, 17′
19′	16.7	CH_3	1.78, *s*	12′, 13′
20′	17.7	CH_3	1.63, *s*	16′, 17′
6′-Me	22.0	CH_3	2.28, *s*	5′, 6′, 7′

1.4.25. Bianthrones J (25, [23])



The structure of compound 25

1.4.25.1. Bianthronea J (25). Yellow-green solid. HREIMS *m/z* $[M]^+$ 674.2864 (calcd for $C_{42}H_{42}O_8$, 674.2880); NMR spectral data ($CDCl_3$) see **Table 20**.

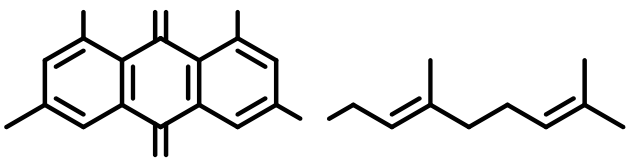
Table 20 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 25**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	161.7	C	12.63, *s*	1, 2, 9a
2	113.4	C		
3	162.0	C		
4	103.1	CH	5.65, *s*	2, 9, 9a
5	120.7	CH	6.34, *br s*	7, 10, 5a, 8a, 6-Me
6	146.9	C		
7	117.0	CH	6.70, *br s*	5
8-OH	161.7	C	11.91, *s*	7, 8, 8a
9	190.7	C		
10	56.8	CH	4.26, *s*	4, 5, 4a, 5a, 8a, 9a
4a	140.1	C		
5a	141.5	C		
8a	114.7	C		
9a	110.6	C		
11	115.6	CH	6.53, *dd*, 0.7, 6.6 Hz	2, 12
12	143.6	CH	6.68, *t*, 6.6 Hz	2, 11, 13
13	33.1	CH	2.48, *m*	11, 12
14	22.6	CH_3	1.20, *d*, 6.6 Hz	12, 13
15	22.6	CH_3	1.20, *d*, 6.6 Hz	12, 13
3-OMe	55.5	CH_3	3.71, *s*	3
6-Me	22.0	CH_3	2.34, *s*	5, 6, 7

Table 20 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 25** (continued)

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1′-OH	161.3	C	12.68, *s*	1′, 2′, 9a′
2′	113.4	C		
3′	162.0	C		
4′	103.0	CH	5.89, *s*	2′, 9′, 10′, 9a′
5′	120.7	CH	6.04, *br s*	7′, 10′, 5a′, 8a′, 6′-Me
6′	146.6	C		
7′	117.0	CH	6.68, *br s*	5′
8′-OH	161.9	C	11.85, *s*	7′, 8′, 8a′
9′	190.6	C		
10′	57.0	CH	4.25, *s*	4′, 5′, 4a′, 5a′
11′	115.6	CH	6.47, *dd*, 0.7, 6.6 Hz	2′, 12′
12′	143.6	CH	6.63, *t,* 6.6 Hz	2′, 11′, 13′
13′	33.1	CH	2.48, *m*	11′, 12′
14′	22.6	CH_3	1.20, *d*, 6.6 Hz	12′, 13′
15′	22.6	CH_3	1.20, *d*, 6.6 Hz	12′, 13′
3′-OMe	55.6	CH_3	3.80, *s*	3′
6′-Me	22.0	CH_3	2.29, *s*	5′, 6′

1.4.26. 3-geranyloxy-6-methyl-1,8-dihydroxyanthraquninone (26, [20])



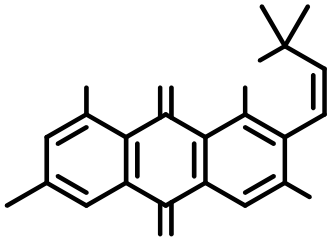
The structure of compound 26

1.4.26.1. 3-geranyloxy-6-methyl-1,8-dihydroxyanthraquninone (26). Orange solid. NMR spectral data ($CDCl_3$) see **Table 21**.

Table 21 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 26**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	165.1	C	12.29, *s*	1, 2, 9a
2	107.4	CH	6.67, *br d*, 2.4 Hz	1, 4
3	165.9	C		
4	108.8	CH	7.36, *br d*, 2.4 Hz	2, 3, 9, 10, 9a
5	121.2	CH	7.61, *br s*	6, 7, 8, 9, 10, 8a, 6-Me
6	148.3	C		
7	124.4	CH	7.07, *br s*	5, 8, 8a, 6-Me
8-OH	162.4	C	12.13, *s*	6, 7,8, 8a
9	190.6	C		
10	181.9	C		
4a	135.1	C		
4b	133.2	C		
8a	113.6	C		
9a	110.1	C		
1′	65.8	CH_2	4.67, *d*, 6.6 Hz	3, 2′, 3′
2′	118.2	CH	5.47, *br t*, 6.6 Hz	3′, 4′, 9′
3′	142.8	C		1′, 2′, 4′, 5′
4′	39.5	CH_2	2.12, *m*	3′, 5′, 6′
5′	26.2	CH_2	2.12, *m*	3′, 4′, 7′
6′	123.6	CH	5.08, *br t*, 6.6 Hz	
7′	132.0	C		
8′	25.7	CH_3	1.68, *s*	6′, 7′, 8′
9′	16.8	CH_3	1.78, *s*	2′, 3′
10′	17.7	CH_3	1.61, *s*	6′, 7′, 10′
6-Me	22.1	CH_3	2.45, *s*	6, 7, 4b

1.4.27. 11-hydroxy-5-methoxy-2,2,9-trimethyl-2*H*-anthra-[1,2-b]pyran-7,12-dione (27, [24]).



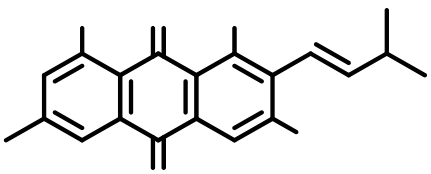
The structure of compound 27

1.4.27.1. 11-hydroxy-5-methoxy-2,2,9-trimethyl-2*H*-anthra-[1,2-b]pyran-7,12-dione (27). Orange solid. UV ($CHCl_3$) λ_{max} (log ε) 224, 264, 285 and 424 nm; IR (KBr) ν_{max} 3414, 1635 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 22**.

Table 22 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 27**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	156.3	C		
2	114.9	C		
3	158.8	C		
4	102.8	CH	7.43, *s*	3, 9, 10,4a, 9a
5	119.8	CH	7.56, *dd,* 0.6, 1.5 Hz	7, 10, 8a, 6-Me
6	146.7	C		
7	124.5	CH	7.67, *dd,* 0.6, 1.5 Hz	5, 8, 8a, 6-Me
8-OH	162.6	C	13.18, *s*	7, 8, 8a
9	187.2	C		
10	182.8	C		
4a	135.4	C		
4b	132.6	C		
8a	115.4	C		
9a	116.3	C		
1′	116.1	CH	6.73, *d*, 10.2 Hz	1, 3, 3′
2′	132.2	CH	5.84, *d*, 10.2 Hz	1′, 3′, 4′, 5′
3′	77.8	C		
4′	28.0	CH_3	1.57, *s*	1′, 2′, 3′
5′	28.0	CH_3	1.57, *s*	1′,2′, 3′
3-OMe	56.2	CH_3	4.03, *s*	3
6-Me	22.0	CH_3	2.42, *s*	5, 6, 7

1.4.28. Vismiaquinone A (28, [25]).



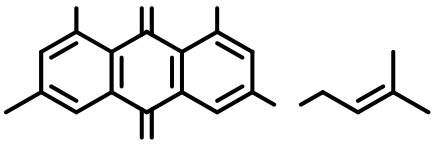
The structure of compound 28

1.4.28.1. Vismiaquinone A (28). Red orange solid. UV ($CHCl_3$) λ_{max} (log ε) 220, 278 and 425 nm; IR (KBr) ν_{max} 3425, 1624 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 23**.

Table 23 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 28**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	162.5	C	12.84, *s*	1, 2, 9, 9a
2	120.0	C		
3	163.0	C		
4	103.4	CH	7.40, *s*	2, 3, 9, 10,4a, 9a
5	121.1	CH	7.61, *br s*	6, 7, 8, 9, 10, 8a, 6-Me
6	148.4	C		
7	124.4	CH	7.07, *br s*	5, 8, 6-Me
8-OH	162.1	C	12.02, *s*	6, 7, 8, 8a
9	191.4	C		
10	181.9	C		
4a	132.1	C		
4b	133.2	C		
8a	113.7	C		
9a	110.5	C		
1′	115.8	CH	6.66, *dd*, 1.2, 16.2 Hz	1, 2, 3
2′	146.8	CH	6.92, *dd*, 1.2, 16.2 Hz	2
3′	33.4	CH	2.50, *m*	1′, 2′, 4′, 5′
4′	22.5	CH_3	1.14, *d*, 6.9 Hz	1′, 3′
5′	22.5	CH_3	1.14, *d*, 6.9 Hz	1′, 3′
3-OMe	56.3	CH_3	4.05, *s*	3
6-Me	22.2	CH_3	2.45, *s*	6, 7, 4b

1.4.29. Madagascin (29, [26])



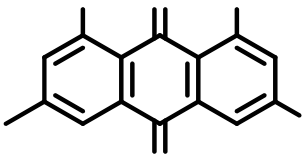
The structure of compound 29

1.4.29.1. Madagascin (29). Red orange solid. UV ($CHCl_3$) λ_{max} (log ε) 221, 253, 265, 286 and 480 nm; IR (KBr) ν_{max} 3338, 1628 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 24**.

Table 24 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 29**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1-OH	165.1	C	12.28, *s*	1, 2, 9a
2	107.5	CH	6.69, *d*, 2.4 Hz	1, 4
3	165.9	C		
4	108.7	CH	7.38, *d*, 2.4 Hz	2, 3, 10, 9a
5	121.2	CH	7.63, *br d*, 1.5 Hz	6, 7, 9, 10, 8a
6	148.3	C		
7	124.4	CH	7.08, *br s*	5, 8, 9, 8a
8-OH	162.5	C	12.11, *s*	6, 7, 8, 8a
9	190.7	C		
10	182.0	C		
4a	135.2	C		
4b	133.2	C		
8a	113.7	C		
9a	110.1	C		
1′	65.8	CH_2	4.66, *d*, 6.9 Hz	3, 2′, 3′, 4′, 5′
2′	118.2	CH	5.50, *br t*, 6.9 Hz	4′, 5′
3′	139.7	C		
4′	18.3	CH_3	1.81, *s*	2′, 3′, 5′
5′	25.8	CH_3	1.84, *s*	2′, 3′, 4′
6-Me	22.1	CH_3	2.46, *s*	5, 6, 7

1.4.30. Physion (30, [27])



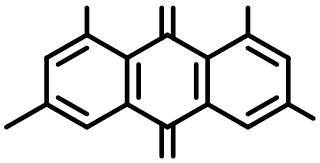
The structure of compound 30

1.4.30.1. Physion (30). Orange solid. UV ($CHCl_3$) λ_{max} (log ε) 222, 267, 284 and 437 nm; IR (KBr) ν_{max} 3350, 1646 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 25**.

Table 25 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 30**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1-OH	165.2	C	12.31, *s*	1, 2, 9a
2	106.8	CH	6.67, *d*, 2.4 Hz	1, 3, 4, 9a
3	166.6	C		
4	108.2	CH	7.35, *d*, 2.4 Hz	2, 3, 9, 10,4a, 9a
5	121.3	CH	7.60, *br d*, 1.5 Hz	7, 9, 10, 8a, 6-Me
6	148.4	C		
7	124.5	CH	7.07, *br s*	5, 8, 8a, 6-Me
8-OH	162.5	C	12.10, *s*	6, 7, 8, 8a
9	190.8	C		
10	182.0	C		
4a	135.3	C		
4b	133.2	C		
8a	113.7	C		
9a	110.3	C		
3-OMe	56.1	CH_3	3.88, *s*	3
6-Me	22.2	CH_3	2.45, *s*	5, 6, 7

1.4.31. Emodin (31, [28])



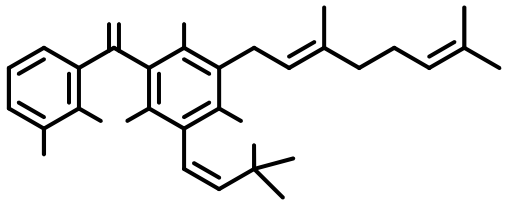
The structure of compound 31

1.4.31.1. Emodin (31). Orange solid. UV ($CHCl_3$) λ_{max} (log ε) 220, 251, 266, 285 and 441 nm; IR (KBr) ν_{max} 3400, 1642 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 26**.

Table 26 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 31**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1-OH	170.0	C	12.20, *s*	1, 2, 9a
2	113.2	CH	6.62, *d*, 2.4 Hz	1, 4
3	170.7	C		
4	114.5	CH	7.24, *d*, 2.4 Hz	2, 3, 10
5	125.6	CH	7.55, *br d*, 2.4 Hz	7, 9, 10, 8a, 6-Me
6	152.8	C		
7	129.0	CH	7.07, *br d*, 2.4 Hz	5, 8, 8a, 6-Me
8-OH	167.0	C	12.12, *s*	7, 8, 8a
9	195.1	C		
10	186.7	C		
4a	138.0	C		
4b	140.1	C		
8a	118.4	C		
9a	113.2	C		
6-Me	20.8	CH_3	2.45, *s*	5, 6, 7

1.4.32. Formoxanthone B (32, [14])



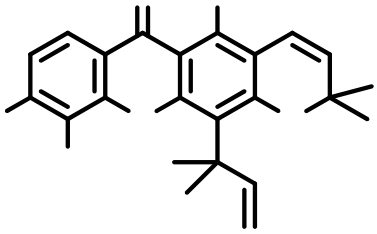
The structure of compound 32

1.4.32.1. Formoxanthone B (32). Yellow solid. mp. 143-145 $^{\circ}$C.; UV ($CHCl_3$) λ_{max} (log ε) 221, 244, 260 and 318 nm; IR (neat) ν_{max} 3424, 1646 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 27**.

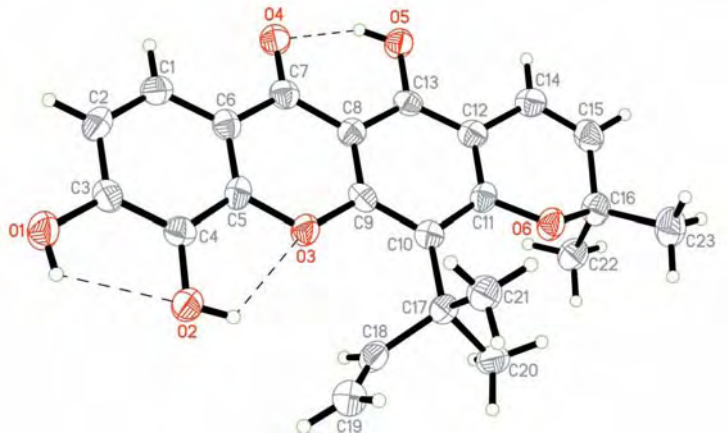
Table 27 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 32**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	160.6	C	13.20, *s*	1, 2, 9a
2	112.3	C		-
3	158.7	C		-
4	100.6	C		-
5	144.2	C		-
6	120.1	CH	7.31, *dd*, 1.8, 7.8 Hz	5, 8
7	124.0	CH	7.25, *t*, 7.8 Hz	5, 8a
8	117.2	CH	7.79, *dd*, 1.8, 7.8 Hz	6, 9, 4b, 8a
9	180.8	C		-
4a	149.2	C		-
4b	144.1	C		-
8a	121.2	C		-
9a	103.2	C		-
1′	21.1	CH_2	3.38, *d*, 7.2 Hz	1, 2, 3, 2′, 3′
2′	121.7	CH	5.26, *br t*, 7.2 Hz	1′, 4′, 9′
3′	135.2	C		-
4′	39.8	CH_2	2.02, *m*	5′, 9′
5′	26.7	CH_2	2.02, *m*	4′
6′	124.4	CH	5.09, *br t*, 7.2 Hz	-
7′	131.3	C		-
8′	25.7	CH_3	1.64, *s*	6′, 7′, 10′
9′	16.3	CH_3	1.82, *s*	2′, 3′, 4′
10′	17.7	CH_3	1.58, *s*	6′, 7′, 8′
1″	115.0	CH	6.80, *d*, 9.9 Hz	3, 4, 4a, 3″
2″	127.4	CH	5.65, *d*, 9.9 Hz	4, 3″, 4″, 5″
3″	78.1	C		-
4″	28.2	CH_3	1.50, *s*	2″, 3″
5″	28.2	CH_3	1.50,*s*	2″, 3″

1.4.33. Macluraxanthone (33, [29])

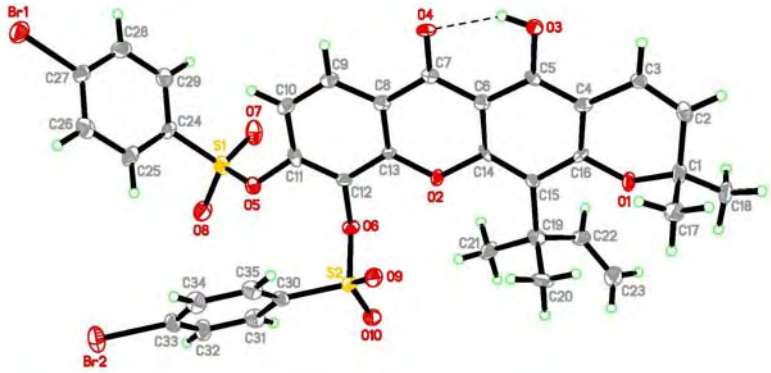


The structure of compound 33



The X-ray structure of compound 33

Fun, H-K. *et al*., *Acta Cryst*. **2006**, *E62*, o130–o132. [**30**]



The X-ray structure of dibrosylated of compound 33

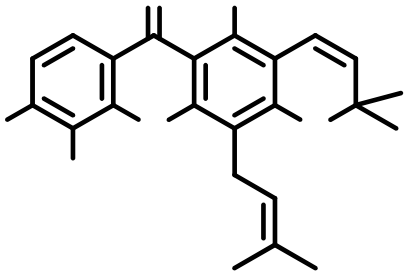
Boonnak, N. *et al*., *Analytical Sciences* **2008**, *24*, 1-2. [**31**]

1.4.33.1. Macluraxanthone (33). Yellow needle-shaped single crystals were obtained from a $CHCl_3$-CH_3OH (9:1, v/v) solvent after several days. mp. 183-184 $^{\circ}$C.; NMR spectral data ($CDCl_3$) see **Table 28**.

Table 28 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 33**

Position	^{13}C	DEPT	HMQC	HMBC (^{1}H$\rightarrow$^{13}C)
1-OH	156.8	C	13.53, *s*	1, 2, 9a
2	105.5	C		
3	158.9	C		
4	113.1	C		
5	131.0	C		
6	149.0	C		
7	112.8	CH	6.94, *d*, 9.0 Hz	5, 6, 8a
8	117.5	CH	7.68, *d*, 9.0 Hz	6, 9, 4b
9	180.8	C		
4a	154.1	C		
4b	144.5	C		
8a	113.7	C		
9a	103.0	C		
1′	116.1	CH	6.76, *d*, 9.9 Hz	1, 2, 3, 3′
2′	127.2	CH	5.61, *d*, 9.9 Hz	2, 3′, 4′, 5′
3′	78.3	C		
4′	27.9	CH_3	1.52, *s*	2′, 3′
5′	27.9	CH_3	1.52, *s*	2′, 3′
1″	41.4	C		
2″	156.8	CH	6.76, *dd*, 10.5, 17.7 Hz	1″, 3″, 4″, 5″
3″	103.3	CH_2	5.22, *dd*, 1.5, 17.7 Hz	1″, 2″
			5.05, *dd*, 1.5, 10.5 Hz	
4″	28.2	CH_3	1.65, *s*	4, 1″, 2″
5″	28.2	CH_3	1.65, *s*	4, 1″, 2″

1.4.34. Xanthone V_1 (34, [32])



The structure of compound 34

The X-ray structure of compound 34

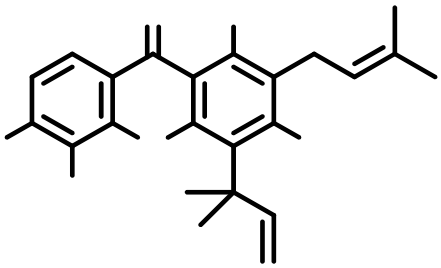
Chantrapromma, S. *Acta Cryst*. **2005**, *E61*, o2136–o2138. [**33**]

1.4.34.1. Xanthone V_1 (34). Yellow needle-shaped single crystals were obtained from a $CHCl_3$-CH_3OH (4:1, v/v) solvent after several days. mp. 218-219 ^{o}C.; NMR spectral data ($CDCl_3$) see **Table 29**.

Table 29 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 34**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	158.0	C	13.25, *s*	-
2	104.2	C		
3	155.3	C		
4	107.8	C		
5	132.3	C		
6	151.7	C		
7	112.4	CH	6.96, *d*, 8.7 Hz	5, 6, 8a
8	116.7	CH	7.73, *d*, 8.7 Hz	6, 9, 4b
9	181.2	C		
4a	154.3	C		
4b	146.4	C		
8a	113.8	C		
9a	102.6	C		
1′	115.6	CH	6.75, *d*, 9.9 Hz	1, 2, 3, 1′, 2′
2′	127.3	CH	5.61, *d*, 9.9 Hz	2, 2′, 3′
3′	78.2	C		
4′	28.0	CH_3	1.49, *s*	1′, 2′, 3′
5′	28.0	CH_3	1.49, *s*	1′, 2′, 3′
1″	21.3	CH_2	3.50, *d*, 7.2 Hz	4, 4a, 2″, 3″
2″	122.3	CH	5.23, *br t*, 7.2 Hz	-
3″	131.4	C		
4″	17.6	CH_3	1.88, *s*	2″, 3″
5″	25.5	CH_3	1.72, *s*	2″, 3″

1.4.35. Gerontaxanthone I (35, [34])



The structure of compound 35

The X-ray structure of compound 35

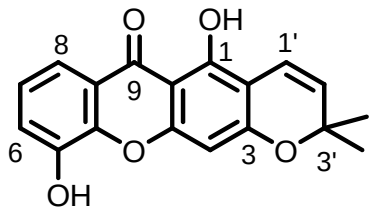
Boonnak, N. *et al*., *Acta Cryst*. **2006**, *E62*, o2034–o2036. [**35**]

1.4.35.1. Gerontaxanthone I (29). Brown-yellow needle-shaped single crystals were obtained from a $CHCl_3$-CH_3OH (4:1, v/v) solvent after several days. mp. 180-181 ^{o}C.; NMR spectral data ($CDCl_3$) see **Table 30**.

Table 30 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 35**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	158.9	C	13.61, *s*	1, 2, 9a
2	110.2	C		
3	161.4	C		
4	111.1	C		
5	131.0	C		
6	149.0	C		
7	112.60	CH	6.94, *d*, 8.7 Hz	5, 6, 8a
8	117.6	CH	7.70, *d*, 8.7 Hz	6, 9, 4b
9	180.8	C		
4a	153.3	C		
4b	144.8	C		
8a	113.8	C		
9a	103.0	C		
1′	21.6	CH_2	3.47, *d*, 6.9 Hz	1, 2, 3, 2′, 3′
2′	121.2	CH	5.24, *br t*, 6.9 Hz	1′, 4′, 5′
3′	135.9	C		
4′	17.9	CH_3	1.86, *br s*	2′, 3′
5′	25.9	CH_3	1.79, *br s*	2′, 3′
1″	41.6	C		
2″	154.6	CH	6.68, *dd*, 10.5, 17.7 Hz	1″, 4″, 5″
3″	106.6	CH_2	5.30, *dd*, 0.9, 17.7 Hz	1″, 2″
			5.15, *dd*, 0.9, 10.5 Hz	
4″	28.0	CH_3	1.69, *s*	4, 1″, 2″
5″	28.0	CH_3	1.69,*s*	4, 1″, 2″

1.4.36. Deoxyjacareubin (36, [36])



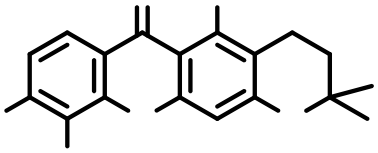
Structure of compound 36

1.4.36.1. Deoxyjacareubin **(36)**. Yellow powder. mp. 222-224 $^{\circ}$C.; UV ($CHCl_3$) λ_{max} (log ε) 260, 309 and 381 nm; IR (neat) ν_{max} 3400, 1640 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 31**.

Table 31 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 36**

Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow ^{13}C$)
1-OH	164.6	C	12.98, *s*	1, 2, 9a
2	103.6	C		
3	161.0	C		
4	99.8	CH	6.30, *s*	2, 3, 4a, 9a
5	144.3	C		
6	120.4	CH	7.33, *dd*, 1.8, 7.8 Hz	5, 4a
7	124.2	CH	7.26, *t*, 7.8 Hz	5
8	117.2	CH	7.78, *dd*, 1.8, 7.8 Hz	-
9	180.7	C		
4a	163.3	C		
4b	144.1	C		
8a	121.1	C		
9a	101.0	C		
1′	114.6	CH	6.79, *d*, 9.9 Hz	2, 3, 3′
2′	127.7	CH	5.65, *d*, 9.9 Hz	2, 3′
3′	78.3	C		
4′	28.2	CH_3	1.50, *s*	1′, 2′, 3′
5′	28.2	CH_3	1.50, *s*	1′, 2′, 3′

1.4.37. 3,4-dihydroxyjacareubin (37, [37])



Structure of compound 37

1.4.37.1. 3,4-dihydroxyjacareubin (37). Yellow powder. mp. 122-124 ^{o}C.; UV ($CHCl_3$) λ_{max} (log ε) 282, 338 and 380 nm; IR (neat) ν_{max} 3415, 1646 cm^{-1}; NMR spectral data ($CDCl_3$) see **Table 32**.

Table 32 ^{1}H, ^{13}C, HMQC and HMBC spectral data of **compound 37**

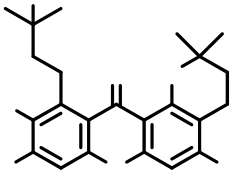
Position	^{13}C	DEPT	HMQC	HMBC ($^{1}H \rightarrow {}^{13}C$)
1-OH	160.1	C	13.38, *s*	1, 2, 9a
2	104.0	C		-
3	161.2	C		-
4	95.0	CH	6.43, *s*	2, 3, 4a, 9a
5	131.8	C		-
6	151.0	C		-
7	112.4	CH	6.89, *d*, 8.7 Hz	5, 6, 8a
8	116.9	CH	7.67, *d*, 8.7 Hz	6, 9
9	180.7	C		-
4a	155.8	C		-
4b	146.1	C		-
8a	114.0	C		-
9a	102.0	C		-
1′	15.9	CH_2	2.73, *br t*, 6.9 Hz	2, 3, 2′, 3′
2′	31.7	CH_2	1.87, *br t*, 6.9 Hz	2, 1′, 3′, 4′, 5′
3′	76.3	C		-
4′	26.6	CH_3	1.39, *s*	1′, 2′, 3′
5′	26.6	CH_3	1.39, *s*	1′, 2′, 3′

1.5. การทดสอบการออกฤทธิ์ทางชีวภาพ

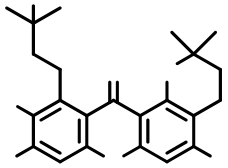
1.5.1. ทดสอบการออกฤทธิ์ต้านเชื้อแบคทีเรีย (Antibacterial activity)

The isolated compounds from roots and barks of *C. formosum* ssp. *pruniflorum* were tested against the microorganisms, *Bacillus substilis* (obtained from Department of Industrial Biotechnology, PSU), *Staphylococcus aureus* (TISTR517) (obtained from Microbial Resources Center (MIRCEN), Bangkok, Thailand), *Streptococcus faecalis*, *Salmonella typhi*, *Shigella sonei* and *Pseudomonas aeruginosa*. The last four microrganism were obtained from Department of Pharmacognosy and Botany, PSU.

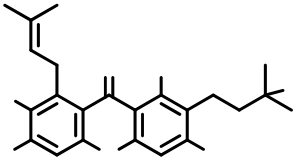
The antibacterial assay employed was the same as described in Boonsri et al [**14**]. Vancomycin, which was used as a standard, showed antibacterial activity of 75 μg/mL.



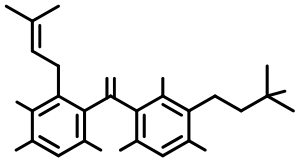
(**1**)



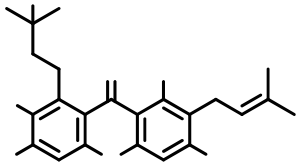
(**2**)



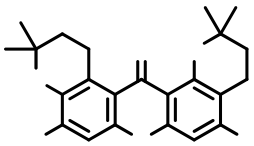
(**3**)



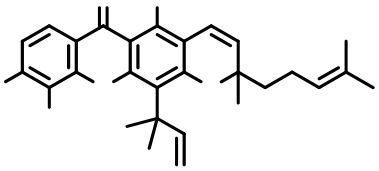
(**4**)



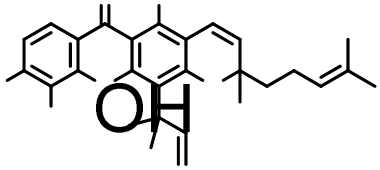
(**5**)



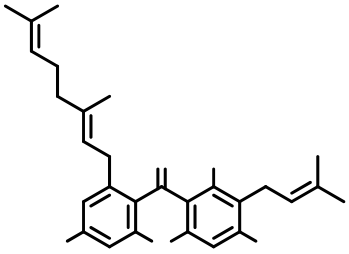
(**6**)



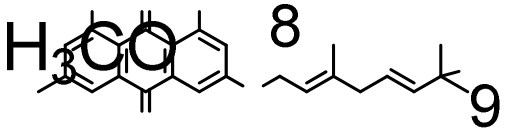
(**7**)



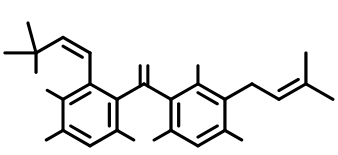
(**8**)



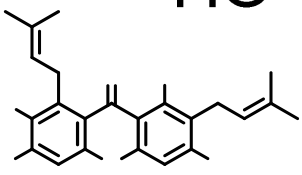
(**9**)



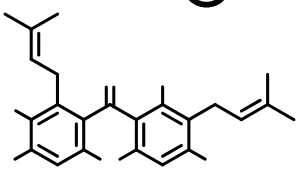
(**10**)



(**11**)



(**12**)



(**13**)

4" 3" 5"

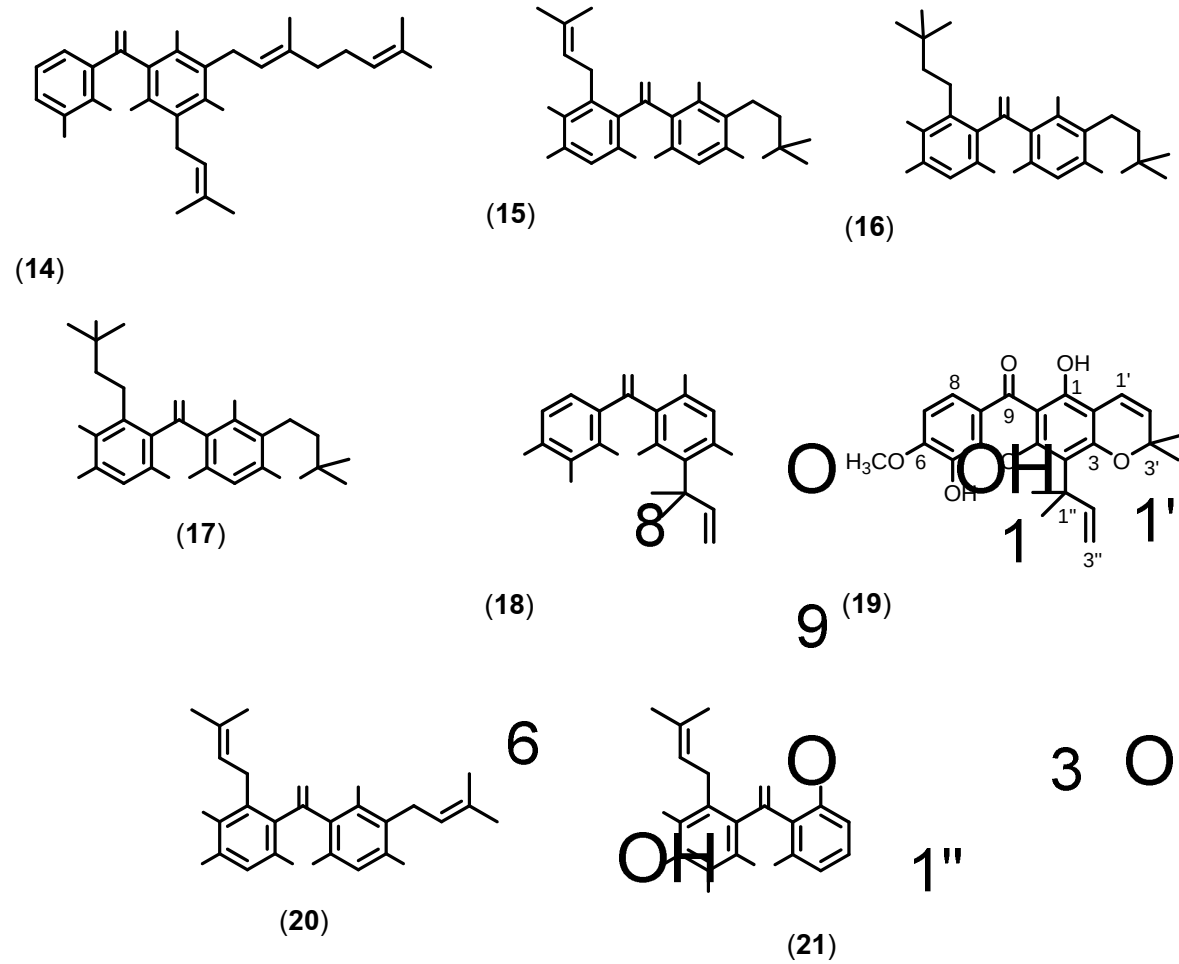


Fig. 1.5.1.1. The isolated compounds the roots of *C. formosum* spp. *Pruniflorum*

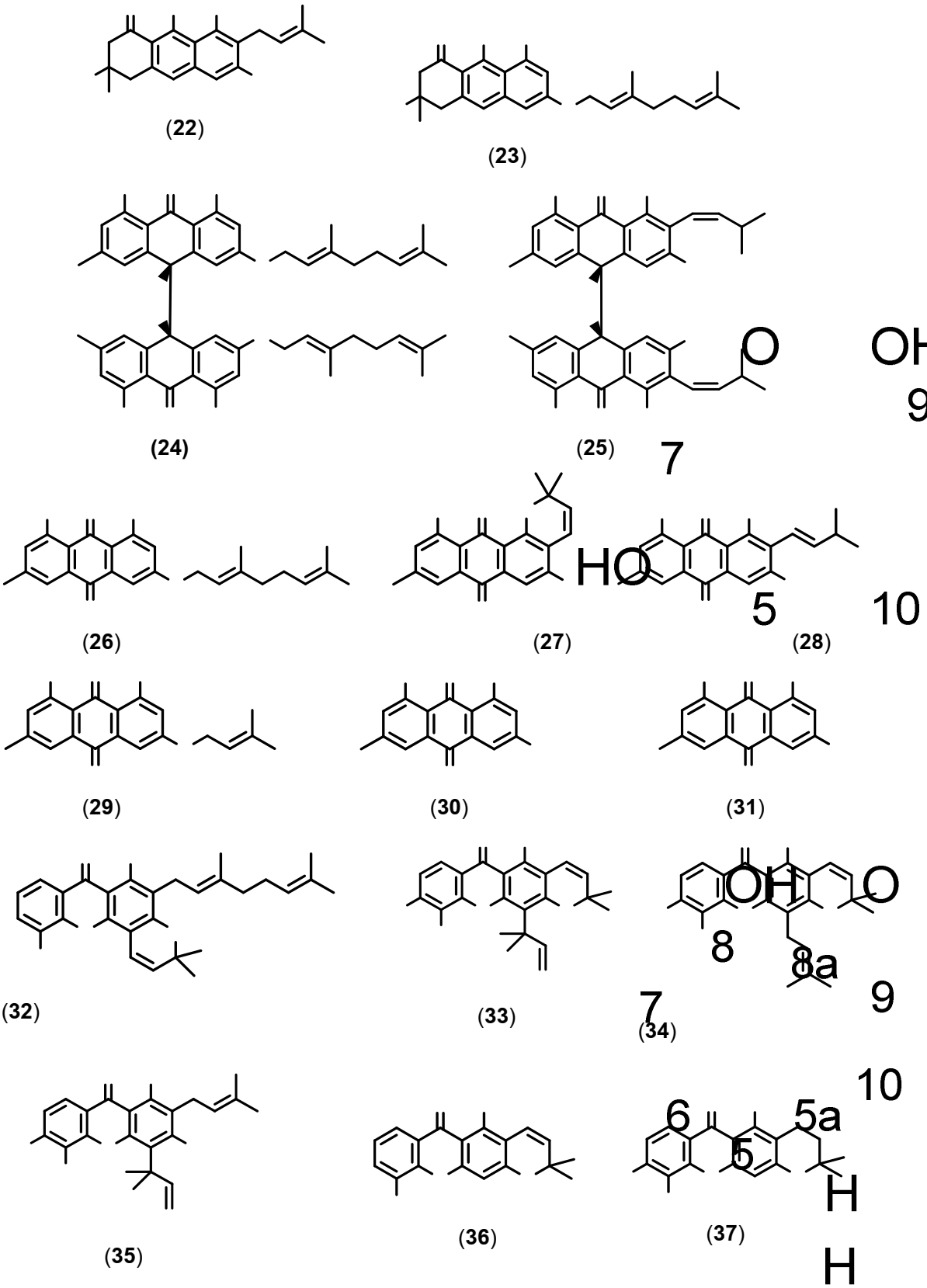


Fig. 1.5.1.2. The isolated compounds the barks of *C. formosum* ssp. *pruniflorum*

Table 33 Antibacterial activity (MIC, μg/ml) of **1**-**37**

No.	Gram-positive bacteria		Gram-negative bacteria			
	B. substilis	*S. aureus*	*S. faecalis*	*S. typhi*	*S. sonei*	*P. aeruginosa*
1	300	18.7	-	-	300	-
2	nt	nt	nt	nt	nt	nt
3	<1.1	<1.1	150	-	300	-
4	nt	nt	nt	nt	nt	nt
5	<1.1	<1.1	<1.1	-	300	18.7
6	300	9.3	4.6	-	300	37.5
7	nt	nt	nt	nt	nt	nt
8	nt	nt	nt	nt	nt	nt
9	nt	nt	nt	nt	nt	nt
10	300	75	150	-	300	-
11	75	18.7	-	-	300	-
12	18.7	<1.1	75	-	-	-
13	<1.1	<1.1	<1.1	-	18.7	18.7
14	18.7	37.5	-	-	-	-
15	nt	nt	nt	nt	nt	nt
16	nt	nt	nt	nt	nt	nt
17	9.3	<1.1	-	-	-	-
18	nt	nt	nt	nt	nt	nt
19	nt	nt	nt	nt	nt	nt
20	nt	nt	nt	nt	nt	nt
21	nt	nt	nt	nt	nt	nt
22	-	150	<1.1	9.4	2.3	-
23	-	75	<1.1	<1.1	2.3	-
24	-	-	-	-	-	-
25	-	-	-	-	-	-
26	-	-	-	-	-	-
27	-	-	-	-	-	-
28	-	-	-	-	-	-

29	-	-	-	-	-	-
30	-	-	-	-	-	-
31	-	-	-	-	-	-
32	nt	nt	nt	nt	nt	nt
33	4.6	4.6	2.3	9.6	-	-
34	<1.1	<1.1	<1.1	<1.1	-	9.3
35	<1.1	<1.1	4.6	37.5	<1.1	<1.1
36	4.6	<1.1	75	-	150	150
37	<1.1	<1.1	37.5	-	-	37.5

- = inactive compound

Nt = not tested

การวิเคราะห์ผลการต้านเชื้อแบคทีเรีย

จากผลการทดสอบฤทธิ์การต้านเชื้อแบคทีเรีย (Antibacterial activity) ในตารางที่ 33 (Table 33) พบว่าสารประกอบที่ 12 (β-mangostin) จะออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะกับ *S. aureus* (<1.1 µg/ml) เท่านั้น ส่วนสารประกอบที่ 3 (pruniflorone C) จะออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะ *B. substilis* (<1.1 µg/ml) และ *S. aureus* (<1.1 µg/ml) สารประกอบที่ 5 (pruniflorone E) จะออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะ *B. substilis* (<1.1 µg/ml) *S. aureus* (<1.1 µg/ml) และ *S. faecalis* (<1.1 µg/ml) จากในรูปที่ 1.5.1.3. (Fig. 1.5.1.3.) แสดงแผนผังการเกิดของสารประกอบที่ 1-5 จากสารประกอบที่ 12 (β-mangostin) ซึ่งจะได้ว่าหากสารประกอบที่ 12 (β-mangostin) เปลี่ยนไปเป็นสารประกอบที่ 3 และ 5 จะทำให้สารออกฤทธิ์ต้านเชื้อแบคทีเรียได้ดีขึ้น ส่วนในกรณีของสารประกอบที่ 12 (β-mangostin) เปลี่ยนไปเป็นสารประกอบที่ 1 2 และ 4 จะทำให้สารไม่แสดงออกฤทธิ์ต้านเชื้อแบคทีเรีย ซึ่งจะได้ว่าหากในโครงสร้างของสารประกอบมีสายโซ่ (side chain) ที่เป็น isoprenyl และ 3,3-dimethyl-propa-3-ol side chains อยู่ในโครงสร้างจะทำให้สารประกอบออกฤทธิ์ต้านเชื้อแบคทีเรียได้ดียิ่งขึ้น

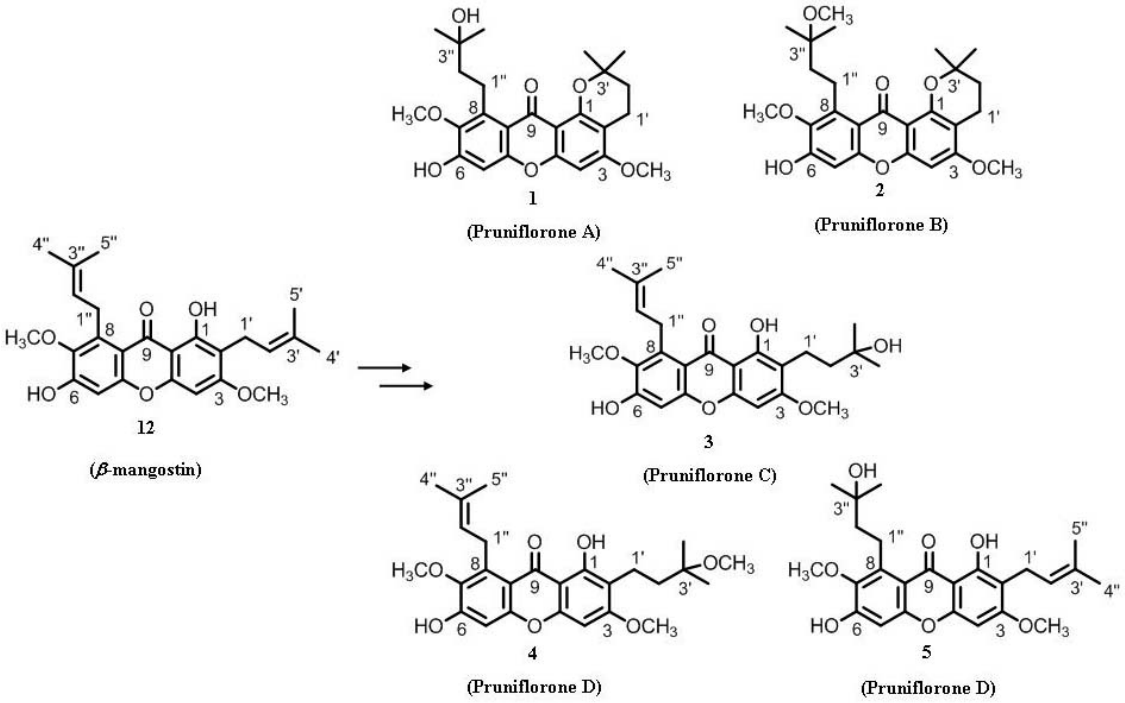


Fig 1.5.1.3. Chemical transformation of isolated compounds **1-5** and **12**

จากผลการทดสอบฤทธิ์การต้านเชื้อแบคทีเรีย (Antibacterial activity) ในตารางที่ 33 (**Table 33**) พบว่าสารประกอบที่ **13** (α-mangostin) จะออกฤทธิ์ต้านเชื้อแบคทีเรีย *B. substilis* (<1.1 µg/ml) *S. aureus* (<1.1 µg/ml) และ *S. faecalis* (<1.1 µg/ml) มีเฉพาะสารประกอบที่ **17** จะออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะ *S. aureus* (<1.1 µg/ml) เท่านั้น ส่วนในสารประกอบที่ **15** และ **16** จะไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรีย จากในรูปที่ **1.5.1.4.** (**Fig. 1.5.1.4.**) แสดงแผนผังการเกิดของสารประกอบที่ **15-17** จากสารประกอบที่ **13** (α-mangostin) ซึ่งจะได้ว่าหากสารประกอบที่ **13** (α-mangostin) เปลี่ยนไปเป็นสารประกอบที่ **15** และ **17** จะทำให้ไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรีย ส่วนในกรณีของสารประกอบที่ **13** (α-mangostin) เปลี่ยนไปเป็นสารประกอบที่ **17** จะทำให้สารแสดงออกฤทธิ์ต้านเชื้อแบคทีเรียต้านเชื้อแบคทีเรียจำเพาะ *S. aureus* ซึ่งจะได้ว่าหากในโครงสร้างของสารประกอบมีสายโซ่ (side chain) ที่เป็น chromane ring กับ isoprenyl และ chromane ring กับ 2-methoxy-2-methylbutane อยู่ในโครงสร้างจะทำให้สารไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรีย แต่หากมี สารประกอบมีสายโซ่ (side chain) ที่เป็น isoprenyl กับ 3,3-dimethyl-propa-3-ol จะทำสารยังแสดงการออกฤทธิ์ต้านเชื้อแบคทีเรีย

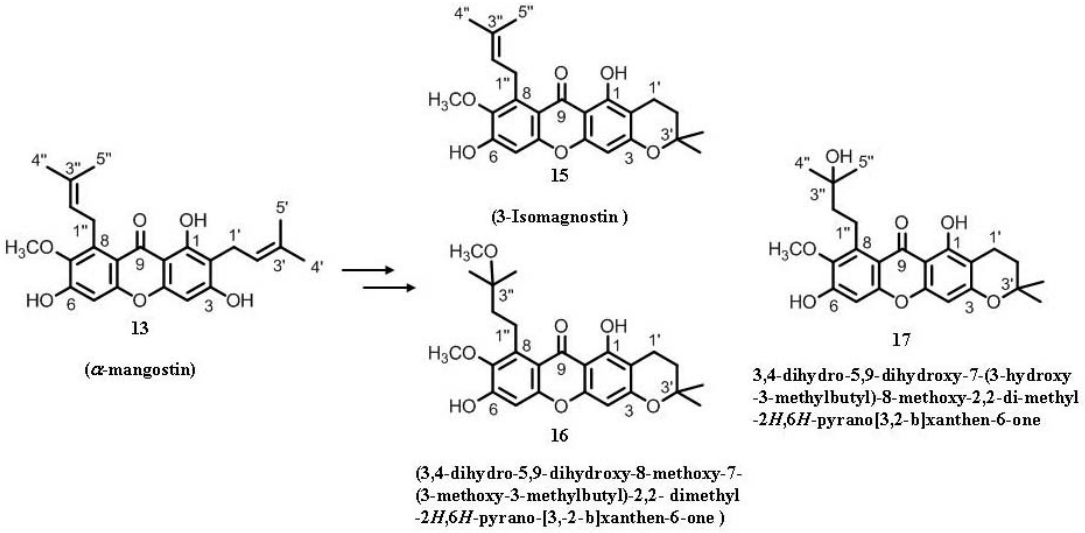


Fig 1.5.1.4. Chemical transformation of isolated compounds **13** and **15-17**

จากผลการทดสอบฤทธิ์การต้านเชื้อแบคทีเรีย (Antibacterial activity) ใน**ตารางที่ 33** (**Table 33**) พบว่าสารประกอบที่ **35** (Gerontoxanthone I) จะออกฤทธิ์ต้านเชื้อแบคทีเรียในช่วงกว้างทั้งแกรมบวกแบคทีเรีย (Gram-positive bacteria) *B. substilis* (<1.1 µg/ml) *S. aureus* (<1.1 µg/ml) และแกรมบวกแบคทีเรีย (Gram-negative bacteria) *S. sonei* (<1.1 µg/ml) และ *P. aureginosa* (<1.1 µg/ml) ส่วนในสารประกอบที่ **27** จะออกฤทธิ์ต้านเชื้อแบคทีเรียเฉพาะแกรมบวกแบคทีเรีย (Gram-positive bacteria) *B. substilis* (<1.1 µg/ml) *S. aureus* (<1.1 µg/ml) แต่ไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรียแกรมบวกแบคทีเรียเลย ส่วนในสารประกอบที่ **28** จะออกฤทธิ์ต้านเชื้อแบคทีเรียทั้งแกรมบวกแบคทีเรีย (Gram-positive bacteria) *B. substilis* (<1.1 µg/ml) *S. aureus* (<1.1 µg/ml)) และแกรมบวกแบคทีเรีย (Gram-negative bacteria) *S. faecalis* (<1.1 µg/ml) และ *S. typhi* (<1.1 µg/ml) จากใน**รูปที่ 1.5.1.5.** (**Fig. 1.5.1.5.**) แสดงแผนผังการเกิดของสารประกอบที่ **33** จากสารประกอบที่ **35** ซึ่งจะได้ว่าหากสารประกอบที่ **33** เปลี่ยนไปเป็นสารประกอบที่ **35** จะทำให้สารออกฤทธิ์ต้านเชื้อแบคทีเรียเฉพาะแกรมบวกแบคทีเรีย (Gram-positive bacteria) เท่านั้น

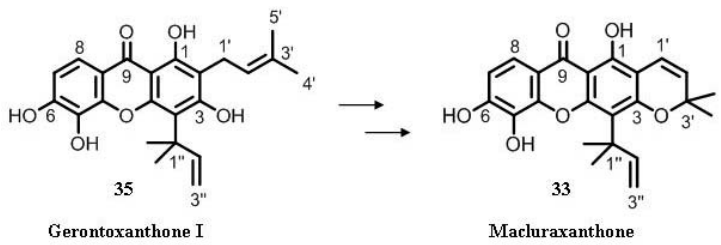


Fig. 1.5.1.5. Chemical transformation of isolated compounds **35** and **33**

จากผลการทดสอบฤทธิ์การต้านเชื้อแบคทีเรีย (Antibacterial activity) ใน**ตารางที่ 33** (**Table 33**) พบว่าสารประกอบที่ **22** (Vismone E) จะออกฤทธิ์ต้านเชื้อแบคทีเรียฉพาะแกรมลบแบคทีเรีย (Gram-negative bacteria) *S. faecalis* (<1.1 µg/ml) และ *S. sonei* (2.3 µg/ml) เท่านั้น ส่วนในสารประกอบที่ **24 27** และ **28** จะไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรียเลย จากใน**รูปที่ 1.5.1.6.** (**Fig. 1.5.1.6.**) แสดงแผนผังการเกิดของสารประกอบที่ **24 27** และ **28** จากสารประกอบที่ **22** ซึ่งจะได้ว่าหากสารประกอบที่ **22** เปลี่ยนไปเป็นสารประกอบที่ **24 27** และ **28** จะทำให้สารไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรียเลย

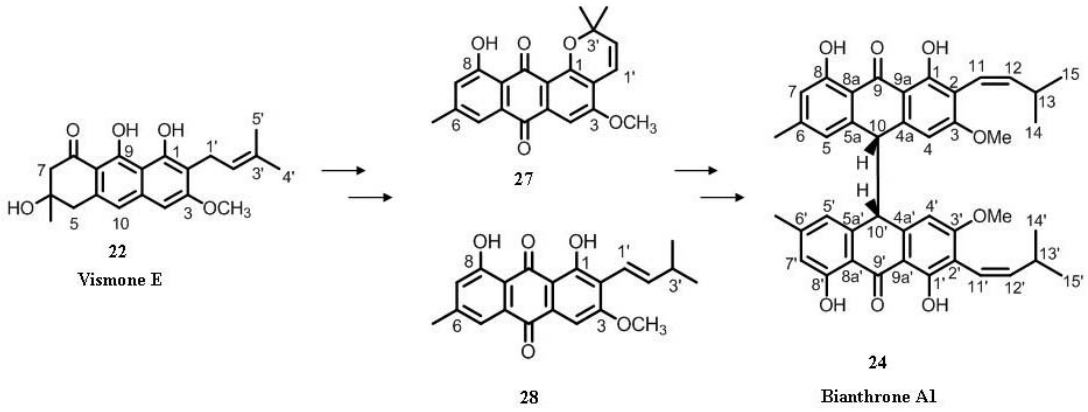


Fig. 1.5.1.6. Chemical transformation of isolated compounds **22, 24, 27** and **28**

จากผลการทดสอบฤทธิ์การต้านเชื้อแบคทีเรีย (Antibacterial activity) ใน**ตารางที่ 33** (**Table 33**) พบว่าสารประกอบที่ **23** (Vismone D) จะออกฤทธิ์ต้านเชื้อแบคทีเรียฉพาะแกรมลบแบคทีเรีย (Gram-negative bacteria) *S. faecalis* (<1.1 µg/ml) และ *S. typhi* (<1.1 µg/ml) เท่านั้น ส่วนในสารประกอบที่ **25** และ **26** จะไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรียเลย จากใน**รูปที่ 1.5.1.7.** (**Fig. 1.5.1.7.**) แสดงแผนผังการเกิดของสารประกอบที่ **25** และ **26** จากสารประกอบที่ **23** ซึ่งจะได้ว่าหากสารประกอบที่ **23** เปลี่ยนไปเป็นสารประกอบที่ **25** และ **26** จะทำให้สารไม่แสดงการออกฤทธิ์ต้านเชื้อแบคทีเรียเลย

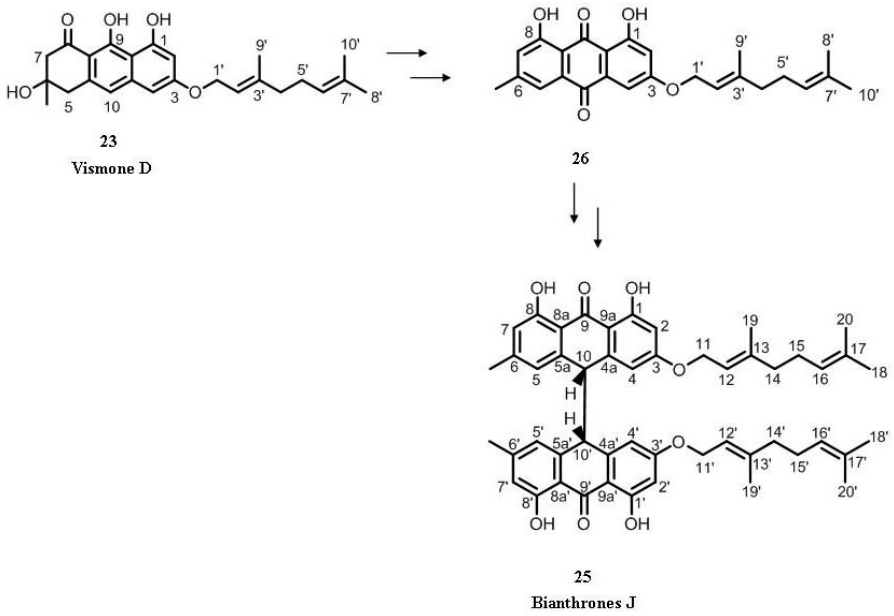


Fig. 1.5.1.7. Chemical transformation of isolated compounds **22, 24, 27** and **28**

1.5.2. ทดสอบการออกฤทธิ์ยับยั้งเซลล์มะเร็ง (Cytotoxicity)

The procedure for cytotoxic assay was performed by the sulphorhodamine B (SRB) assay as described by Skehan et al [**38**]. In this study, four cancer cell lines obtained from National Cancer Institute, Bangkok, Thailand, were used: MCF-7 (breast adenocarcinoma), KB (human oral cancer), HeLa (Human cervinal cancer) and HT-29 (colon cancer). Camptothecin, which was used as a standard, showed cytotoxic activity in the range of 0.2-2.0 μg/mL.

Table 34 In vitro cytotoxicity of **1**-**37**.

No.	Cell lines – IC_{50} (µg/ml)			
	MCF-7	**HeLa**	**HT-29**	**KB**
1	-	-	-	-
2	nt	nt	nt	nt
3	nt	nt	nt	nt
4	nt	nt	nt	nt
5	-	-	-	-
6	-	-	-	-
7	nt	nt	nt	nt
8	nt	nt	nt	nt
9	nt	nt	nt	nt
10	nt	nt	nt	nt
11	-	-	-	-
12	3.6	4.9	4.8	4.6
13	3.7	3.2	4.5	3.2
14	nt	nt	nt	nt
15	nt	nt	nt	nt
16	nt	nt	nt	nt
17	nt	nt	nt	nt
18	nt	nt	nt	nt
19	nt	nt	nt	nt
20	nt	nt	nt	nt
21	nt	nt	nt	nt
22	-	-	-	4.0
23	0.7	0.6	-	0.2
24	-	-	-	-
25	-	-	-	-
26	-	-	-	-
27	-	-	-	-
28	-	-	-	-
29	-	-	-	-
30	-	-	-	-

- = inactive

nt = not tested

Table 34 In vitro cytotoxicity of **1**-**39** (continued)

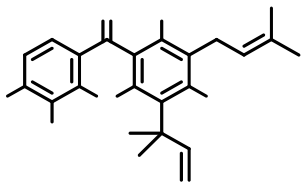
No.	Cell lines – IC_{50} (μg/ml)			
	MCF-7	**HeLa**	**HT-29**	**KB**
31	-	-	-	-
32	nt	nt	nt	nt
33	nt	nt	nt	nt
34	>25.0	4.7	6.0	2.7
35	0.6	0.7	0.7	0.6
36	nt	nt	nt	nt
37	>5.0	3.4	>5.0	>5.0

- = inactive

nt = not tested

การวิเคราะห์ผลการยับยั้งเซลล์มะเร็ง

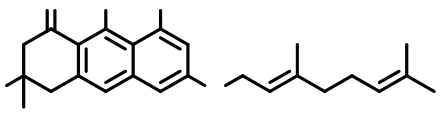
จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 34** (**Table 34**) พบว่าสารประกอบที่ **35** (Gerontoxanthone I) ออกฤทธิ์การยับยั้งเซลล์มะเร็งในช่วงกว้างทั้ง MCF-7 (0.6 μg/ml) HeLa (0.7 μg/ml) HT-29 (0.7 μg/ml) และ KB (0.6 μg/ml)



35

Gerontoxanthone I

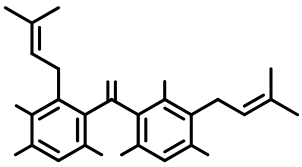
จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 34** (**Table 34**) พบว่าสารประกอบที่ **23** (Visomone D) ออกฤทธิ์การยับยั้งเซลล์มะเร็งในช่วงกว้างทั้ง MCF-7 (0.7 μg/ml) HeLa (0.6 μg/ml) และ KB (0.2 μg/ml)



23

Vismone D

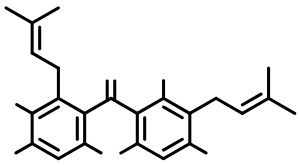
จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 34** (**Table 34**) พบว่าสารประกอบที่ **12** (β-mangostin) ออกฤทธิ์การยับยั้งเซลล์มะเร็งในช่วงกว้างทั้ง MCF-7 (3.6 μg/ml) HeLa (4.9 μg/ml) HT-29 (4.8 μg/ml) และ KB (4.6 μg/ml)



12

(β-mangostin)

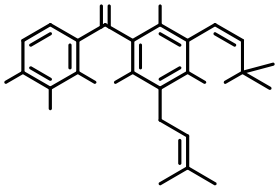
จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 34** (**Table 34**) พบว่าสารประกอบ**13** (α-mangostin) ออกฤทธิ์การยับยั้งเซลล์มะเร็งในช่วงกว้างทั้ง MCF-7 (3.7 μg/ml) HeLa (3.2 μg/ml) HT-29 (4.5 μg/ml) และ KB (3.2 μg/ml)



13

(α-mangostin)

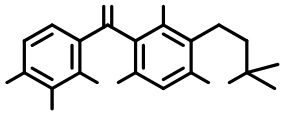
จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 34** (**Table 34**) พบว่าสารประกอบ**34** (Xanthone V_1) ออกฤทธิ์การยับยั้งเซลล์มะเร็งในช่วงกว้างทั้ง HeLa (4.7 μg/ml) HT-29 (6.0 μg/ml) และ KB (2.7 μg/ml)



34

(Xanthone V_1)

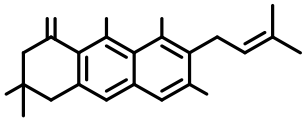
จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 34** (**Table 34**) พบว่าสารประกอบ**37** (3,4-dihydroxyjacareubin) ออกฤทธิ์การยับยั้งเซลล์มะเร็งในช่วงกว้าง ทั้ง MCF-7 (>5.0 μg/ml) HeLa (3.4 μg/ml) HT-29 (>5.0 μg/ml) และ KB (>5.0 μg/ml)



37

(3,4-dihydroxyjacareubin)

จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 34** (**Table 34**) พบว่าสารประกอบที่ **22** (Visomone E) ออกฤทธิ์การยับยั้งเซลล์มะเร็งเฉพาะ KB (4.0 μg/ml)



22

Vismone E

เอกสารอ้างอิง

1[1]. Munekazu, L., Hideki, T., Toshiyuki, T., Tetsuro, I. & Fujio, A. *TYKYDS Journal* **1996**, *38*, 409-414.

1[2]. Seo, E. K., Kim, N. C., Wani, M. C., Wall, M. E., Navarro, H. A., Burgess, J. P., Kawanishi, K., Kardono, L. B. S., Riswan, S., Rose, W. C., Fairchild, C. R., Farnsworth, N. R., Kinghorn A. D. *J. Nat. Prod*., **2002**, *65*, 299-305.

1[3]. Pattanaprateeb, P., Nijsiri, R., Cordell G. A. *Planta Medica* **2005**, *71*(*2*), 181-183.

1[4]. Pinto, M., Nascimento, M. S. J., Gonzalez, M. J., Mondranondra, I. O. *Pharmaceutical and Pharmacological Letters* **1997**, *7*(*2*/*3*), 128-130.

1[5]. Bennett, G. J. *et al*., *Phytochemistry* **1995**, *32*(*5*), 1245-1251.

1[6]. Sia, G. L. *et al*., *Phytochemistry* **1995**, *38*(*6*), 1521-1528.

1[7]. Linuma, M. *et al*., *Phytochemistry* **1996**, *42*(*4*), 1195-1198.

1[8]. Kijjoa, A. *et al*., *Phytochemistry* **1998**, *49*(*7*), 2159-2162.

1[9]. Nguyen, L. H. D. *et al*., *Phytochemistry* **1998**, *50*, 471-476.

1[10]. Boonnak, N., Karalai, C., Chantrapromma, S., Ponglimanont, C., Fun, H-K. Kanjana-Opas, A., Laphookhieo, S. *Tetrahedron* **2006**, *62*, 8850–8859.

1[11]. Deachathai, S., Mahabusarakam,W., Phongpaichit, S., Taylor, W. C., Zhang, Y. J., Yang, C. R. *Phytochemistry* **2006**, 67, 464–469.

1[12]. Mahabusarakam, W.; Wiriyachitra, P.; Taylor, W. C. *J. Nat. Prod*. **1987**, 50, 474-478.

1[13]. Chantrapromma, S., Boonnak, N., Fun, H-K., Karalai, C. *Acta Cryst*. **2006**, *E62*, o360–o362.

1[14]. Boonsri, S., Karalai, C., Ponglimanont, C., Kanjana-Opas, A., Chantrapromma, K. *Phytochemistry* **2006**, *67*, 723-727.

1[15]. Dutta, P. K., Sen, A. K., Sarkar, K. K., Banerji, N. *Indian J. Chem., Sect. B*: *Org. Chem. Incl. Med. Chem*. **1987**, *26B*, 281–282.

1[16]. Kobayashi, M., Mahmud, T., Yoshioka, N., Shibuya, H., Kitagawa, I. *Chem. Pharm. Bull*. **1997**, *45*, 1615–1619.

1[17]. Gunasekera, S. P., Selliah, S., Sultanbawa, M. *U. S. J. Chem. Soc., Perkin Trans. 1*. **1975**, 1539–1544.

1[18]. Deachathai, S., Mahabusarakam,W., Phongpaichit, S., Taylor, W. C. *Phytochemistry* **2005**, 66, 2368-2375.

1[19]. Boonnak, N. Chantrapromma, S., Fun, H-K., Karalai, C. *Acta Cryst*. **2005**, *E61*, o4376–o4378

1[20]. Botta, B., Delle Monache, F., Delle Monache, G., Marini Bettolo, FG. B., Oguakwa, J. U. *Phytochemistry* **1983**, *22*, 539-5421.

1[21]. Sibanda, S., Nyanyira, C., Nicoletti, M., Galeffi, C. *Phytochemistry* **1993**, *34*, 1650.

1[22]. Botta, B., Delle Monache, F., Delle Monache, G., Marini Bettolo, G. B., Msonthi, J. D. *Phytochemistry* **1985**, *24*, 827.

1[23]. Boonnak, N., Karalai, C., Chantrapromma, S., Ponglimanont, C., Kanjana-Opas, A., Chantrapromma, K., Fun, H-K. *Can. J. Chem*. **2007**, *85*, 341-345.

1[24]. Delle Monache, F., Ferrari, F., Marini-Bettolo, G. B., Maxfield, P., Cerrini, S., Fedeli, W., Gavuzzo, E., Vaciago, A. *Gazz. Chim. Ital*. **1979**, *109*, 301-310.

1[25]. Goncalves, M. L. S., Mors, W. B. *Phytochemistry* **1981**, *20*, 1947-1950.

1[26]. Ritchie, E., Taylor, W. C. *Tetrahedron Lett*. **1964**, *23*, 1431-1436.

1[27]. Kalidhar, S. B. *Phytochemistry* **1989**, *28*, 2455–2458.

1[28]. Cohen, P. A., Towers, G. H. N. *Phytochemistry* **1995**, *40*, 911–915.

1[29]. Delle Monache, F., Botta, B., Nicoletti, M., De Barros Coelho, J. S., Lyra, F. D., De Andrade Lyra, F. D. *J. Chem. Soc., Perkin Trans. I*. **1981**, 484–488.

1[30]. Fun, H-K., Ng, S-L., Razak, I. A., Boonnak, N., Chantrapromma, S. *Acta Cryst*. **2006**, *E62*, o130–o132.

1[31]. Boonnak, N,. Chantrapromma, S., Fun, H-K., Karalai, C. *Analytical Sciences* **2008**, *24*, 1-2.

1[32]. Botta, B., Delle Monache, G., Delle Monache, F., Marini Bettolo, G. B., Menichini, F. *Phytochemistry* **1986**, *25*, 1217-1219.

1[33]. Chantrapromma, S., Boonnak, N., Fun, H-K. Anjum, S., Atta-ur-Rahman. *Acta Cryst*. **2005**, *E61*, o2136–o2138

1[34]. Chang, C.-H., Lin, C.-C., Kawata, Y., Hattori, M., Namba, T. *Phytochemistry* **1989**, *28*, 2823–2826.

1[35]. Boonnak, N., Chantrapromma, S., Fun, H-K. *Acta Cryst*. **2006**, *E62*, o2034–o2036

1[36]. Rocha, L., Marston, A., Kaplan, M. A. C., Stoeckli-Evans, H., Thull, U., Testa, B., Hostettmann, K. *Phytochemistry* **1994**, *36*, 1381–1385.

1[37]. King, F. E., King, T. J., Manning, L. C. *J. Chem. Soc*. **1953**, 3932–3937.

1[38]. Skehan, P., Storeng, R., Scudiero, D., Monks, A., McMahon, J., Vistica, D., Warren, J. T., Bokesch, H., Kenney, S., Boyd, M. R. *J. Natl. Cancer Inst*. **1990**, *82*, 1107–1112.

2. การสกัดและแยกสารจากต้นกำจาย

การทดลอง

2.1. General experimental procedures

Melting points were determined on the Fisher-John melting point apparatus. Optical rotations were measured on a JASCO P-1020 digital polarimeter. UV and IR spectra were recorded on SPECORD S 100 (Analytikjena) and Perkin-Elmer FTS FT-IR spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz Varian UNITY INOVA and/or 300 MHz Bruker FTNMR Ultra Shield^{TM} spectrometers in $CDCl_3$ or CD_3OD with TMS as the internal standard. Chemical shifts are reported in δ (ppm) and coupling constants (*J*) are expressed in hertz. EI and HREI mass spectra were measured on a Kratos MS 25 RFA spectrometer. Quick column chromatography (QCC) and column chromatography (CC) were carried out on silica gel 60 F_{254} (Merck) and silica gel 100 (Merck), respectively.

2.2. Plant material

Air-dried twigs and stems of *C. digyna* were collected in 2005 from from Songkhla province in the southern part of Thailand. Identification was made by Prof. Puangpen Sirirugsa, Department of Biology, Faculty of Science, Prince of Songkla University and a plant sample was deposited at Prince of Songkla University Herbarium.

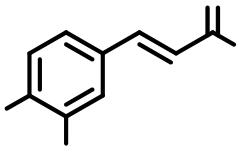
2.3. Extraction and Isolation

1.3.1. Extraction and Isolation of the crude CH_2Cl_2 of the twigs and stems of *C. digyna*.

Air-dried twigs and stems of *C. digyna* were extracted with CH_2Cl_2 (2 × 20 L, for 5 days) at room temperature. The crude CH_2Cl_2 extracts were evaporated under reduced pressure to afford a brownish crude (14.52 g) extract. The crude extract was subjected to QCC on silica gel using hexane as the first eluent and then increasing polarity with acetone, respectively, to give 12 fractions (F1-F12). Rechromatography of the all fractions yielded **4** compounds including of the (*E*)-3-(3-hydroxy-4-methoxyphenyl)acrylaldehyde (**38,** [**6**]) Bonducillin (**39,** [**7**,**8**]) 8-methoxy-bonducellin (**40**, [**9**]) and Intricatinol (**41,** [**10**,**11**]).

2.4. Characterization of isolated compounds

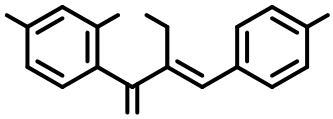
2.4.1. (*E*)-3-(3-hydroxy-4-methoxyphenyl)acrylaldehyde (38, [6])



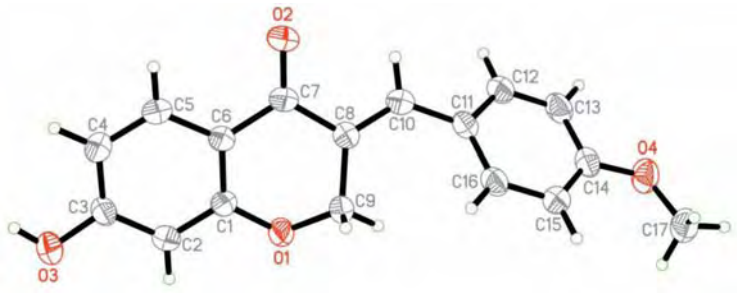
The structure of compound **38**

2.4.1.1. (*E*)-3-(3-hydroxy-4-methoxyphenyl)acrylaldehyde (**38**) ^{1}H NMR spectral data (300, MHz, $CDCl_3$) ; 9.65 (*d*, *J* = 7.5 Hz, H-3′), 7.41 (*d*, *J* = 15.9 Hz, H-1′), 7.13 (*dd*, *J* = 8.1, 1.5 Hz, H-6), 7.07 (*d*, *J* = 1.5 Hz, H-2), 6.96 (*d*, *J* = 8.1 Hz, H-5), 6.60 (*dd*, *J* = 15.9, 7.5 Hz, H-2′), 3.95 (*s*, 4-OCH_3); ^{13}C NMR spectral data (300, MHz, $CDCl_3$) ; 193.6 (C-3′), 153.1 (C-1′), 148.9 (C-3), 146.9 (C-4), 126.7 (C-1), 126.4 (C-2′), 124.1 (C-2), 114.9 (C-5), 109.5 (C-6), 56.0 (4-OCH_3)

2.4.2. Bonducillin (39, [7])



The structure of compound **39**

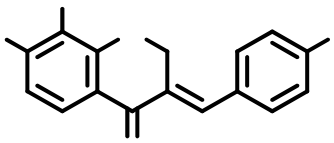


The X-ray structure of compound **39**

Boonsri, S. *et al*., Acta Cryst, **2005**, E61, o3930–o3932. [**8**]

2.4.2.1. Bonducillin (**39**). Colorless needle single crytals were obtained from a $CHCl_3$-CH_3OH (4:1, v/v) solvent after several days. m.p. = 215-217 C°; UV (CH_3OH) λ_{max} 318 and 358 nm; IR (KBr) v_{max} 1655, 1615 cm^{-1}; ^1H NMR spectral data (300, MHz, CD_3OD+$CDCl_3$) ; 7.87 (*d*, *J* = 8.7 Hz, H-5), 7.78 (*br s*, H-9), 7.27 (*d*, *J* = 8.7 Hz, H-2′ and H-6′), 6.97 (*d*, *J* = 8.7 Hz, H-3′ and H-5′), 6.56 (*dd*, *J* = 8.7, 2.4 Hz, H-6), 6.35 (*d*, *J* = 2.4 Hz, H-8), 5.33 (*d*, *J* = 1.8 Hz, H-2), 3.86 (*s*, 4′-OCH_3); ^{13}C NMR spectral data (300, MHz, CD_3OD+$CDCl_3$) ; 181.6 (C-4), 164.6 (C-7), 163.1 (C-8a), 160.5 (C-4′), 136.7 (C-9), 131.9 (C-2′/C-6′), 129.9 (C-5), 128.9 (C-3), 127.1 (C-1′),114.2 (C-3′/C-5′), 114.9 (C-4a), 111.2 (C-6), 102.8 (C-8), 67.8 (C-2)

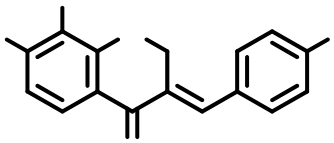
2.4.3. 8-methoxybonducellin (40, [9])



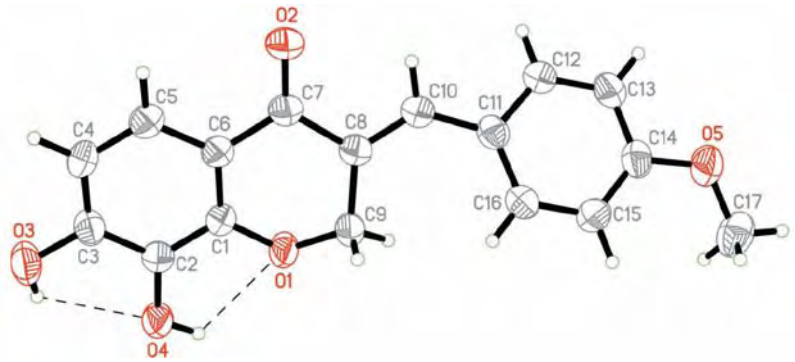
The structure of compound **40**

2.4.3.1. 8-methoxybonducellin (40) Yellow powder. m.p. = 184-186 C°; UV (CH_3OH) λ_{max} 318 and 358 nm; IR (KBr) v_{max} 1655, 1615 cm^{-1}; ^1H NMR spectral data (300, MHz, CD_3OD+$CDCl_3$) ; 7.83 (*br s*, H-9), 7.74 (*d*, *J* = 8.7 Hz, H-5), 7.28 (*d*, *J* = 8.4 Hz, H-2′ and H-6′), 6.97 (*d*, *J* = 8.7 Hz, H-3′ and H-5′), 6.70 (*d*, *J* = 8.7 Hz, H-6), 5.43 (*d*, *J* = 1.8 Hz, H-2), 3.93 (*s*, 8-OCH_3), 3.87 (*s*, 4′-OCH_3); ^{13}C NMR spectral data (300, MHz, CD_3OD+$CDCl_3$) ; 181.0 (C-4), 160.7 (C-4′), 155.1 (C-7), 137.1 (C-9), 134.3 (C-8), 131.9 (C-2′/C-6′), 128.5 (C-3), 127.1 (C-1′), 124.2 (C-5), 116.7 (C-4a), 114.3 (C-3′, C-5′), 109.8 (C-6), 68.3 (C-2), 61.3 (8-OCH_3), 55.4 (4′-OCH_3)

2.4.4. Intricatinol (41, [10])



The structure of compound **41**



The X-ray structure of compound **41**

Chantrapromma, S., *et al*., *Acta Cryst*. **2006**, E62, o1254-o1256. [**11**]

2.4.4.1. Intricatinol (41). Yellow single crytals were obtained from a CH_2Cl_2-CH_3OH (4:1, v/v) solvent after several days. m.p. = 184-186 C°; UV (CH_3OH) λ_{max} 318 and 358 nm; IR (KBr) ν_{max} 1655, 1615 cm^{-1}; ^1H NMR spectral data (300, MHz, CD_3OD+$CDCl_3$) ; 7.85 (*br s*, H-9), 7.58 (*d*, *J* = 9.0 Hz, H-5), 7.27 (*d*, *J* = 8.4 Hz, H-2′ and H-6′), 6.98 (*d*, *J* = 8.7 Hz, H-3′ and H-5′), 6.70 (*d*, *J* = 9.0 Hz, H-6), 5.86 (*br s*, 7-OH), 5.43 (*d*, *J* = 1.8 Hz, H-2), 5.34 (*br s*, 8-OH), 3.87 (*s*, 4′-OCH_3)

2.5. การทดสอบการออกฤทธิ์ทางชีวภาพ

2.5.1. การทดสอบการออกฤทธิ์ต้านเชื้อแบคทีเรีย (Antibacterial activity)

The isolated compounds from twigs and stems of *C. digyna* were tested against the microorganisms, *Bacillus substilis* (obtained from Department of Industrial Biotechnology, PSU), *Staphylococcus aureus* (TISTR517) (obtained from Microbial

Resources Center (MIRCEN), Bangkok, Thailand), *Streptococcus faecalis*, *Salmonella typhi*, *Shigella sonei* and *Pseudomonas aeruginosa*. The last four microrganism were obtained from Department of Pharmacognosy and Botany, PSU. The antibacterial assay employed was the same as described in Boonsri et al. [**12**] Vancomycin, which was used as a standard, showed antibacterial activity of 75 μg/mL.

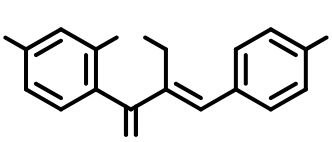
Table 35 Antibacterial activity (MIC, μg/ml) of **38-41**

No.	Gram-positive bacteria		Gram-negative bacteria			
	B. substilis	*S. aureus*	*S. faecalis*	*S. typhi*	*S. sonei*	*P. aeruginosa*
38	9.3	37.5	150	-	-	37.5
39	<1.1	-	-	-	-	-
40	18.7	150	150	-	-	37.5
41	4.6	4.6	37.5	-	-	75

- = inactive compound

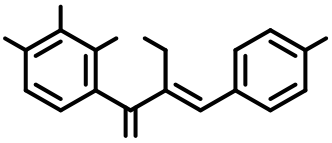
การวิเคราะห์ผลการต้านเชื้อแบคทีเรีย

จากผลการทดสอบฤทธิ์การต้านเชื้อแบคทีเรีย (Antibacterial activity) ใน**ตารางที่ 35** (**Table 35**) พบว่าสารประกอบที่ **39** (Bonducillin) จะออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะกับ *B. substilis* (<1.1 μg/ml) เท่านั้น ส่วนสารประกอบที่ **41** (Intricatinol) จะออกฤทธิ์ต้านเชื้อแบคทีเรียทั้ง *B. substilis* (4.6 μg/ml) และ *S. aureus* (4.6 μg/ml)



39

(Bonducillin)



41

(Intricatinol)

เอกสารอ้างอิง

2[1]. Linn, *et al*., *J. Nat. Prod*. **2005**, *68*, 706-710.

2[2]. Ragasa, *et al*., 2002, *J. Nat. Prod*. **2002**, *65*, 1107-1110.

2[3]. Reddy, *et al*., *Fitoterapia* **2003**, *74*, 600-602.

2[4]. Hong-Xi, *et al*., *Phytotherapy Research* **2004**, *18*(*8*), 647-651.

2[5]. Hiroshi, *et al*., *Planta Medica* **1977**, *31*(*3*), 214-220.

2[6]. Barakat, H. H.; Nawwar, M. A. M.; Buddrusa, J.; Linscheida, M. *Phytochemistry* **1987**, *26*, 1837-1838.

2[7]. McPherson, D.D., Cordell, G.A., Soejarto, D.D., Pezzuto, J.M., Fong, H.H.S., *Phytochemistry* **1983**, *22*, 2835–2838.

2[8]. Boonsri, S., Chantrapromma, S., Fun, H-K., Karalai, C., Kanjana-Opas, A., Anjumd, S. *Acta Cryst*, **2005**, *E61*, o3930-o3932

2[9]. Chen, P., Yang, J-S. *Chem. Pharm. Bull.* **2007***, 55*(*4*), 655-657.

2[10]. Wall M. E., Wani M. C., Manikumar G., Talor H., Mcgivney N., *J. Nat. Prod.*, **1989**, *52*, 774-778.

2[11]. Chantrapromma, S., Boonsri, S., Fun, H-K., Anjum, S., Kanjana-Opas, A. *Acta Cryst*. **2006**, *E62*, o1254-o1256.

2[12]. Boonsri, S., Karalai, C., Ponglimanont, C., Kanjana-Opas, A., Chantrapromma, K. *Phytochemistry* **2006**, *67*, 723-727.

3. การสกัดและแยกสารจากต้นโพทะเล

การทดลอง

3.1. General experimental procedures

Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. UV spectra were measured with a SPECORD S100 spectrophotometer (Analytikjena). The IR spectra were measured with a FTS 165 FT-IR Perkin Elmer spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using Bruker Avance 300 MHz spectrometers. Optical rotation was measured in MeOH solution at the sodium D line (589 nm) on JASCO D-1020 polarimeter. The EI-MS and HREIMS mass spectra were obtained from a Micromass LCT mass spectrometer. Quick column chromatography (QCC) and column chromatography (CC) were carried out on silica gel 60 F_{254} (Merck) and silica gel 100, respectively. Precoated plates of silica gel 60 GF_{254} were used for analytical purposes.

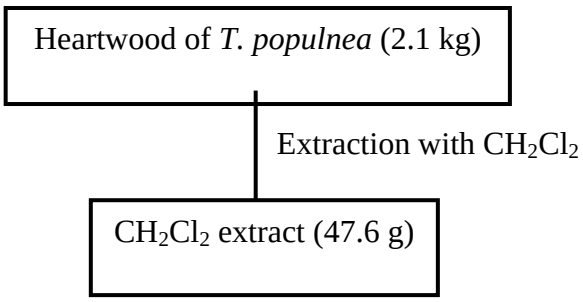
3.2. Plant material

The fresh stem of *T. populnea* was collected from Suratthani Province in the Southern part of Thailand in 2005. The plant was identified by Prof. Puangpen Sirirugsa and a voucher specimen (no SB 01-001) has been deposited at the Herbarium of Department of Biology, Prince of Songkla University (PSU).

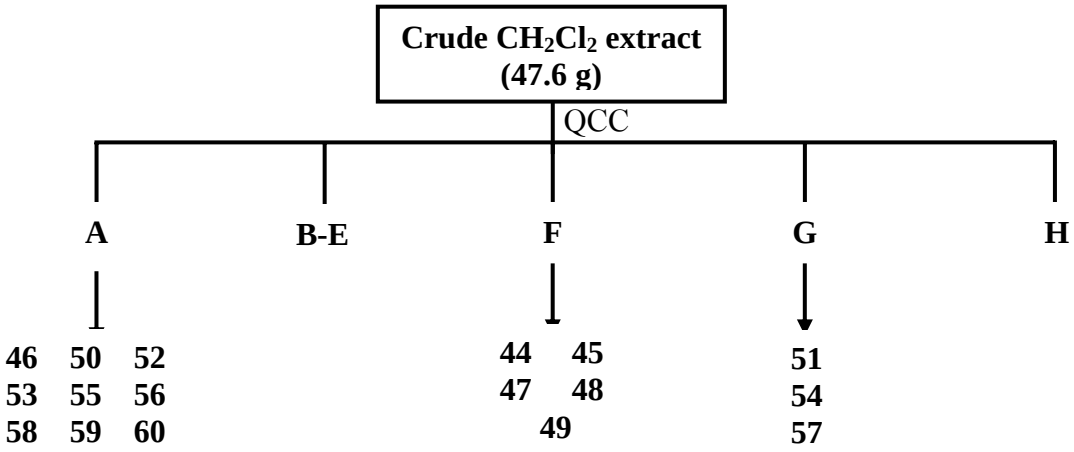
3.3. Extraction and Isolation

3.3.1. Extraction and isolation of the crude CH_2Cl_2 from the heartwood of *T. populnea*

The air-dried heartwood of *T. populnea* (2.10 kg) was extracted with CH_2Cl_2 over a period of 5 days at room temperature. Evaporation of the solvent under reduced pressure furnished a dark residue (37.5 g).



Scheme 3.3.1a. Extraction the heartwodd of *T. populnea*



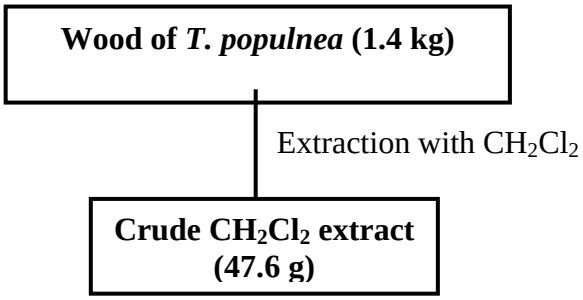
Scheme 3.3.1b. Isolation of compounds **44-60** from the heartwood of *T. populnea*

The crude dichloromethane extract was subjected to QCC on silica gel, eluting with CH_2Cl_2 and separated into 8 fractions (A-H). Fraction A was purified by QCC using a gradient of hexane-acetone to afford nine subfractions (A_1-A_9). Subfraction A_2 and A_3 were combined and purified by QCC using a gradient of acetone-hexane as a mobile phase to give **56** (10.2 mg), **58** (8.3 mg) and **50** (2.5 mg), respectively. Subfraction A_5 and A_6 were combined and then purified by QCC with a gradient system of acetone-hexane to afford **46** (2.0 mg) and **53** (2.0 mg). Subfraction A_7 and A_8 were separately purified by QCC using a gradient of CH_2Cl_2-hexane as a mobile phase to yield **60** (4.0 mg) from A_7 and **55** (4.5 mg), **52** (18.1 mg) and **59** (3.3 mg) from A_8. Fraction F was separated by QCC with a gradient system of increasing polarity (CH_2Cl_2-hexane) to afford nine subfractions (F_1- F_9). Subfraction F_4 was further purified by QCC using a gradient of CH_2Cl_2- hexane to give **44** (10.0 mg) and **45** (14.9 mg). Subfraction F_6 was

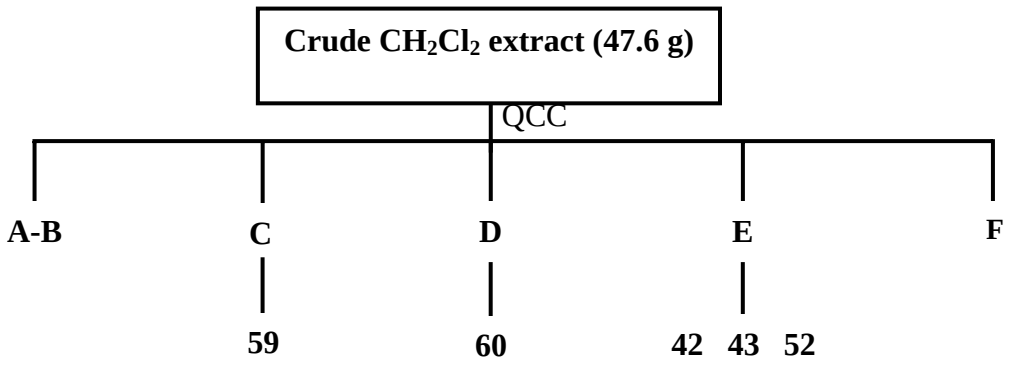
subjected to QCC using 20% acetone in hexane to afford four subfractions (F_{6A}-F_{6D}). Subfraction F_{6B} was further separated by QCC with a solvent system of 2% acetone-$CHCl_3$ to afford **47** (12.6 mg). Subfraction F_{6C}, upon standing overnight at room temperature gave yellow solid of **49** (4.2 mg) and the mother liquor gave **7** (4.1 mg). Fraction G was purified by QCC with a gradient of acetone-CH_2Cl_2 to give five subfractions (G_A-G_E). Subfraction G_A was subjected to precoated TLC using 50% CH_2Cl_2-hexane as a mobile phase (4 runs) to give **57** (5.1 mg). Subfraction G_C gave **51** (93.0 mg). Fraction H, upon standing overnight at room temperature gave red-brown crystal of **54** (30.5 mg).

3.3.2. The extraction and isolation of compounds from the wood of *T. populnea*

The air-dried wood of *T. populnea* (1.40 kg) was extracted with CH_2Cl_2 over a period of 5 days at room temperature. Evaporation of the solvent under reduced pressure furnished a dark-green residue (10.2 g).



Scheme 3.3.2a. Extraction of wood of *T. populnea*

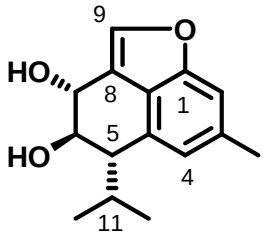


Scheme 3 Isolation of compounds **42**, **43**, **52**, **59** and **60** from the wood of *T. populnea.*

This was subjected to QCC on silica gel, and eluted with a gradient of hexane-acetone to give six fractions (A-F). Fraction C was then purified by QCC using a gradient of hexane-acetone to afford **59** (22.6 mg). Fraction D, upon standing overnight at room temperature gave **60** (20.3 mg). Fraction E was separated by QCC with a gradient system of increasing polarity (acetone-hexane) to afford five subfractions (E_1-E_5). Subfraction E_2 was subjected to precoated plates using 50% CH_2Cl_2-hexane as a mobile phase (4 runs) to give **52** (1.6 mg). Subfraction E_3 was subjected to precoated plates using 3% MeOH-CH_2Cl_2 as a mobile phase (4 runs) to give **42** (2.3 mg) and **43** (2.1 mg).

3.4. Characterization of isolated compounds

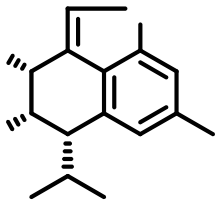
3.4.1. Populene A (42, [4])



The structure of compound 42

3.4.1.1. Populene A (**42**): yellow gum; $[\alpha]^{25}_{D}$ +57.9 (*c* 0.54, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 216 (4.22), 251 (3.98), 259 (3.91), 279 (3.44), 289 (3.40) nm; IR (Neat) ν_{max} 3365, 2959, 2870, 1617, 1591, 758 cm^{-1}; NMR data see **Table 36**; EIMS *m/z* , 246 $[M]^+$ (8), 211 (18), 185 (33), 169 (25), 72 (100), 69 (47); HREIMS *m/z* 246.1262 (calcd for $C_{15}H_{18}O_3$, 246.1256).

3.4.2. Populene B (43, [4])



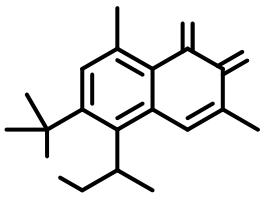
The structure of compound 43

3.4.2.1. Populene B (**43**): yellow gum; $[\alpha]^{25}_{D}$ -63.6 (*c* 0.37, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 213 (4.15), 251 (3.85), 259 (3.80), 278 (3.32), 290 (3.29) nm; IR (Neat) ν_{max} 3387, 2959, 2871, 1716, 1524, 754 cm^{-1}; NMR data see **Table 36**; EIMS *m/z* ,246 $[M]^+$ (50), 199 (31), 185 (100), 157 (23), 129 (46); HREIMS *m/z* 246.1255 (calcd for $C_{15}H_{18}O_3$, 246.1256).

Table 36 NMR data of compounds 42 and 43

Position	42		43	
	δ_H (mult, *J* in Hertz	δ_C	δ_H (mult, *J* in Hertz	δ_C
1		153.5		153.6
2	7.10, *br s*	109.3	7.14, *br s*	109.8
3		135.8		135.7
4	7.02, *br s*	121.6	6.91, *br s*	124.5
4a		131.4		129.8
5	3.02, *dd*, 7.8, 3.9	49.8	2.90, *dd*, 8.7, 3.3	53.5
6	4.01, *dd*, 7.8. 7.8	75.7	4.38, *dd*, 3.3, 3.3	73.4
7	4.90, *dd*, 7.8, 0.9	70.5	5.08, *m*	65.6
8		118.7		118.2
8a		123.7		123.4
9	7.50, *d*, 0.9	138.8	7.57, *d*, 1.5	140.9
10	2.48, *s*	22.4	2.48, *s*	22.2
11	2.58, *m*	27.8	1.63, *m*	31.0
12	1.16, *d*, 7.2	20.0	1.12, *d*, 6.6	21.3
13	1.18, *d*, 7.2	20.8	0.94, *d*, 6.6	21.6

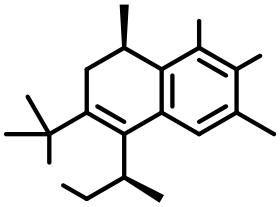
3.4.3. Populene C (44, [4])



The structure of compound 44

3.4.3.1. Populene C (**44**): orange solid; mp 168-170 $^{\circ}$C; $[\alpha]^{25}_{D}$ -46.0 (*c* 0.27, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 213 (4.18), 242 (3.79), 259 (3.98), 380 (3.03) nm; IR (Neat) ν_{max} 2974, 2930, 2871, 1757, 1698, 1657 cm^{-1}; NMR data see **Table 37**; EIMS *m/z* , 286.1556 $[M+2]^+$ (17), 271 (53), 241 (72), 85 (66), 83 (100); HREIMS *m/z* 286.1556 $[M+2]^+$ (calcd for $C_{18}H_{24}O_3$, 284.1412).

3.4.4. Populene D (45, [4])



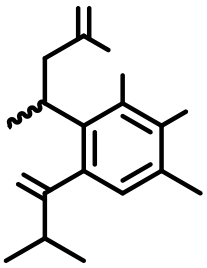
The structure of compound 45

3.4.4.1. Populene D (**45**): brown gum; $[\alpha]^{25}_{D}$ -21.9 (*c* 0.75, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 219 (4.10), 264 (3.92), 277sh (3.81), 366 (2.86) nm; IR (Neat) ν_{max} 3417, 2967, 2930, 2863, 1653, 754 cm^{-1}; NMR data see **Table 37**; EIMS *m/z* , 288 $[M]^+$ (15), 274 (21), 241 (20), 273 (100); HREIMS *m/z* 288.1736 (calcd for $C_{18}H_{24}O_3$, 288.1725).

Table 37 NMR data of compounds 44 and 45.

Position	44		45	
	δ_H (mult, *J* in Hertz	δ_C	δ_H (mult, *J* in Hertz	δ_C
1		181.7		140.3
2		181.6		140.9
3		135.8		121.0
4	7.02, *d*, 1.2	137.3	6.65, *s*	117.0
4a		128.4		125.0
5		135.8		128.7
6		150.1		132.2
7	6.95, *s*	131.2	2.00, *d*, 15.3	31.0
			2.36, *dd*, 15.3, 5.1	
8		142.6	3.19, *br dq*, 6.9, 6.9	25.2
8a		133.1		125.2
9	2.62, *s*	23.0	1.04, *d*, 6.9	17.9
10	2.09, *d*, 1.2	16.0	2.25, *s*	15.8
11	3.01, *br q*, 6.9	29.9	2.68, *m*	28.4
12	1.40, *d*, 6.9	21.2	1.14, *d*, 6.9	17.6
13	3.97, *dd*, 11.7, 2.4	64.9	3.90, *dd*, 11.1, 3.0	65.7
	3.79, *dd*, 11.7, 1.2		3.66, *dd*, 11.1, 2.4	
14		74.9		75.0
15	1.53, *s*	31.3	1.26, *s*	23.6
16	1.57, *s*	27.8	1.41, *s*	27.6

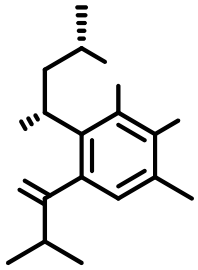
3.4.5. Populene E (46, [4])



The structure of compound 46

3.4.5.1. Populene E (**46**): yellow-brown gum; $[\alpha]^{25}_{D}$ +30.1 (*c* 0.58, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 228 (4.11), 273 (3.86) nm; IR (Neat) ν_{max} 3410, 2970, 2925, 2873, 1776, 1675, 1616 cm^{-1}; NMR data see **Table 38**; EIMS *m/z* , 262 $[M]^+$ (31), 220 (34), 191 (43), 219 (100); HREIMS *m/z* 262.1210 (calcd for $C_{15}H_{18}O_4$, 262.1205).

3.4.6. Populene F (47, [4])



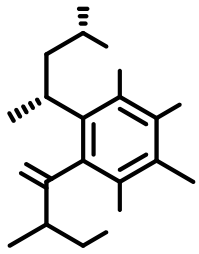
The structure of compound 47

3.4.6.1. Populene F (**47**): yellow gum; $[\alpha]^{25}_{D}$ +7.5 (*c* 0.23, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 219 (4.23), 232 (4.14), 281 (3.00) nm; IR (Neat) ν_{max} 3417, 2967, 2930, 2871, 1668, 1576 cm^{-1}; NMR data see **Table 38**; EIMS *m/z* , 264 $[M]^+$ (27), 221 (100), 203 (22), 193 (26), 179 (44), 177 (25), 151 (20); HREIMS *m/z* 264.1353 (calcd for $C_{15}H_{20}O_4$, 264.1362).

Table 38 NMR data of compounds 46 and 47

Position	46		47	
	δ_H (mult, *J* in Hertz	δ_C	δ_H (mult, *J* in Hertz	δ_C
2		167.4	5.65, *dd*, 9.0, 3.0	92.6
3	2.72, *d*, 3.6	36.3	1.87, *ddd*, 13.5, 9.0, 5.1	36.6
			2.07, *td*, 13.5, 3.0	
4	3.88, *tq*, 7.2, 3.6	27.5	3.84, *m*	26.2
4a		127.9		126.3
5		126.2		127.1
6	7.40, *s*	127.8	7.18, *s*	125.0
7		123.5		121.0
8		145.4		146.2
8a		139.2		140.0
1′		205.8		207.1
2′	3.47, *sept*, 6.9	37.2	3.45, *sept*, 6.9	37.4
3′	1.21, *d*, 6.9	19.0	1.17, *d*, 6.9	19.1
4′	1.14, *d*, 6.9	19.4	1.15, *d*, 6.9	19.6
4-CH_3	1.31, *d*, 7.2	20.2	1.25, *d*, 6.9	22.3
7-CH_3	2.30, *s*	15.5	2.23, *s*	15.3

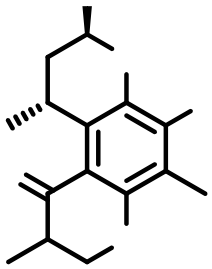
3.4.7. Populene G (48, [4])



The structure of compound 48

3.4.7.1. Populene G (**48**): yellow gum; $[\alpha]^{25}_{D}$ +62.7 (*c* 0.07, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 214 (4.09), 235 (3.98), 286 (3.95), 339 (3.66) nm; IR (Neat) ν_{max} 3424, 2959, 2930, 2871, 1661, 1591, 1429 cm^{-1}; NMR data see **Table 39**; EIMS *m/z*, 278 $[M]^+$ (98), 249 (27), 239 (100), 208 (36), 192 (35); HREIMS *m/z* 278.1196 (calcd for $C_{15}H_{18}O_5$, 278.1154).

3.4.8. Populene H (49, [4])



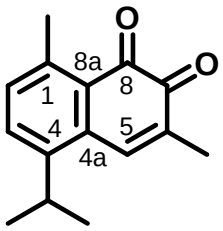
The structure of compound 49

3.4.8.1. Populene H (**49**): yellow gum; $[\alpha]^{25}_{D}$ +43.7 (*c* 0.04, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 214 (4.06), 237 (3.95), 286 (3.96), 339 (3.60) nm; IR (Neat) ν_{max} 3417, 2967, 2930, 2871, 1661, 1587 cm^{-1}; NMR data see **Table 39**; EIMS *m/z*, 278 $[M]^+$ (54), 234 (56), 208 (25), 192 (24), 72 (100); HREIMS *m/z* 278.1159 (calcd for $C_{15}H_{18}O_5$, 278.1154).

Table 39 NMR data of compounds 48 and 49.

Position	48		49	
	δ_H (mult, *J* in Hertz	δ_C	δ_H (mult, *J* in Hertz	δ_C
2	5.56, *dd*, 9.9, 2.7	92.2	5.81, *dd*, 7.5, 4.5	95.9
3	1.84, *ddd*, 13.5, 9.9, 5.4	36.8	2.00, *m*	36.1
	2.04, *ddd*, 13.5, 13.5, 2.7			
4	4.09, *m*	27.2	4.10, *m*	27.1
4a		125.1		127.2
5		109.4		111.4
6		157.7		158.7
7		110.4		110.6
8		149.3		149.9
8a		134.6		134.9
1′		195.3		196.1
2′	2.75, *dq*, 6.9, 5.1	41.2	2.75, μ	42.1
3′	1.16, *d*, 6.9	11.0	1.17, *d*, 6.5	11.8
4′	4.03, l*dd*, 11.1, 11.1	71.6	4.05, l*dd*, 11.5, 11.5	72.6
	4.43, *dd*, 11.1, 5.1		4.45, *dd*, 11.5, 5.5	
4-CH_3	1.28, *d*, 6.9	22.4	1.32, *d*, 6.9	23.0
7-CH_3	2.09, *s*	8.1	2.11, *s*	9.0

3.4.9. Mansonone C (**50**, [**5**])



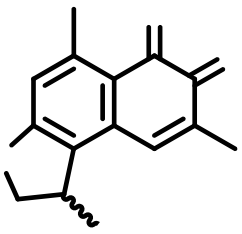
The structure of compound 50

3.4.9.1. Mansonone C (**50**): Yellow gum. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 40**.

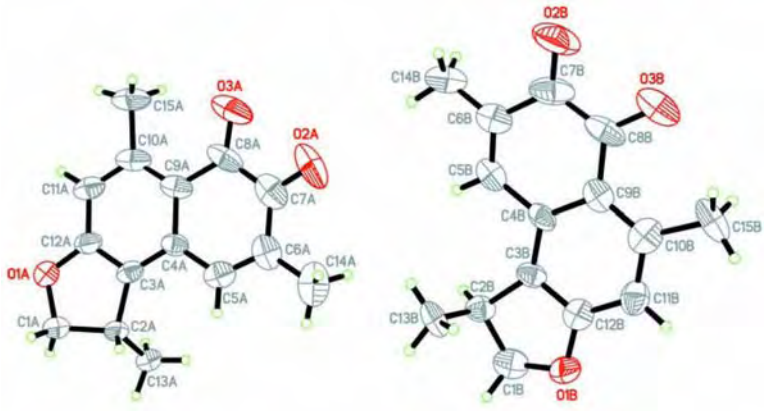
Table 40 NMR spectral data of compounds 50

Position	50		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1		143.0(C)	
2	7.19 (*d*, J = 8.1)	134.1 (CH)	3, 8a, 9
3	7.43 (*d*, J = 8.1)	132.0 (CH)	1, 2, 4
4		132.5 (C)	
4a		145.3 (C)	
5	7.66 (*brd*, 1.5)	138.0 (CH)	4a, 8a, 6, 13
6		135.0 (C)	
7		182.0 (C)	
8		180.0 (C)	
8a		129.3 (C)	
9	2.63 (*s*)	22.8 (CH_3)	1, 2, 8, 8a
10	3.39 (*sept*, 6.9)	28.3 (CH)	11, 12
11	1.30 (*d*, 6.9)	23.7 (CH_3)	10, 12
12	1.30 (*d*, 6.9)	23.7 (CH_3)	10, 11
13	2.08 (*d*, 1.5)	16.0 (CH_3)	5, 6, 7

3.4.10. Mansonone D (51, [**3**])



The structure of compound 51



The X-ray structure of compound 51

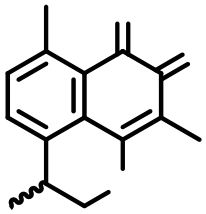
Boonsri, S. *et al*., *Acta Cryst*. **2007**, *E63*, o4901. [**6**]

3.4.10.1. Mansonone D (**51**): Intense yellow solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 41**.

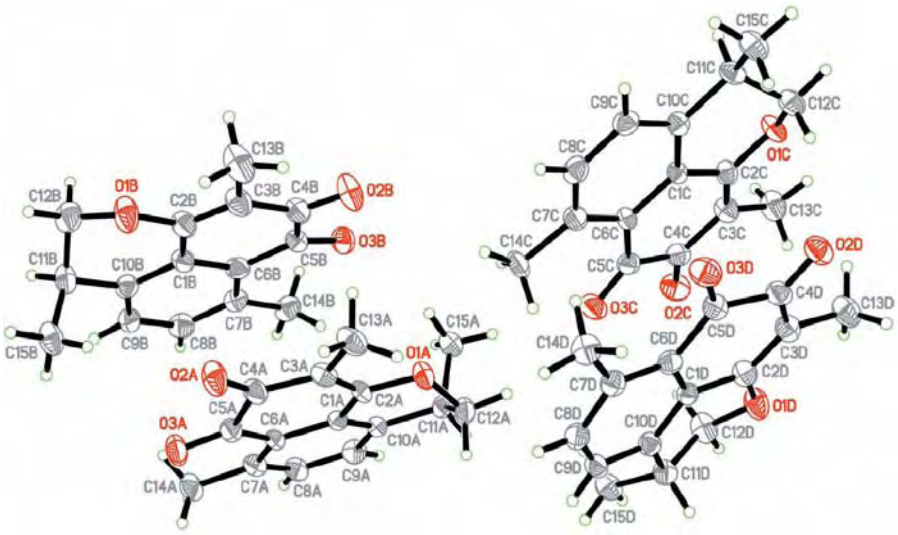
Table 41 NMR spectral data of compounds 51

Position	51		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1		149.4 (C)	
2	6.44 (*s*)	113.3 (CH)	3, 4, 8a, 9
3		165.3 (C)	
4		131.1 (C)	
4a		132.9 (C)	
5	7.11 (*s*)	137.4 (CH)	4, 4a, 6, 7, 8a, 13
6		136.6 (C)	
7		182.5 (C)	
8		178.7 (C)	
8a		122.4 (C)	
9	2.49 (*s*)	23.6 (CH_3)	1, 2, 8a
10	3.54 (*dq*, 7.2, 2.7)	34.5 (CH)	3
11	4.27 (*dd*, 8.7, 2.7)	80.0 (CH_2)	3, 4, 10, 12
	4.64 (*t*, 8.7)		
12	1.43 (*d*, 7.2)	21.9 (CH_3)	4, 10, 11
13	1.94 (*s*)	15.7 (CH_3)	5, 6, 7

3.4.11. Mansonone E (**52**, [7])



The structure of compound 52



The X-ray structure of compound 52

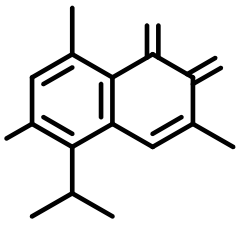
Fun, H.-K. *et al*., *Acta Cryst*. **2007**, *E63*, o2127–o2129. [**8**]

3.4.11.1. Mansonone E (**52**): Red-brown solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 42**.

Table 42 NMR spectral data of compounds 52

Position	52		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1		127.4 (C)	
2	7.26 (*d*, 8.1)	134.9 (CH)	1, 9
3	7.35 (*d*, 8.1)	132.6 (CH)	4, 4a, 10
4		136.9 (C)	
4a		126.9 (C)	
5		162.5 (C)	
6		116.3 (C)	
7		180.2 (C)	
8		182.2 (C)	
8a		142.9 (C)	
9	2.65 (*s*)	22.5 (CH_3)	1, 2, 8a
10	3.09 (*m*)	31.1 (CH)	3, 4, 4a
11	1.37 (*d*, 7.2)	17.6 (CH_3)	4, 10, 12
12	4.41 (*dd*, 10.8, 3.9)	71.5 (CH_2)	4, 5
	4.23 (*dd*, 10.8, 5.1)		
13	1.96 (*s*)	7.8 (CH_3)	5, 6, 7

3.4.12. Mansonone G (53, [3])



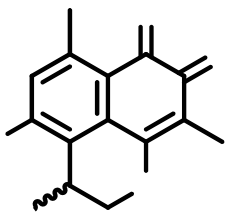
The structure of compound 53

3.4.12.1. Mansonone G (**53**): Orange solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 43**.

Table 43 NMR spectral data of compounds 53

Position	53	
	δ_H (mult, *J* in Hertz	δ_C
1		134.5 (C)
2	6.56 (*s*)	119.9 (CH)
3		162.2 (C)
4		133.2 (C)
4a		146.6 (C)
5	7.72 (*s*)	139.1 (CH)
6		135.3 (C)
7		182.8 (C)
8		180.0 (C)
8a		122.7 (C)
9	2.58 (*s*)	23.3 (CH_3)
10	3.58 (*sept*, 7.2)	26.8 (CH)
11	1.43 (*d*, 7.2)	21.2 (CH_3)
12	1.43 (*d*, 7.2)	21.2 (CH_3)
13	2.07 (*s*)	15.9 (CH_3)

3.4.13. Mansonone H (54, [**9**])



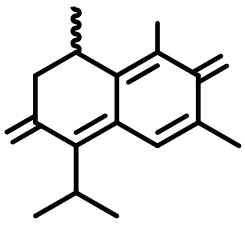
The structure of compound 54

3.4.13.1. Mansonone H (**54**): Red-brown solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 44**.

Table 44 NMR spectral data of compounds 54

Position	54		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1		128.3 (C)	
2	6.74 (*s*)	119.5 (CH)	3, 4, 8, 9
3		159.7 (C)	
4		125.4 (C)	
4a		128.3 (C)	
5		162.4 (C)	
6		115.5 (C)	
7		181.0 (C)	
8		180.1 (C)	
8a		145.6 (C)	
9	2.59 (*s*)	23.0 (CH_3)	1, 2, 8, 8a
10	3.25 (*dq*, 6.9, 3.3)	26.1 (CH)	3, 4, 4a, 11
11	1.31 (*d*, 6.9)	17.2 (CH_3)	4, 10, 12
12	4.41 (*d*, 10.8)	72.0 (CH_2)	4, 10, 11, 5
	4.29 (*dd*, 10.8, 3.3)		
13	1.90 (*s*)	7.9 (CH_3)	5, 6, 7

3.4.14. Mansonone S (55, [**10**])



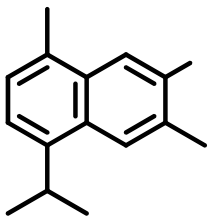
The structure of compound 55

3.4.14.1. Mansonone S (**55**): Intense yellow solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 45**.

Table 45 NMR spectral data of compounds 55

Position	55		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1	3.57 (*dquint*, 6.6,1.8)	28.1 (CH)	3, 4a, 8, 8a
2	2.50 (*dd*, 14.7, 1.8)	46.1 (CH_2)	1, 3, 4, 8a, 9
	2.81 (*dd*, 14.7, 6.6)		
3		200.1 (C)	
4		150.2 (C)	
4a		135.3 (C)	
5	7.55 (*d*, 1.5)	132.5 (CH)	4, 4a, 8a, 13
6		136.1 (C)	
7		180.8 (C)	
8		144.7 (C)	
8a		123.0(C)	
9	1.18 (*d*, 6.6)	20.5 (CH_3)	2, 8a
10	3.42 (*hept*, 6.9)	28.5 (CH)	3, 4a, 11, 12
11	1.28 (*d*, 6.9)	21.0 (CH_3)	4, 10, 12
12	1.38 (*d*, 6.9)	22.8 (CH_3)	4, 10, 11
13	2.07 (*s*)	16.2 (CH_3)	5, 6, 7

3.4.15. 7-hydroxycadalene (56, [**3**])



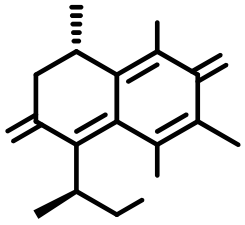
The structure of compound 57

3.4.15.1. 7-hydroxycadalene (**57**): Orange solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 46**.

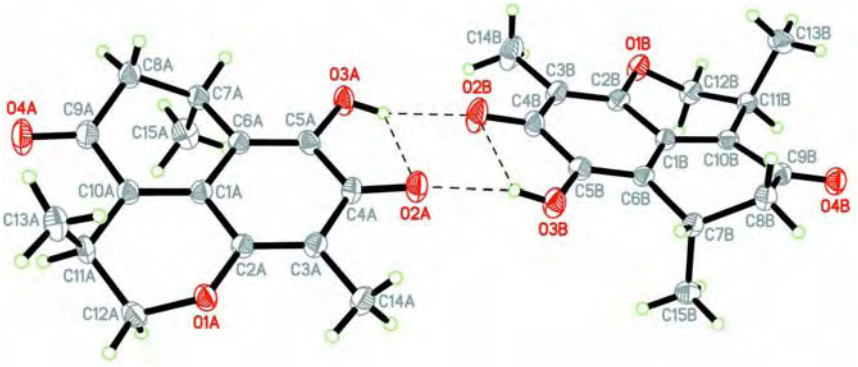
Table 46 NMR spectral data of compounds 57

Position	57		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1		130.1 (C)	
2	7.19 (*d*, J = 7.5)	126.2 (CH)	3, 4, 8a, 9
3	7.13 (*d*, J = 7.5)	119.1 (CH)	1, 4a, 9, 10
4		142.2 (C)	
4a		126.9 (C)	
5	7.89 (*s*)	125.6 (CH)	13, 4, 8a
6		125.1 (C)	
7		152.1 (C)	
8	7.27 (*s*)	106.9 (CH)	4a, 6, 13
8a		133.1 (C)	
9	2.56 (*s*)	19.5 (CH_3)	3, 8a
10	3.67 (*sept*)	28.4 (CH)	3, 4, 4a
11	1.37 (*d*, 6.6)	23.7 (CH_3)	4, 10, 12
12	1.37 (*d*, 6.6)	23.7 (CH_3)	4, 10, 11
13	2.47 (*s*)	16.8 (CH_3)	5, 6, 7

3.4.16. 7-hydroxy-2,3,5,6-tetrahydro-3,6,9-trimethyl-naphtho-[1,8-b,c]pyran-4,8-dione (**58**, [**2**])



The structure of compound 58



The X-ray structure of compound 58

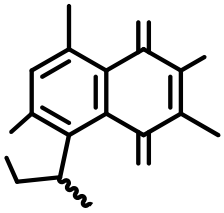
Chantrapromma, S. *et al*., *Acta Cryst*. **2007**, *E63*, o2749–o2750. [**11**]

3.4.16.1. 7-hydroxy-2,3,5,6-tetrahydro-3,6,9-trimethyl-naphtho[1,8-b,c]-pyran-4,8-dione (**58**): Red-brown solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 47**.

Table 47 NMR spectral data of compounds 58

Position	58		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1			
2	4.22 (*d*, 10.8)	71.9 (CH_2)	3, 3a, 3-Me, 9a
	4.09 (*dd*, 10.8, 3.3)		
3	3.05 (*dq*, 6.9, 3.3)	26.5 (CH)	4, 9a
3a		139.5 (CH)	
4		197.1 (C)	
5	2.71 (*dd*, 16.2, 6.6)	44.6 (CH_2)	3a, 4, 6, 6a, 6-Me
	2.53 (*dd*, 16.2, 1.8)		
6	3.54 (*dquint*, 6.9, 1.8)	27.6 (CH)	4, 6a, 7, 9a
6a		115.2 (C)	
7		143.5 (C)	
8		181.3 (C)	
9		115.1 (C)	
9a		157.1 (C)	
9b		131.0 (C)	
3-Me	1.09 (*d*, 6.9)	16.1 (CH_3)	2, 3, 3a
6-Me	1.11 (*d*, 6.9)	20.7 (CH_3)	5, 6, 6a
9-Me	1.90 (*s*)	8.0 (CH_3)	8, 9, 9a

3.4.17. Thespesone (58, [**3**])



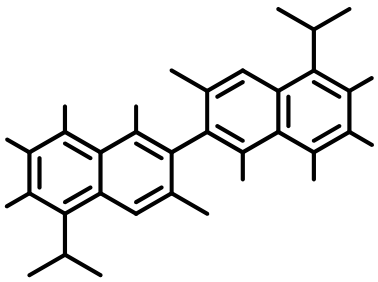
The structure of compound 58

3.4.17.1. Thespesone (58): Yellow solid. NMR spectral data ($CDCl_3$, 300 MHz) see **Table 48**.

Table 48 NMR spectral data of compounds 58

Position	58		
	δ_H (mult, *J* in Hertz	δ_C	HMBC
1		146.0 (C)	
2	6.82 (*s*)	116.2 (CH)	3, 4, 9
3		165.7 (C)	
4		134.2 (C)	
4a		128.1(C)	
5		186.3 (C)	
6		117.7 (C)	
7		153.8 (C)	
8		180.6 (C)	
8a		120.7 (C)	
9	2.72 (*s*)	23.9 (CH_3)	1, 2, 8a
10	4.14 (*dquint*, 6.9, 2.4)	37.1 (CH)	11
11	4.41 (*dd*, 4.4, 2.4)	80.5 (CH_2)	3, 4, 10, 12
	4.62 (*t*, 8.4)		
12	1.29 (*d*, 6.9)	19.8 (CH_3)	4, 10, 11
13	2.40 (*s*)	8.4 (CH_3)	5, 6, 7
7-OH	7.75 (*s*)		6, 7, 78

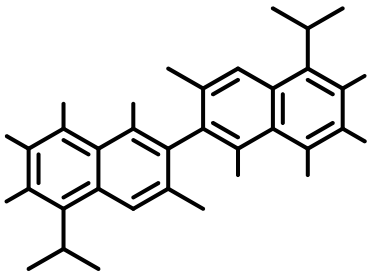
3.4.18. (+)-gossypol (59, [**12**])



The structure of compound 59

3.4.18.1. (+)-gossypol (59): Yellow solid; mp 171-173°C; UV (MeOH) λ_{max} (log ε) 237 (4.26), 276 sh (3.90), 290 (3.84), 379 (3.61) nm; IR (neat) ν_{max} 3410, 2959, 2930, 1626, 1314, 754 cm^{-1}.

3.4.19. (+)-6,6′-dimethoxy gossypol (60, [**13**])



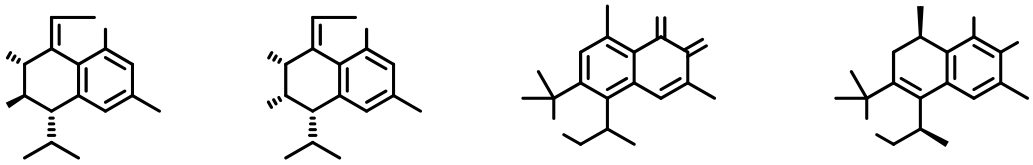
The structure of compound 60

3.4.19.1. (+)-6,6′-dimethoxy gossypol (60): Yellow solid; mp 165-167 $^{\circ}$C; UV (MeOH) λ_{max} (log ε) 229 (4.77), 252 sh (4.65), 286 (4.44), 360 (4.00) nm; IR (neat) ν_{max} 3373, 2962, 2932, 1608, 1444, 1332, 754 cm^{-1}.

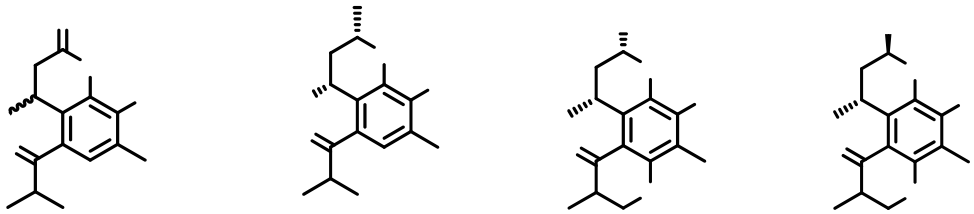
3.5. Bioassays

3.5.1. Antibacterial assay

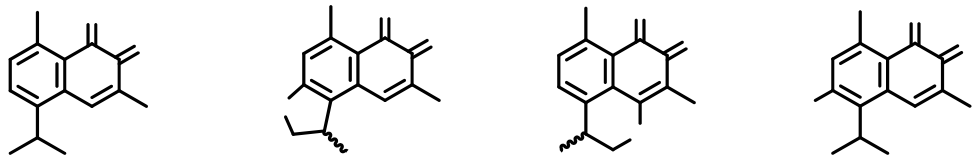
The isolated compounds from air-dried heartwood and wood of *T. populnea* were tested against the microorganisms, *Bacillus substilis* (obtained from Department of Industrial Biotechnology, PSU), *Staphylococcus aureus* (TISTR517) (obtained from Microbial Resources Center (MIRCEN), Bangkok, Thailand), *Streptococcus faecalis*, *Salmonella typhi*, *Shigella sonei* and *Pseudomonas aeruginosa*. The last four microrganism were obtained from Department of Pharmacognosy and Botany, PSU. The antibacterial assay employed was the same as described in Boonsri et al [**14**]. Vancomycin, which was used as a standard, showed antibacterial activity of 75 μg/mL.



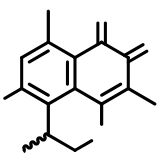
42 **43** **44** **45**



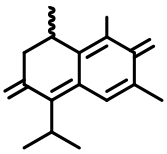
46 **47** **48** **49**



50 **51** **52** **53**



54



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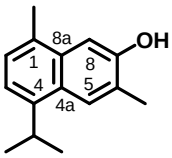

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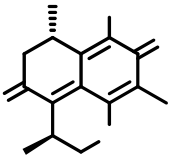

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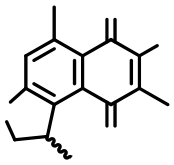

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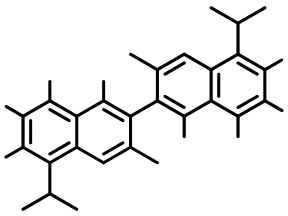

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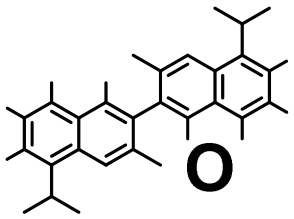

59

Fig. 3.5.1a. The isolated compounds from *T. populnea*

Table 49 Antibacterial activity (MIC, µg/ml) of **42-60.**

No.	Gram-positive bacteria			Gram-negative bacteria		
	B. substilis	***S. aureus***	***E. faecalis***	***S. typhi***	***S. sonie***	***P. aeruginosa***
42	nt	nt	nt	nt	nt	nt
43	nt	nt	nt	nt	nt	nt
44	4.69	-	-	-	-	-
45	4.69	-	-	-	-	-
46	nt	nt	nt	nt	nt	nt
47	-	-	-	-	-	-
48	-	-	-	-	-	-
49	nt	nt	nt	nt	nt	nt
50	nt	nt	nt	nt	nt	nt
51	2.34	-	-	-	-	-
52	2.69	-	-	-	-	-
53	nt	nt	nt	nt	nt	nt
54	-	-	-	-	-	-
55	-	-	-	-	-	-
56	0.59	-	-	-	-	-
57	-	-	-	-	-	-
58	-	-	-	-	-	-
59	1.17	1.17	-	-	-	-
60	2.34	4.69	1.17	-	-	-

- = inactive compound

nt = not tested

การวิเคราะห์ผลการต้านเชื้อแบคทีเรีย

จากผลการทดสอบฤทธิ์การต้านเชื้อแบคทีเรีย (Antibacterial activity) ใน**ตารางที่ 49** (**Table 33**) พบว่าสารประกอบที่ **56** (**7-hydroxycadalene**) ออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะกับ *B. substilis* (0.59 µg/ml) พบว่าสารประกอบที่ **59** (**(+)-gossypol**) ออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะกับแบคทีเรียแกรมบวกทั้ง *B. substilis* (1.1 µg/ml) และ *S. aureus* (1.1 µg/ml) และในทางเดียวกัน สารประกอบที่ **60** (**(+)-6,6′-dimethoxy gossypol**) ออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะกับแบคทีเรียแกรมบวกทั้ง *E. faecalis* (1.1 µg/ml) *B. substilis* (2.34

µg/ml) และ *S. aureus* (4.67 µg/ml) สารประกอบที่ **44** (**Populene C**, (4.69 µg/ml)) **45** (**Populene D**, (4.69 µg/ml)) **51** (**Mansonone D**, (2.34 µg/ml)) และ **52** (**Mansonone E**, (4.69 µg/ml)) ออกฤทธิ์ต้านเชื้อแบคทีเรียจำเพาะกับ *B. substilis*

3.5.2. Cytotoxic assay

The procedure for cytotoxic assay was performed by the sulphorhodamine B (SRB) assay as described by Skehan et al [**15**]. In this study, four cancer cell lines obtained from National Cancer Institute, Bangkok, Thailand, were used: MCF-7 (breast adenocarcinoma), KB (human oral cancer), HeLa (Human cervinal cancer) and HT-29 (colon cancer). Camptothecin, which was used as a standard, showed cytotoxic activity in the range of 0.2-2.0 µg/mL.

Table 50 In vitro cytotoxicity of **42-60**.

No.	Cell lines – IC_{50} (µg/ml)			
	MCF-7	**HeLa**	**HT-29**	**KB**
42	nt	nt	nt	nt
43	nt	nt	nt	nt
44	2.35			
45	1.85			
46	nt	nt	nt	nt
47	-	-	-	-
48	-	-	-	-
49	nt	nt	nt	nt
50	nt	nt	nt	nt
51	0.80	2.80	>5	4.90
52	0.05	0.55	0.18	0.40
53	nt	nt	nt	nt
54	-	-	-	-
55	>5	>5	>5	>5
56	>5	>5	>5	>5
57	>5	>5	>5	>5
58	-	-	-	-
59	nt	0.08	>5	0.04
60	4.00	>5	3.00	>5

- = inactive compound

nt = not tested

การวิเคราะห์ผลการยับยั้งเซลล์มะเร็ง

จากผลการทดสอบฤทธิ์การยับยั้งเซลล์มะเร็ง (Cytotoxicity) ใน**ตารางที่ 50** (**Table 50**) พบว่าสารประกอบที่ **59** (**(+)-gossypol**) ออกฤทธิ์การยับยั้งเซลล์มะเร็งได้ดีมากทั้ง HeLa (0.08 μg/ml) และ KB (0.04 μg/ml) ส่วนในสารประกอบที่ **52** (**Mansonone E**) ออกฤทธิ์การยับยั้งเซลล์มะเร็งได้ดีในช่วงกว้างทั้ง MCF-7 (0.05 μg/ml) HeLa (0.55 μg/ml) HT-29 (0.18 μg/ml) และ KB (0. 40 μg/ml) ส่วนในสารประกอบที่ **45** (**Populene D**) ออกฤทธิ์การยับยั้งเซลล์มะเร็งเฉพาะ HeLa (0.95 μg/ml) และในทำนองเดียวกัน สารประกอบที่ **51** (**Mansonone D**) ออกฤทธิ์การยับยั้งเซลล์มะเร็งเฉพาะ MCF-7 (0.95 μg/ml) เท่านั้น

เอกสารอ้างอิง

3[1]. Datta, S. C., Murti, V. V. S., Seshadri, T. R. *Indian Journal of Chemistry* **1972**, *10*, 263-266.

3[2]. Milbrodt, M., Konig, W. A., Hausen, B. M. *Phytochemistry* **1997**, *45*, 1523-1525.

3[3]. Puckhaber, L. S.; Stipanovic, R. D. *J. Nat. Prod.* **2004**, *67*, 1571-1573.

3[4]. Boonsri, S., Karalai, C., Ponglimanont, C., Chantrapromma, S., Kanjana-Opas, A. *J. Nat. Prod.* **2008**, *71*(*7*), 1173-1177.

3[5]. Tiew, P., Puntumchai, A., Kokpol, U., Chavasiri, W. *Phytochemistry* **2002**, *60*, 773–776.

3[6]. Boonsri, S., Chantrapromma, S., Fun, H-K., Karalai, C. *Acta Cryst*. **2007**, *E63*, o4901.

3[7]. Kim, J.-P., Kim, W.-G., Koshino, H., Jung, J., Yoo, I.-D. *Phytochemistry* **1996**, *43*, 425–430.

3[8]. Fun, H-K., Boonsri, S., Chantrapromma, S., Boonnak, N., Karalai, C. *Acta Cryst*. **2007**, *E63*, o2127–o2129.

3[9]. Kim, J.-P., Kim, W.-G., Koshino, H., Jung, J., Yoo, I.-D. *Phytochemistry* **1996**, *43*, 425–430.

3[10]. Tiew, P., Takayama, H., Kitajima, M., Aimi, N., Kokpol, U., Chavasiri, W. *Tetrahedron Letts.* **2003**, *44*, 6759–6761.

3[11]. Chantrapromma, S., Boonsri, S., Fun, H-K., Karalai, C. *Acta Cryst*. **2007**, *E63*, o2749–o2750.

3[12]. Badria, F. A., Houssein, W. E., Zaghloul, M. G., Halim, A. F. *Pharm. Biol.* **2001**, *39*, 120–126.

3[13]. Alois, A., Mace, M. E., Howell, C. R. *Phytochemistry* **1975**, *14*, 1077–1081.

3[14]. Boonsri, S., Karalai, C., Ponglimanont, C., Kanjana-Opas, A., Chantrapromma, K. *Phytochemistry* **2006**, *67*, 723-727.

3[15]. Skehan, P., Storeng, R., Scudiero, D., Monks, A., McMahon, J., Vistica, D., Warren, J. T., Bokesch, H., Kenney, S., Boyd, M. R. *J. Natl. Cancer Inst*. **1990**, *82*, 1107–1112.

ผลงานตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

ได้ตีพิมพ์ผลงานวิจัยในวารสารวิชาการระดับนานาชาติ จำนวน 16 เรื่อง ดังนี้
(Reprints 1 –16 ดังภาคผนวก)

1. Nawong Boonnak, Chatchanok Karalai*, Suchada Chantrapromma, Chanita Ponglimanont, Hoong-Kun Fun, Akkharawit Kanjana-Opas and Surat Laphookhieod (2006)

   "Bioactive prenylated xanthones and anthraquinones from *Cratoxylum formosum* ssp. *pruniflorum*"

   Tetrahedron. **62**, 8850-8859. (Impact Factor = 3.219 Reprints 1)

2. Sompong Boonsri, Suchada Chantrapromma*, Hoong-Kun Fun, Chatchanok Karalai, Akkharawit Kanjana-opas and Shazia Anjum (2005)

   "2,3-Dihydro-7-hydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one"

   Acta Crystallographica. E**61**, o3930-3932. (Impact Factor = 0.411 Reprints 2)

3. Nawong Boonnak, Suchada Chantrapromma*, Hoong-Kun Fun and Chatchanok Karalai (2005)

   "1,6,7-Trihydroxy-3-methoxy-2,8-bis(3-methyl-2-butenyl)-9*H*-xanthen-9-one chloroform solvate"

   Acta Crystallographica. E**61**, o4376-o4378. (Impact Factor = 0.411 Reprints 3)

4. Hoong-Kun Fun, Shea-Lin Ng, Ibrahim Abdul Razak, Nawong Boonnak and Suchada Chantrapromma* (2006)

   "12-(1,1-Dimethyl-2-propenyl)-5,9,10-trihydroxy-2,2-dimethyl-*2H*,*6H* pyrano[3,2-*b*]xanthen-6-one"

   Acta Crystallographica. E**62**, o130-o132. (Impact Factor = 0.411 Reprints 4)

5. Suchada Chantrapromma*, Nawong Boonnak, Hoong-Kun Fun and Chatchanok Karalai (2006)

“1,6-Dihydroxy-3,7-dimethoxy-2,8-bis(3-methyl-2-butenyl)-9*H*-xanthene-9-one”

Acta Crystallographica. E**62**, o360-o362. (Impact Factor = 0.411 Reprints 5)

6. Suchada Chantrapromma*, Sompong Boonsri, Hoong-Kun Fun, Shazia Anjum and Akkharawit Kanjana-opas (2006)

“2,3-dihydro-7,8-dihydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one”

Acta Crystallographica. E**62**, o1254-o1256. (Impact Factor = 0.411 Reprints 6)

7. Nawong Boonnak, Suchada Chantrapromma* and Hoong-Kun Fun (2006)

“4-(1,1-Dimethylprop-2-enyl)-1,3,5,6-tetrahydroxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one monohydrate”

Acta Crystallographica. E**62**, o2034-o2036. (Impact Factor = 0.411 Reprints 7)

8. Nawong Boonnak, Chatchanok Karalai*, Suchada Chantrapromma, Chanita Ponglimanont, Akkharawit Kanjana-Opas, Kan Chantrapromma and Hoong-Kun Fun (2007)

“Quinonoids from the barks of *Cratoxylum formosum* ssp. *pruniflorum* barks”

Canadian Journal of Chemistry, **85**, 341-345. (Impact Factor = 1.423 Reprints 8)

9. Hoong-Kun Fun, Sompong Boonsri, Suchada Chantrapromma*, Nawong Boonnak and Chatchanok Karalai (2007)

“3,6,9-Trimethyl-2,3-dihydrobenzo[*de*]chromene-7,8-dione”

Acta Crystallographica, E**63**, o2127-o2129. (Impact Factor = 0.411 Reprints 9)

10. Suchada Chantrapromma*, Sompong Boonsri, Hoong-Kun Fun and Chatchanok Karalai (2007)

“7-Hydroxy-3,6,9-trimethyl-2,3,5,6-tetrahydronaphtho[1,8-b,c]pyran-4,8- dione”

Acta Crystallographica, E**63**, o2749-o2750. (Impact Factor = 0.411 Reprints 10)

11. Nawong Boonnak, Hoong-Kun Fun, Suchada Chantrapromma* and Chatchanok Karalai (2007)

“Gerontoxanthone I methanol solvate”

Acta Crystallographica, E**63**, o3958-o3959. (Impact Factor = 0.411 Reprints 11)

12. Sompong Boonsri, Suchada Chantrapromma, Hoong-Kun Fun and Chatchanok Karalai (2007)

“1,5,8-Trimethyl-1,2-dihydronaphtho-[2,1-*b*]furan-6,7-dione”

Acta Crystallographica. E**63**, o4901. (Impact Factor = 0.411 Reprints 12)

13. Nawong Boonnak, Suchada Chantrapromma*, Hoong-Kun Fun and Chatchanok Karalai (2007)

“4,8-Dihydroxy-2,3-dimethoxy-1-(3-methylbut-2-enyl)-9*H*-xanthene-9-one”

Acta Crystallographica, E**63**, o4903-o4904. (Impact Factor = 0.411 Reprints 13)

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Journal of Natural Products. ***71****,* 1173–1177. (Impact Factor = 3.159 Reprints 15)

16. Hoong-Kun Fun, Suchada Chantrapromma* and Nawong Boonnak (2009)

“X-ray Structure Determination: A Powerful Technique for Natural Products Research and Drug Discovery”

Malaysian Journal of Science. **28**, 55-62. (SCOPUS Reprints 16)

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Bioactive prenylated xanthones and anthraquinones from *Cratoxylum formosum* ssp. *pruniflorum*

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Abstract—Ten new compounds (**1**–**10**), pruniflorone A–J, together with 21 known compounds (**11**–**31**) were isolated from the roots and barks of *Cratoxylum formosum* ssp. *pruniflorum*. Their structures were determined by spectroscopic methods. Compounds **1** and **11** were also confirmed by X-ray diffraction data. In addition, antibacterial and cytotoxic activities of the isolates were also evaluated.

1. Introduction

Cratoxylum belongs to the family Guttiferae, which is distributed in several Southeast Asian countries. Six species are found in Thailand;[1] *Cratoxylum arboresens*, *Cratoxylum cochinchinense*, *Cratoxylum maingayi*, *Cratoxylum sumatranum* ssp. *neriifolium*, *Cratoxylum formosum* ssp. *formosum* (Jack) Dyer and *Cratoxylum formosum* (Jack) Dyer ssp. *pruniflorum* (Kurz) Gogel. The last two species, which are subspecies of *C. formosum*, can be differentiated through the young twigs, leaves, pedicels and sepals. Those of *C. formosum* ssp. *formosum* are glabrous, whereas *C. formosum* ssp. *pruniflorum* are densely villous.[2] Some species of this genus have been used for the treatment of diuretic, stomachic and tonic effects,[3] as well as for diarrhoea and flatulence,[4] and for food poisoning and internal bleeding.[5] They produce various types of secondary metabolites, including xanthones,[6a–c] triterpenoids[6b,7] and flavonoids.[3] We have previously isolated a number of xanthones from the roots of *C. formosum* ssp. *formosum*.[8] As a continuation of our study on this genus, we report herein nine new xanthones (**1**–**9**): pruniflorones A–I, and nine known xanthones (**11**–**19**) from the roots, a new anthraquinone (**10**): pruniflorone J, six known anthraquinones (**20**–**25**) and six known xanthones (**26**–**31**) from the barks of *C. formosum* ssp. *pruniflorum*. In addition, the antibacterial and cytotoxic activities of selected compounds are also reported.

2. Results and discussion

The CH_2Cl_2 extracts of the roots and barks of *C. formosum* ssp. *pruniflorum* were subjected to column chromatography to give nine new xanthones (**1**–**9**) and a new anthraquinone (**10**). All isolated new xanthones gave characteristic signals in the UV spectrum, showing absorption bands in the range of 236–261 and 312–380 nm. The IR spectra also exhibited characteristic conjugated carbonyl and hydroxyl functionalities in the range of 1632–1646 and 3170–3414 cm^{-1}, respectively. Moreover, the ^1H and ^{13}C NMR spectral data suggested that the isolated new xanthones **1**–**6** had the 1,3,6,7-oxygenated xanthone skeleton, whereas xanthones **7**–**8** and **9** were 1,3,5,6- and 1,3,6-oxygenated xanthones, respectively.

Pruniflorone A (**1**) was isolated as a pale yellow powder, which was further recrystallized from $CHCl_3$–MeOH (4:1, v/v) to yield pale yellow single crystals. The X-ray structure (Fig. 1) confirmed a molecular structure with a prenylated xanthone skeleton and a molecular formula $C_{25}H_{30}O_7$. Its structure was supported by ^1H and ^{13}C NMR spectral data (Tables 1 and 2). The ^1H NMR spectral data of **1** (Table 1) showed two aromatic protons at δ 6.29 (s, H-4) and 6.72 (s, H-5), and two methoxyl groups at δ 3.90 (s, 3-OMe) and 3.84 (s, 7-OMe). In addition, the ^1H NMR spectral data also exhibited a dimethylchromane ring[9] at δ 2.73 (2H, br t,

Keywords: *Cratoxylum formosum* ssp. *pruniflorum*; Pruniflorone; Xanthone; Anthraquinone; Antibacterial activity; Cytotoxic activity.
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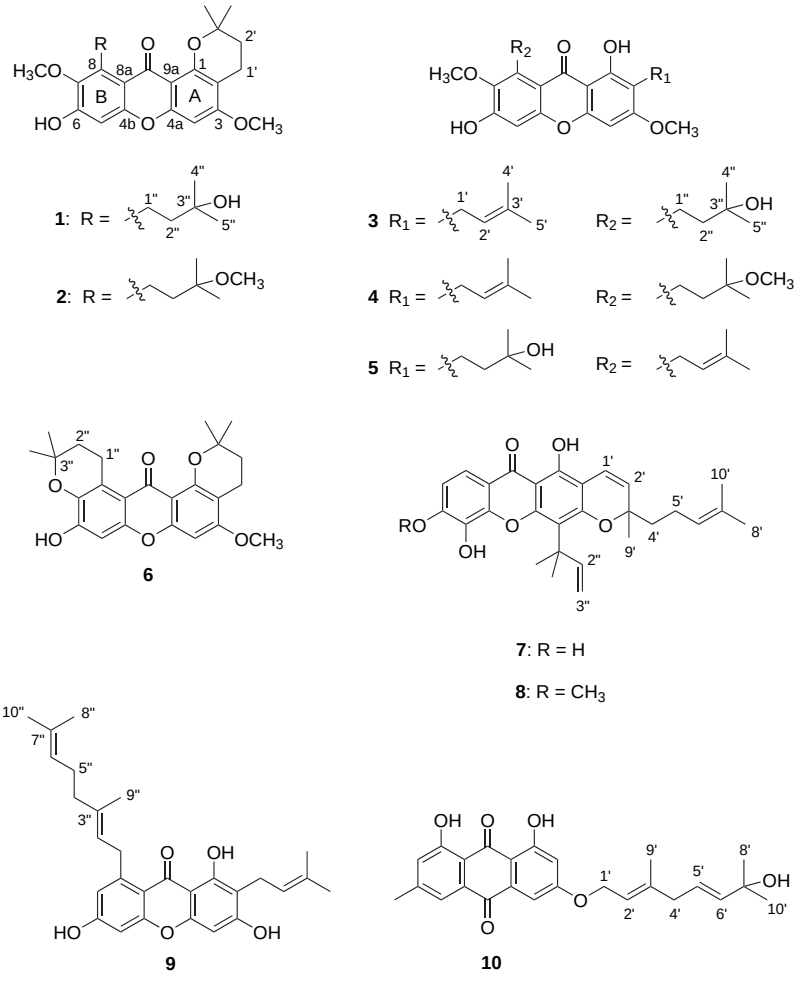


Structures of pruniflorone A-J

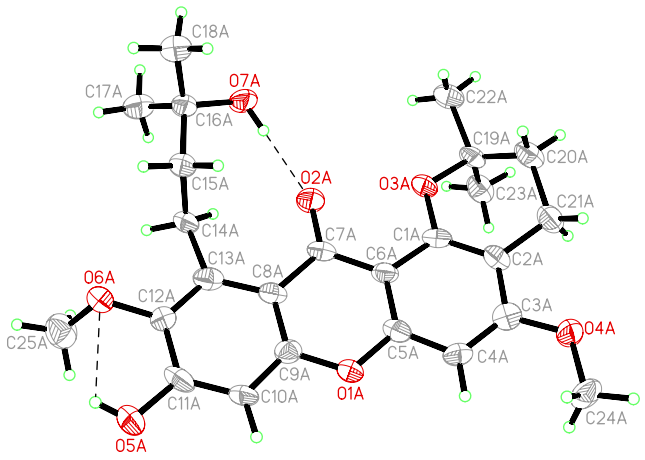


Figure 1. The ORTEP plot of **1**. There are two molecules in asymmetric unit of **1**, only one molecule was shown for clarity.

J=7.5 Hz, H-1′), 1.72 (2H, br t, J=7.5 Hz, H-2′) and 1.34 (6H, s, H-4′ and H-5′). A 3-hydroxyl-3-methylbutyl group[9] was evident from signals at δ 3.38 (2H, m, H-1″), 1.78 (2H, m, H-2″) and 1.30 (6H, s, H-4″ and H-5″). From these data, the structure of pruniflorone A was deduced to be **1**.

Pruniflorone B (**2**) was obtained as a yellow powder with a molecular ion peak at m/z 456.2116 $[M]^+$ in the HREIMS, corresponding to a molecular formula of $C_{26}H_{32}O_7$. The UV, ^1H and ^{13}C NMR spectral data of **2** (Tables 1 and 2) were similar to those of **1**, indicating the presence of a xanthone skeleton. However, an additional methoxyl singlet signal was apparent in both the ^1H+^{13}C spectra (δ_H 3.35, δ_C 49.2). This methoxyl group was located at C-3″ from the HMBC correlation with C-3″ (75.1). The completed HMBC correlations were summarized in Table 3. Thus, the structure of pruniflorone B was assigned as **2**.

Pruniflorone C (**3**) showed a molecular formula of $C_{25}H_{30}O_7$ by HREIMS. The ^1H and ^{13}C NMR spectra of **3** (Tables 1 and 2) were similar to those of **1**, except for the presence of signals for a prenyl group at δ_H 3.33 (2H, d, J=7.2 Hz, H-1′), δ_C 21.1; δ_H 5.21 (1H, br t, J=7.2, H-2′), δ_C 122.1; δ_H 1.79 (3H, s, H-4′), δ_C 17.5; δ_H 1.68 (3H, s, H-5′), δ_C 25.6 and δ_C 131.6 (C-3′) instead of the dimethylchromane ring present in **1**. HMBC data confirmed the position of the prenyl group in **3** (Table 3) at C-2 by the ^2J correlation of H-1′ with C-2, and the ^3J correlations of H-1′ with C-1 and C-3. The structure of pruniflorone C was therefore assigned as **3**.

Pruniflorone D (**4**) showed a molecular formula of $C_{26}H_{32}O_7$ by HREIMS. The ^1H NMR spectral data (Table 1) of **4** were similar to those of **3**, except for an additional methoxyl singlet signal at δ_H 3.32, δ_C 49.2. This group replaced the hydroxyl group at C-3″ in **3**. HMBC correlations between

Table 1. ^{1}H NMR spectral data of **1–6** (δ in ppm, multiplicities, J in Hz)

Position	**1**[a]	**2**[b]	**3**[c]	**4**[b]	**5**[c]	**6**[a]
4	6.29 s	6.33 s	6.32 s	6.34 s	6.38 s	6.35 s
5	6.72 s	6.76 s	6.75 s	6.82 s	6.78 s	6.74 s
1′	2.73 br t (7.5)	2.63 br t (7.0)	3.33 d (7.2)	3.36 d (7.5)	2.72 m	2.64 t (6.9)
2′	1.72 br t (7.5)	1.83 br t (7.0)	5.21 br t (7.2)	5.23 br t (7.5)	1.71 m	1.82 t (6.9)
4′	1.34 s	1.41 s	1.79 s	1.81 s	1.29 s	1.46 s
5′	1.34 s	1.41 s	1.68 s	1.69 s	1.29 s	1.46 s
1″	3.38 m	3.37 m	3.39 m	3.38 m	4.12 d (6.9)	3.58 t (6.9)
2″	1.78 m	1.79 m	1.77 m	1.77 m	5.26 m	1.84 t (6.9)
4″	1.30 s	1.31 s	1.32 s	1.30 s	1.85 s	1.36 s
5″	1.30 s	1.31 s	1.32 s	1.30 s	1.69 s	1.36 s
1-OH			[d]	13.60 s	[d]	
3-OMe	3.90 s	3.89 s	3.90 s	3.91 s	3.92 s	3.90 s
7-OMe	3.84 s	3.83 s	3.84 s	3.86 s	3.80 s	
3″-OMe		3.35 s		3.32 s		

[a] Recorded at 300 MHz in $CDCl_3$.
[b] Recorded at 500 MHz in $CDCl_3$.
[c] Recorded at 300 MHz in $CD_3OD/CDCl_3$.
[d] Exchangeable with CD_3OD.

3″-OMe and δ_C 74.9 (C-3″), and H-2″ with δ_C 22.2 (C-1″) and 74.9 (C-3″) (Table 3) proved this assignment. Thus, the structure of pruniflorone D was assigned as **4**.

Pruniflorone E (**5**) was isolated as a yellow gum, which showed a molecular ion peak at m/z 442.2000 $[M]^+$ in the HREIMS, corresponding to a molecular formula of $C_{25}H_{30}O_7$. The UV and IR spectra of **5** exhibited the same patterns as those of **3** and **4**. Extensive 1D and 2D NMR analysis of **5** showed that this xanthone has the same substituents as **3**; a 3-hydroxyl-3-methylbutyl, a prenyl and two methoxyl groups (Tables 1 and 2). However, the ^{1}H NMR spectral data of **5** (Table 1) and **3** exhibited different chemical shifts for the 3-hydroxyl-3-methylbutyl and prenyl moieties. From HMBC spectral data (Table 3), the methylene protons of H-1′ of a 3-hydroxyl-3-methylbutyl group showed correlations with δ_C 163.3 (C-3), 159.8 (C-1) and 103.6 (C-2), and the methoxyl group at δ_H 3.92 showed a cross peak with δ_H 6.38 (H-4) in the NOESY spectrum (Table 4). It was therefore apparent there that the 3-hydroxyl-3-methylbutyl and methoxyl substituent groups were located at C-2 and C-3 in ring A, respectively. In addition, the signal for H-1″ of the prenyl group (δ 4.12, 2H, d, J=6.9 Hz) in **5** appears further downfield than the expected values for this functionality (ca. δ 3.5–3.3).[10] This can be explained by the fact that H-1″ is in a deshielding region of the carbonyl functionality. The HMBC experiment was also used to confirm the position of attachment of the prenyl group in **5** (Table 3) at C-8 by the ^2J correlation of H-1″ with C-8. Thus, the structure of pruniflorone E was assigned as **5**, a constitutional isomer of **3**.

Table 2. ^{13}C NMR (75 MHz) spectral data of **1–6** in $CD_3OD/CDCl_3$

Position	**1**	**2**[a]	**3**[a]	**4**[a,b]	**5**[a]	**6**[b]
1	155.2	155.3	159.1	159.8	159.8	155.6
2	105.6	105.4	111.3[c]	111.5	103.6	105.2
3	162.0	161.4	163.3	163.5	163.3	161.3
4	89.6	89.6	88.7	88.8	88.9	89.7
5	101.3	100.8	101.7	101.4	101.7	99.7
6	154.6	154.5	156.0	154.5	155.1	150.1
7	143.3	142.3	143.1	142.6	143.0	137.7
8	138.4	138.5	138.4	138.8	137.2	122.0
9	177.5	176.4	181.8	182.0	181.9	177.4
4a	157.1	156.9	155.1	155.2	155.4	157.2
4b	155.2	152.9	155.6	155.8	155.6	151.7
8a	113.8	115.5	111.2[c]	112.5	112.0	114.1
9a	107.2	107.9	103.5	103.8	111.9	107.8
1′	16.9	17.1	21.1	21.4	16.9	17.1
2′	31.3	31.4	122.1	122.3	42.1	31.5
3′	75.7	75.2[c]	131.6	131.7	71.1	75.2[c]
4′	26.1	26.5	17.5	17.8	28.9	26.6
5′	26.1	26.5	25.6	25.8	28.9	26.6
1″	21.8	21.8	21.8	22.2	26.4	22.6
2″	43.9	39.7	44.0	39.9	123.2	33.1
3″	70.7	75.1[c]	70.8	74.9	131.9	75.3[c]
4″	28.7	25.3	28.7	25.2	18.1	26.5
5″	28.7	25.3	28.7	25.2	25.8	26.5
3-OMe	55.6	55.7	55.3	55.8	55.8	55.7
7-OMe	60.9	62.0	61.2	62.2	61.4	
3″-OMe		49.2		49.2		

[a] Recorded at 125 MHz.
[b] Recorded in $CDCl_3$.
[c] May be interchangeable.

Pruniflorone F (**6**), a pale yellow powder, was deduced as $C_{24}H_{26}O_6$ from an exact mass measurement. The ^{1}H and ^{13}C NMR spectral data of **6** (Tables 1 and 2) were closely related to those of **1**. The major difference was the replacement of the ^{1}H NMR signals for the methoxyl and 3-hydroxyl-3-methylbutyl groups at C-7 and C-8, respectively, of **1** with a dimethylchromane ring at δ 3.58 (2H, t, J=6.9 Hz, H-1″), 1.84 (2H, t, J=6.9 Hz, H-2″) and 1.36 (6H, s, H-4″ and H-5″) in **6**. The observed HMBC correlations (Table 3) confirmed the assignment of this structure.

Pruniflorone G (**7**), a brown powder, was deduced as $C_{28}H_{30}O_6$ from an exact mass measurement. The ^{1}H NMR spectral data of **7** (Table 5) were similar to those of gerontoxanthone I (29),[11] except for the appearance of the signal of a chromene ring bearing a methyl group and six-carbon side chain (Table 5) instead of the prenyl moiety present in gerontoxanthone I. The proposed structure was further supported by the appearance of an abundant fragment ion m/z 379 ($[M]^+ -83$), resulting from loss of the 4-methylpent-3-enyl moiety. The location of a chromene ring was confirmed by HMBC (Table 6), in which the methine proton H-1′ at δ_H 6.83 was correlated with δ_C 81.1 (C-3′), 105.2 (C-2), 156.8 (C-1) and 159.2 (C-3), while the methine proton H-2′ at δ_H 5.58 was correlated with δ_C 26.9 (C-9′), 41.8

Table 3. HMBC (300 MHz) spectral data of **1**–**6** in $CDCl_3$

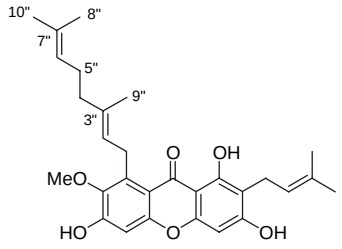
Position	**1**[a]	**2**[b]	**3**[a]	**4**[b]	**5**[a]	**6**
4	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-2, C-3, C-9, C-4a, C-9a	C-3, C-9, C-4a, C-9a
5	C-7, C-8, C-9, C-4b, C-8a	C-6, C-7, C-9, C-4b, C-8a	C-6, C-7, C-8, C-4b, C-8a, C-9	C-6, C-9, C-4b, C-8a	C-6, C-7, C-9, C-4b, C-8a	C-6, C-7, C-9, C-4b, C-8a
1′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′, C-3′	C-1, C-2, C-3, C-2′	C-1, C-2, C-3, C-2′, C-3′
2′	C-2, C-1′, C-3′, C-4′, C-5′	C-2, C-1′, C-3′, C-4′, C-5′		C-2, C-4′, C-5′	C-3′, C-4′, C-5′	C-2, C-1′, C-3′, C-4′, C-5′
4′	C-1, C-1′, C-2′	C-2′, C-3′	C-2′, C-3′, C-5′	C-2′, C-3′	C-2′, C-3′	C-2′, C-3′
5′	C-1, C-1′, C-2′	C-2′, C-3′	C-2′, C-3′, C-4′	C-2′, C-3′	C-2′, C-3′	C-2′, C-3′
1″	C-7, C-8, C-8a, C-3″	C-7, C-8, C-8a, C-2″, C-3″	C-7, C-8, C-8a, C-3″	C-7, C-8, C-8a, C-2″	C-8	C-7, C-8, C-8a, C-2″, C-3″
2″	C-8, C-3″, C-4″, C-5″	C-8, C-1″, C-3″, C-4″, C-5″	C-8, C-3″	C-1″, C-3″, C-4″, C-5″		C-8, C-1″, C-3″, C-4″, C-5″
4″	C-1″, C-2′, C-3″	C-2″, C-3″	C-1″, C-2″, C-3″	C-2″, C-3″	C-2″, C-3″, C-5″	C-2″, C-3″
5″	C-1″, C-2″, C-3″	C-2″, C-3″	C-1″, C-2″, C-3″	C-2″, C-3″	C-2″, C-3″, C-4″	C-2″, C-3″
1-OH				C-1, C-2, C-9a		
3-OMe	C-3	C-3	C-3	C-3	C-3	C-3
7-OMe	C-7	C-7	C-7	C-7	C-7	
3″-OMe		C-3″		C-3″		

[a] Recorded in $CD_3OD/CDCl_3$.
[b] Recorded at 500 MHz.

(C-4′), 81.1 (C-3′), 105.2 (C-2) and 159.2 (C-3), respectively. From these data, the structure of pruniflorone G was assigned as **7**.

Pruniflorone H (**8**) was obtained as a yellow powder, which showed a molecular ion peak at *m*/*z* 476.2215 $[M]^+$ in the HREIMS corresponding to a molecular formula of $C_{29}H_{32}O_6$. The ^1H and ^{13}C NMR spectral data of **8** (Table 5) showed characteristics similar to those of **7**, except that an additional signal of a methoxyl group was observed at δ_H 3.32, δ_C 56.6 in **8**, this methoxyl group was located at C-6 due to the correlation with δ_C 149.0 (C-6) from HMBC experiment (Table 6). Thus, the structure of pruniflorone H was assigned as **8**.

Pruniflorone I (**9**) showed a molecular formula of $C_{28}H_{32}O_5$ by HREIMS. The ^1H and ^{13}C NMR spectral data of **9** (Table 7) showed characteristics similar to those of cowanin,[12] except for the appearance of an aromatic proton at δ_H 7.18 (s, H-7), δ_C 123.7 instead of the methoxyl group at δ_H 3.80 (s, 7-OMe) present in cowanin. Therefore, the structure of pruniflorone I was deduced as **9**.



cowanin

Pruniflorone J (**10**) was isolated as orange viscous oil, which was assigned as $C_{25}H_{26}O_6$ from an exact mass measurement. The UV spectrum of **10** exhibited absorption maxima at 269, 283, 366 and 440 nm, suggesting an anthraquinone as a basic structure.[13] IR absorption bands at 1673 and 1625 $cm^{-1}$and ^{13}C NMR chemical shifts at 190.8 and 182.0 also indicated the presence of carbonyl and chelated carbonyl groups, respectively. Chelated hydroxyl protons were shown at δ_H 12.30 (1H, s) and 12.13 (1H, s). The ^1H and ^{13}C NMR spectral data of **10** (Table 8) showed characteristics similar to those of 3-geranyloxy-6-methyl-1,8-dihydroxyanthraquinone,[14] except for the appearance of *trans*-olefinic protons at δ_H 5.62 (1H, dd, J=6.5, 15.5 Hz, H-5′) and 5.69 (1H, d, J=15.5 Hz, H-6′) in **10** instead of methylene protons at C-5′ and an olefin at C-6′. The chemical shift of the methylene protons at C-4′ was shifted downfield (δ_H 2.79 (2H, d, J=6.5 Hz, H-4′)) compared to δ_H 2.11,[14] due to the double allylic status of these protons. The location of H-4′ at C-4′ was supported by HMBC correlations. The chemical shift of C-7′ (δ 70.8) suggested an oxy-quarternary carbon, whose position was confirmed by HMBC correlations with H-5′ and H-6′. Thus, the structure of pruniflorone J was assigned as **10**.

The following known compounds were also isolated from the roots and barks of *C. formosum* ssp. *pruniflorum*: dulxisxanthone F (**11**),[15] β-mangostin (**12**),[16] α-mangostin (**13**),[16] formoxanthone A (**14**),[8] 3-isomangostin (**15**),[16] 3,4-dihydro-5,9-dihydroxy-8-methoxy-7-(3-methoxy-3-methylbutyl)-2,2-dimethyl-2*H*,6*H*-pyrano-[3,2-*b*]xanthen-6-one (**16**),[17]

Table 4. NOESY (300 MHz) spectral data of **1–6** in $CDCl_3$

Position	**1**[a]	**2**[b]	**3**[a]	**4**[b]	**5**[a]	**6**
4	3-OMe	3-OMe	3-OMe	3-OMe	3-OMe	3-OMe
5						
1′	H-2′	H-2′	H-2′, H-4′	H-2′		H-2′
2′	H-1′, H–4′, H-5′	H-1′, H-4′, H-5′	H-1′, H-5′	H-1′, H-5′	H-4′, H-5′	H-1′, H-4′, H-5′
4′	H-2′	H-2′	H-1′		H-2′	H-2′
5′	H-2′	H-2′	H-2′	H-2′	H-2′	H-2′
1″	7-OMe, H-2″	H-2″	H-2″	H-2″		H-2″
2″	H-1″, H-4″, H-5″	H-4″, H-5″, 3″-OMe	H-1″, H-4″, H-5″	H-1″, H-4″, H-5″, 3″-OMe	H-5″	H-1″, H-4″, H-5″
4″	H-2″	H-2″	H-2″	H-3″		H-2″
5″	H-2″	H-2″	H-2″	H-3″	H-2″	H-2″
1-OH						
3-OMe	H-4	H-4	H-4	H-4		H-4
7-OMe						
3″-OMe				H-4″, H-5″, 3″-OMe		

[a] Recorded in $CD_3OD/CDCl_3$.
[b] Recorded at 500 MHz.

3,4-dihydro-5,9-dihydroxy-7-(3-hydroxy-3-methylbutyl)-8-methoxy-2,2-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one (**17**),[17] isocudraniaxanthone B (**18**),[18] 10-*O*-methylmacluraxanthone (**19**),[19] 3-geranyloxy-6-methyl-1,8-dihydroxyanthraquinone (**20**),[14] 11-hydroxy-5-methoxy-2,2,9-trimethyl-2*H*-anthra-[1,2-*b*]pyran-7,12-dione (**21**),[20] vismiaquinone A (**22**),[21] madagascin (**23**),[22] physcion (**24**),[23] emodin (**25**),[24] formoxanthone B (**26**),[8] macluraxanthone (**27**),[25] xanthone V_1 (**28**),[26] gerontoxanthone I (**29**),[11] 6-deoxyjacareubin (**30**)[27] and 3,4-dihydrojacareubin (**31**).[28] These compounds were identified by comparison of their spectroscopic data with those reported in the literature. In addition, the X-ray structure of **11** was reported here for the first time (Fig. 2).

Table 5. ^1H and ^{13}C NMR spectral data of **7** and **8** in $CDCl_3$

Position	**7**		**8**	
	^1H (J in Hz)[a]	^{13}C (δ)[b]	^1H (J in Hz)[a]	^{13}C (δ)[b]
1		156.8		156.6
2		105.2		104.9
3		159.2		159.3
4		112.7		113.0
5		131.0		133.4
6		149.0		151.4
7	6.96 d (9.0)	112.8	6.97 d (9.0)	108.2
8	7.69 d (9.0)	117.5	7.75 d (9.0)	116.8
9		180.7		181.0
4a		154.1		154.8
4b		144.5		144.3
8a		113.7		114.2
9a		102.9		103.0
1′	6.83 d (9.9)	116.7	6.81 d (9.9)	116.7
2′	5.58 d (9.9)	125.6	5.56 d (9.9)	125.6
3′		81.1		81.1
4′	1.91 m[c]	41.8	1.89 m[c]	41.7
	1.72 m[c]		1.70 m[c]	
5′	2.14 m	23.2	2.10 m	23.3
6′	5.13 br t (7.2)	123.7	5.12 br t (7.5)	123.7
7′		132.1		132.0
8′	1.60 s	17.6	1.59 s	17.6
9′	1.47 s	26.9	1.45 s	26.9
10′	1.69 s	25.7	1.68 s	25.6
1″		41.4		41.3
2″	6.75 dd (10.8, 17.7)	156.7	6.66 dd (10.5, 17.4)	154.9
3″	5.05 dd (1.2, 10.8)	103.3	5.04 dd (1.2, 10.5)	104.5
	5.23 dd (1.2, 17.7)		5.18 dd (1.2, 17.4)	
4″	1.66 s	28.0	1.66 s	28.4
5″	1.66 s	28.4	1.66 s	28.4
1-OH	13.50 s		13.50 s	
6-OMe			3.32 s	56.6

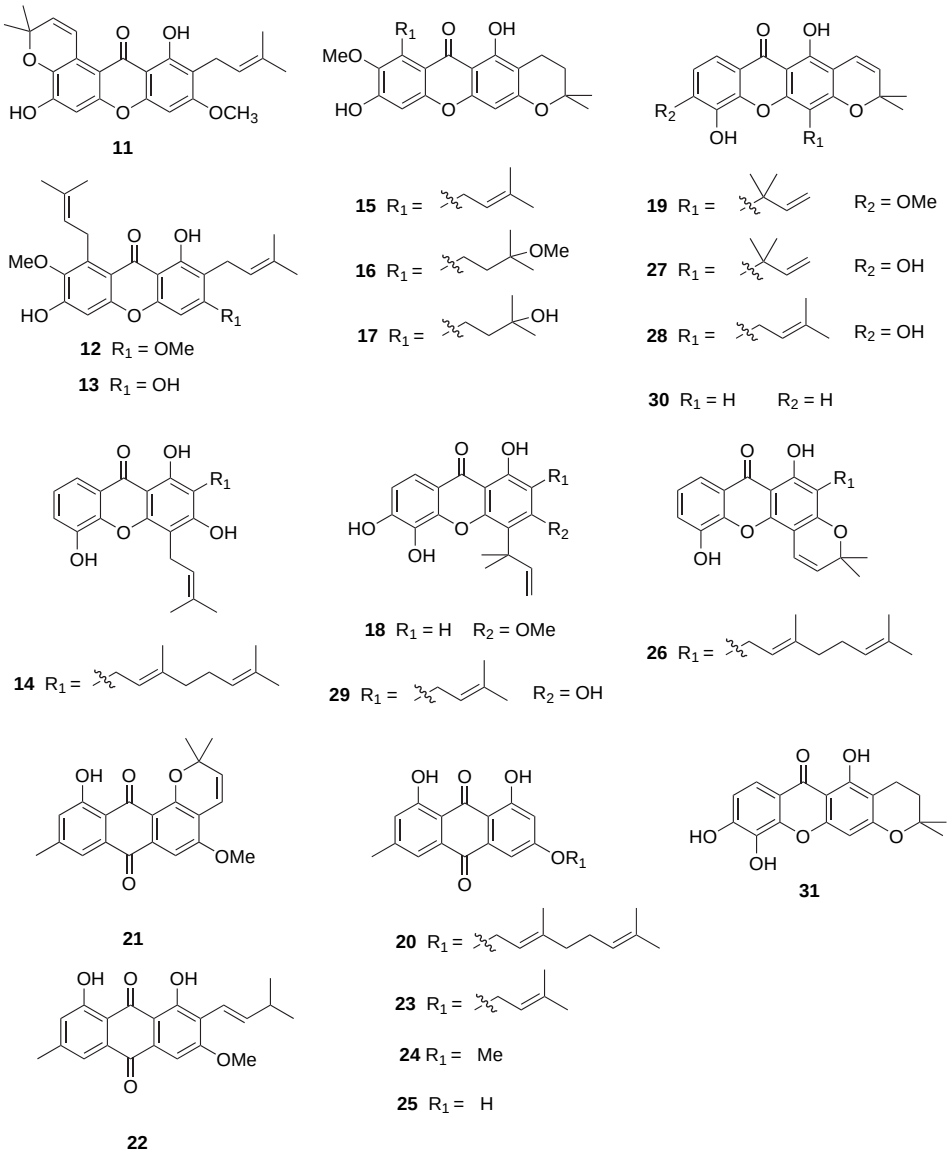
[a] Recorded at 300 MHz.
[b] Recorded at 75 MHz.
[c] Reduced from HMQC experiment.

Only stable compounds of sufficient quantity were evaluated for their antibacterial activity against both Gram-positive (*Bacillus substilis* and *Staphylococcus aureus*) and Gram-negative (*Streptococcus faecalis*, *Salmonella typhi*, *Shigella sonei* and *Pseudomonas aeruginosa*) bacteria. Cytotoxicity against MCF-7 (breast adenocarcinoma), HeLa (Human cervical cancer), HT-29 (colon cancer) and KB (human oral cancer) cell lines was also evaluated. The results of antibacterial activity of the tested compounds are given in Table 9. Pruniflorone E (**5**) and **13** showed potent antibacterial activity against *B. substilis*, *S. aureus* and *S. faecalis*, whereas pruniflorone C (**3**) and **31** exhibited strong activity against *B. substilis* and *S. aureus*. Compounds **28** and **29** showed strong and broad spectrum of antibacterial activity compared to vancomycin. For this investigation, only **29** showed inhibition against *S. sonei* and *P. aeruginosa*. It is interesting to note that, compounds **12**, **17** and **30** were highly active specifically against *S. aureus* therefore it might be worthwhile to further investigate the structure–activity relationships (SAR) of these compounds against *S. aureus*. Compounds **20**–**25** exhibited no antibacterial activity. According to the MIC values shown in Table 9, it seems that the isoprenyl or 3-hydroxyl-3-methylbutyl moiety at C-2 and C-8, and the catechol unit are both important for antibacterial activity, whereas isoprenyl unit at C-8, which was cyclized to 3,3-dimethylchromene or 3,3-dimethylchromane rings might decrease the antibacterial activity as shown in compounds **6** and **11**. In addition to antibacterial activity, compound **29** strongly inhibited all cancer cell lines used in this investigation compared to camptothecin, whereas compounds **12**, **13**, **28** and **31** showed less inhibitory activity. Compounds **1**, **5**, **6**, **11** and **20**–**25** were found to be inactive for cytotoxic activity (Table 10).

3. Experimental

3.1. General experimental procedures

Melting points were determined on the Fisher-John melting point apparatus. Optical rotations were measured on



a JASCO P-1020 digital polarimeter. UV and IR spectra were recorded on SPECORD S 100 (Analytikjena) and Perkin–Elmer FTS FTIR spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz Varian UNITY INOVA and/or 300 MHz Bruker FTNMR Ultra Shield™ spectrometers in $CDCl_3$ or CD_3OD with TMS as

Table 6. HMBC and NOESY (300 MHz) spectral data of **7** and **8** in $CDCl_3$

Position	**7**		**8**	
	HMBC	NOESY	HMBC	NOESY
7		H-8	C-5, C-6, C-8a	H-8, 6-OMe
8	C-6, C-9	H-7	C-6, C-9	H-7
1′	C-1, C-2, C-3, C-3′	H-2′	C-1, C-2, C-3, C-3′	H-2′
2′	C-2, C-3, C-3′ C-4′, C-9′	H-1′, H-4′	C-2, C-3′	H-1′
4′	C-3′, C-5′	H-2′, H-6′	C-3′	
5′	C-3′, C-4′, C-6′, C-7′	H-6′	C-4′	
6′	C-5′, C-8′, C-10′	H-4′, H-5′	C-4′	
8′	C-6′, C-7′		C-6′, C-7′	
9′	C-2′, C-3′, C-4′		C-3′, C-4′	
10′	C-6′, C-7′		C-6′, C-7′	
2″	C-4, C-1″	H-3″	C-4, C-1″	H-3″
3″	C-1″, C-2″	H-2″	C-1″, C-2″, C-4″, C-5″	H-2″, H-4″, H-5″
4″	C-4, C-1″		C-4, C-1″, C-2″	H-3″
5″	C-4, C-1″		C-4, C-1″, C-2″	H-3″
1-OH	C-1, C-2, C-9a		C-1, C-2, C-9a	
6-OMe			C-6	H-7

Table 7. NMR (300 MHz) spectral data of **9** in $CDCl_3$

Position	**9**			
	^1H (J in Hz)	^{13}C (δ)	HMBC	NOESY
1		160.7		
2		108.5		
3		162.1		
4	6.19 s	93.2	C-2, C-3, C-9, C-4a, C-9a	
5	7.17 s	116.7	C-6, C-9, C-4b, C-8a	
6		152.0		
7	7.18 s	123.7	C-6, C-8	
8		127.1		
9		183.4		
4a		155.3		
4b		151.3		
8a		118.4		
9a		104.1		
1′	3.35 d (6.9)	21.5	C-1, C-2, C-3, C-2′, C-3′	H-2′, H-4′
2′	5.19 br t (6.9)	121.4	C-4′	H-1′, H-5′
3′		135.5		
4′	1.66 s	25.8	C-2′, C-3′	H-1′
5′	1.74 s	17.9	C-2′, C-3′	H-2′
1″	4.20 d (6.6)	25.6	C-7, C-8, C-4a, C-8a, C-2′, C-3′	H-2″, H-9″
2″	5.16 br t (6.6)	121.5	C-8, C-4′, C-9′	H-1″, H-4″
3″		138.6		
4″	1.98 m	39.7	C-3′, C-9′	H-2″
5″	1.98 m	26.4	C-4′, C-6′, C-7′	H-6″
6″	4.94 m	123.8	C-4′, C-5′, C-8′	H-5″, H-8″
7″		132.0		
8″	1.55 s	25.8	C-6′, C-7′	H-6″
9″	1.77 s	16.4	C-2′, C-3′	H-1″
10″	1.48 s	17.7	C-6′, C-7′	
1-OH	13.54 s		C-1, C-2, C-9a	

Table 8. NMR (500 MHz) spectral data of **10** in $CDCl_3$

Position	**10**			
	^1H (J in Hz)	^{13}C (δ)	HMBC	NOESY
1-OH	12.30 s	165.1	C-1, C-2, C-9a	
2	6.68 d (2.5)	107.6	C-1, C-4	H-1′
3		165.8		
4	7.37 d (2.5)	108.7	C-3, C-10, C-9a	H-1′
5	7.62 br s	121.3	C-7, C-10, C-8a, C-6(Me)	6-Me
6		148.4		
7	7.08 br s	124.5	C-5, C-8, C-8a, C-6(Me)	6-Me
8-OH	12.13 s	163.0	C-7, C-8, C-8a	
9		190.8		
10		182.0		
4a		135.2		
4b		133.2		
8a		113.7		
9a		110.1		
1′	4.68 d (6.5)	65.8	C-3, C-2′, C-3′	
2′	5.50 br t (6.5)	119.0	C-4′	
3′		141.5		
4′	2.79 d (6.5)	42.1	C-2′, C-3′, C-5′, C-6′, C-9′	
5′	5.62 dd (6.5, 15.5)	123.9	C-4′, C-7′	
6′	5.69 d (15.5)	140.5	C-4′, C-7′, C-8′, C-10′	
7′		70.8		
8′	1.33 s	29.8	C-6′, C-7′	
9′	1.77 s	16.8	C-2′, C-3′, C-4′	
10′	1.33 s	29.8	C-6′, C-7′	
6-Me	2.45 s	22.2	C-5, C-6, C-7	H-5, H-7

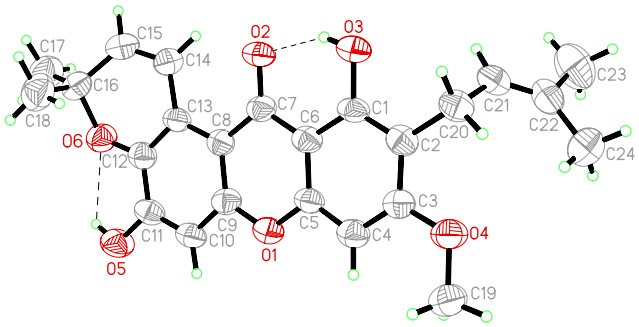


Figure 2. The ORTEP plot of **11**.

the internal standard. Chemical shifts are reported in δ (ppm) and coupling constants (J) are expressed in Hertz. EI and HREIMS were measured on a Kratos MS 25 RFA spectrometer. Quick column chromatography (QCC) and column chromatography (CC) were carried out on silica gel 60 F_{254} (Merck) and silica gel 100 (Merck), respectively.

3.2. Plant material

Barks and roots of *C. formosum* ssp. *pruniflorum* were collected in May 2004 from Nong Khai Province, northeastern part of Thailand. Identification was made by Professor Puangpen Sirirugsa, Department of Biology, Faculty of Science, Prince of Songkla University and a specimen (No. 0012677) was deposited at Prince of Songkla University Herbarium.

3.3. Isolation and extraction

Air-dried roots (5.30 kg) were extracted with CH_2Cl_2 (2×20 L, for 5 days) at room temperature. The crude CH_2Cl_2 extracts were evaporated under reduced pressure to afford a brownish crude (30.04 g) extract. The crude extract was subjected to QCC on silica gel using hexane as the first eluent and then increasing polarity with EtOAc and acetone, respectively, to give eight fractions (FR1–FR8). Fraction FR2 was separated by CC eluting with CH_2Cl_2–hexane (4:1, v/v) to afford four subfractions (FR2A–FR2D). Subfraction FR2A was further purified by CC with EtOAc–hexane (3:7, v/v) to give **12** (45.0 mg). Subfraction FR2B was further purified by CC eluting with acetone–hexane (1:9, v/v) to give **13** (15.0 mg). Subfraction FR2C was further purified by CC on reversed-phase silica gel C-18 with MeOH to give **7** (8.0 mg) and **18** (2.5 mg). Fraction FR3 (2.56 g) was separated by CC with acetone–hexane (3:17, v/v) to give **14** (15.0 mg), **6** (5.8 mg) and **11** (10.2 mg), which was further recrystallized in $CHCl_3$–MeOH (4:1, v/v) to yield yellow needle single crystals. Fraction FR4 was subjected to CC with acetone–hexane (1:4, v/v) to afford five subfractions (FR4A–FR4E). Subfraction FR4B was separated by CC with acetone–hexane to give three fractions (FR4BA–FR4BC). Subfraction FR4BC was further purified by CC on reversed-phase silica gel C-18 with MeOH to give **9** (15.0 mg). Subfraction FR4D was further purified by CC on reversed-phase silica gel C-18 with MeOH to give **8** (3.0 mg) and **19** (3.0 mg). Fraction FR6 was purified by CC with acetone–hexane (1:4, v/v) to give **2** (3.3 mg), **15** (5.0 mg) and **16** (5.0 mg). Fraction FR7 was further purified by CC with EtOAc–hexane (2:3, v/v) to give **3** (8.2 mg),

Table 9. Antibacterial activity of compounds isolated from *C. formosum* ssp. *pruniflorum*

Compound	Minimum inhibitive concentration (μg/mL)					
	B. substilis	*S. aureus*	*S. faecalis*	*S. typhi*	*S. sonei*	*P. aeruginosa*
1	300	18.7	—	—	300	—
3	<1.1	<1.1	150	—	300	—
5	<1.1	<1.1	<1.1	—	300	18.7
6	300	9.3	4.6	—	300	37.5
10	300	75	150	—	300	—
11	75	18.7	—	—	300	—
12	18.7	<1.1	75	—	—	—
13	<1.1	<1.1	<1.1	—	18.7	18.7
14	18.7	37.5	—	—	—	—
17	9.3	<1.1	—	—	—	—
27	4.6	4.6	2.3	9.6	—	—
28	<1.1	<1.1	<1.1	<1.1	—	9.3
29	<1.1	<1.1	4.6	37.5	<1.1	<1.1
30	4.6	<1.1	75	—	150	150
31	<1.1	<1.1	37.5	—	—	37.5

— = Inactive at >50 μg/mL.

Table 10. In vitro cytotoxic activity of compounds isolated from *C. formosum* ssp. *pruniflorum*

Compound	Cell line			
	MCF-7	HeLa	HT-29	KB
	IC_{50} (μg/mL)			
12	3.6	4.9	4.8	4.6
13	3.7	3.2	4.5	3.2
28	>25.0	4.7	6.0	2.7
29	0.6	0.7	0.7	0.6
31	>5.0	3.4	>5.0	>5.0

4 (1.5 mg) and **5** (2.0 mg). Fraction FR8 was separated by CC with a gradient of acetone–hexane to give four fractions (FR8A–FR8D). Subfraction FR8C was further purified by CC with a gradient of acetone–hexane to give **17** (2.1 mg) and **1** (32.2 mg), which was further recrystallized from $CHCl_3$–MeOH (4:1, v/v) to yield pale yellow single crystals.

Ground-dried barks (4.00 kg) were extracted with CH_2Cl_2 and acetone (each 2×20 L, for 5 days) at room temperature, successively. The crude extracts were evaporated under reduced pressure to afford brownish crude CH_2Cl_2 (76.28 g) and acetone (21.74 g) extracts. The crude CH_2Cl_2 extract was subjected to QCC eluting with increasing polarities of EtOAc and acetone in hexane to afford 10 fractions (F1–F10). Fraction F1 (2.01 g) was separated by CC with acetone–hexane (1:19, v/v) to afford three subfractions (F1A–F1C). Subfraction F1B was further purified by CC with EtOAc–hexane (1:9, v/v) to give **22** (3.3 mg) and **23** (5.6 mg). Fraction F2 (58.06 g) was further separated by CC using a gradient of hexane with EtOAc to afford eight subfractions (F2A–F2H) and **27** (150.0 mg). Subfraction F2C (120.02 g) was further purified by CC with EtOAc–hexane (1:4, v/v) to give **10** (5.2 mg) and **20** (68.2 mg). Subfraction F2D was purified by CC with CH_2Cl_2–hexane (3:2, v/v) to give three fractions (F2DA–F2DC). Subfraction F2DB was further purified by prep TLC with CH_2Cl_2–hexane (3:7, v/v) to give **26** (1.5 mg). Subfraction F2G was subjected to CC with acetone–hexane (1:9, v/v) to give **24** (5.0 mg). Fraction F3 was separated by CC with acetone–hexane (1:9, v/v) to afford five fractions (F3A–F3E). Subfraction F3D was purified by CC with acetone–hexane (3:17, v/v) to give **29** (25.0 mg). Fraction F6 was separated by CC with acetone–hexane (3:17, v/v) to afford seven subfractions (F6A–F6G). Subfraction F6B was further purified by CC with EtOAc–hexane (3:7, v/v) to give **28** (8.0 mg). The crude acetone was subjected to QCC eluting with a gradient of hexane–acetone to afford 12 fractions (FA1–FA12). Fraction FA2 (1.98 g) was further separated by CC with acetone–hexane (3:97, v/v) to give six subfractions (FA2A–FA2F). Subfraction FA2B (422.0 mg) was further purified by CC with acetone–hexane (1:19, v/v) to give **21** (3.0 mg). Fraction FA3 was further purified by CC with EtOAc–hexane (1:9, v/v) to give **30** (4.0 mg). Fraction FA7 was separated by CC with acetone–hexane (1:4, v/v) to give **25** (3.1 mg) and **31** (5.0 mg).

3.3.1. Pruniflorone A (1). Pale yellow needle crystals, mp 259-260 °C, $[\alpha]_D^{26}$ −5.1 (*c* 0.430, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 247 (4.29), 261 (4.34), 314 (4.17), 355 (3.55) nm; IR (KBr) ν_{max} 3414, 1642, 1614 cm^{-1}; HREIMS *m/z* $[M]^+$ 442.1994 (calcd for $C_{25}H_{30}O_7$, 442.1992); ^1H NMR ($CDCl_3$, 300 MHz), see Table 1; ^{13}C NMR (CD_3OD/$CDCl_3$, 75 MHz), see Table 2.

3.3.2. Pruniflorone B (2). Yellow powder, mp 215–217 °C, $[\alpha]_D^{26}$ −4.0 (*c* 0.165, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 246 (4.01), 299 (3.79), 334 (3.40) nm; IR (neat) ν_{max} 3177, 1639, 1611 cm^{-1}; HREIMS *m/z* $[M]^+$ 456.2116 (calcd for $C_{26}H_{32}O_7$, 456.2148); ^1H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR (CD_3OD/$CDCl_3$, 125 MHz), see Table 2.

3.3.3. Pruniflorone C (3). Yellow solid, mp 134–136 °C, $[\alpha]_D^{27}$ −5.5 (*c* 0.145, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 245 (3.89), 259 (3.86), 313 (3.75), 353 (3.25) nm; IR (KBr) ν_{max} 3414, 1632, 1614 cm^{-1}; HREIMS *m/z* $[M]^+$ 442.1995 (calcd for $C_{25}H_{30}O_7$, 442.1992); ^1H NMR (CD_3OD/$CDCl_3$, 300 MHz), see Table 1; ^{13}C NMR ($CDCl_3$/CD_3OD, 125 MHz), see Table 2.

3.3.4. Pruniflorone D (4). Yellow viscous oil, $[\alpha]_D^{26}$ 17.5 (*c* 0.075, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 249 (5.00), 259 (4.98), 312 (4.92), 352 (4.35) nm; IR (neat) ν_{max} 3170, 1646, 1597 cm^{-1}; HREIMS *m/z* $[M]^+$ 456.2198 (calcd for

$C_{26}H_{32}O_7$, 456.2148); ^{1}H NMR ($CD_3OD/CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CD_3OD/CDCl_3$, 125 MHz), see Table 2.

3.3.5. Pruniflorone E (5). Yellow gum, $[\alpha]_D^{27}$ −4.4 (*c* 0.130, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 245 (3.91), 260 (3.88), 312 (3.78), 353 (3.25) nm; IR (KBr) ν_{max} 3414, 1635, 1614 cm^{-1}; HREIMS *m/z* [M]$^+$ 442.2000 (calcd for $C_{25}H_{30}O_7$, 442.1992); ^{1}H NMR ($CD_3OD/CDCl_3$, 300 MHz), see Table 1; ^{13}C NMR ($CD_3OD/CDCl_3$, 125 MHz), see Table 2.

3.3.6. Pruniflorone F (6). Pale yellow powder, mp 235–236 °C, $[\alpha]_D^{26}$ −9.2 (*c* 0.290, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 255 (3.94), 258 (3.99), 302 (3.77), 349 (3.40) nm; IR (KBr) ν_{max} 3177, 1614 cm^{-1}; HREIMS *m/z* [M]$^+$ 410.1728 (calcd for $C_{24}H_{26}O_6$, 410.1729); ^{1}H NMR ($CDCl_3$, 300 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 75 MHz), see Table 2.

3.3.7. Pruniflorone G (7). Brown powder, mp 143–145 °C, $[\alpha]_D^{27}$ −7.4 (*c* 0.425, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 243 (4.56), 288 (4.81), 335 (4.53) nm; IR (KBr) ν_{max} 3414, 1646, 1628, 1580 cm^{-1}; EIMS *m/z* 462 (11) [M]$^+$, 447 (5), 379 (100); HREIMS *m/z* [M]$^+$ 462.2063 (calcd for $C_{28}H_{30}O_6$, 462.2042); ^{1}H NMR ($CDCl_3$, 300 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 75 MHz), see Table 3.

3.3.8. Pruniflorone H (8). Yellow powder, mp 175–177 °C, $[\alpha]_D^{27}$ −56.5 (*c* 0.050, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 252 (4.06), 289 (4.22), 336 (4.01) nm; IR (KBr) ν_{max} 3400, 1632, 1597, 1573 cm^{-1}; EIMS *m/z* 476 (31) [M]$^+$, 461 (15), 393 (100), 279 (15), 167 (39), 149 (94), 97 (21), 85 (22), 83 (29); HREIMS *m/z* [M]$^+$ 476.2215 (calcd for $C_{29}H_{32}O_6$, 476.2199); ^{1}H NMR ($CDCl_3$, 300 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 75 MHz), see Table 3.

3.3.9. Pruniflorone I (9). Brown viscous oil, $[\alpha]_D^{27}$ −11.3 (*c* 1.150, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 264 (4.70), 310 (4.45), 380 (3.94) nm; IR (neat) ν_{max} 3400, 1642, 1608 cm^{-1}; HREIMS *m/z* [M]$^+$ 448.2277 (calcd for $C_{28}H_{32}O_5$, 448.2250); ^{1}H NMR ($CDCl_3$, 300 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 75 MHz), see Table 4.

3.3.10. Pruniflorone J (10). Orange viscous oil, $[\alpha]_D^{27}$ −98.4 (*c* 0.250, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 269 (4.33), 283 (4.32), 366 (3.37), 440 (3.86) nm; IR (neat) ν_{max} 3414, 1673, 1625 cm^{-1}; HREIMS *m/z* [M]$^+$ 422.1737 (calcd for $C_{25}H_{26}O_6$, 422.1729); ^{1}H NMR ($CDCl_3$, 500 MHz), see Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 5.

3.4. X-ray crystallographic studies of 1 and 11

Crystallographic data were collected at 100.0(1) K with the Oxford Cyrosystem Cobra low-temperature attachment. The data were collected using a Bruker Apex2 CCD diffractometer with a graphite monochromated Mo Kα radiation at a detector distance of 5 cm and with APEX2 software.[29] The collected data were reduced using *SAINT* program,[29] and the empirical absorption corrections were performed using *SADABS* program.[29] The structures were solved by direct methods and refined by least-squares using the *SHELXTL* software package.[30] All non-hydrogen atoms were refined anisotropically, whereas all H atoms were placed in calculated positions with an O–H distance of 0.82 Å and C–H distances in the range 0.93–0.98 Å after checking their positions in the difference map. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atoms for methyl H atoms and $1.2U_{eq}$ for hydroxyl and the other H atoms. The final refinement converged well. Materials for publication were prepared using *SHELXTL*[30] and *PLATON*.[31]

Crystal data for **1**: $C_{25}H_{30}O_7$, M=442.49, 0.52×0.19×0.05 mm^3, monoclinic, $P2_1/n$, a=11.9303(4) Å, b=19.3361(7) Å, c=19.6631(7) Å, β=96.64(2), V=4505.1(3) Å^3, Z=8, D_x=1.305 Mg m^{-3}, μ(Mo Kα)=0.097 mm^{-1}, 79,107 reflection measured, 7928 unique reflections, R=0.0759, R_w=0.1699.

Crystal data for **11**: $C_{24}H_{24}O_6$, M=408.43, 0.54×0.22×0.08 mm^3, triclinic, P-1, a=8.1342(6) Å, b=8.9103(6) Å, c=14.2437(9) Å, α=82.229(4)°, β=80.494(4)°, γ=83.065(4)°, V=1003.70(12) Å^3, Z=2, D_x=1.351 Mg m^{-3}, μ(Mo Kα)=0.097 mm^{-1}, 25,932 reflection measured, 3926 unique reflections, R=0.1064, R_w=0.2883

The crystallographic-information files for **1** and **11** have been deposited in the Cambridge Crystallographic Data Center as CCDC293266 and CCDC293267, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

3.5. Bioassays

3.5.1. Antibacterial assay. The isolated compounds from roots and barks of *C. formosum* ssp. *pruniflorum* were tested against the microorganisms, *B. substilis* (obtained from Department of Industrial Biotechnology, PSU), *S. aureus* (TISTR517) (obtained from Microbial Resources Center (MIRCEN), Bangkok, Thailand), *S. faecalis*, *S. typhi*, *S. sonei* and *P. aeruginosa*. The last four microorganisms were obtained from Department of Pharmacognosy and Botany, PSU. The antibacterial assay employed was the same as described in Boonsri et al.[8] Vancomycin, which was used as a standard, showed antibacterial activity of 75 μg/mL.

3.5.2. Cytotoxic assay. The procedure for cytotoxic assay was performed by the sulphorhodamine B (SRB) assay as described by Skehan et al.[32] In this study, four cancer cell lines obtained from National Cancer Institute, Bangkok, Thailand, were used: MCF-7 (breast adenocarcinoma), KB (human oral cancer), HeLa (Human cervical cancer) and HT-29 (colon cancer). Camptothecin, which was used as a standard, showed cytotoxic activity in the range of 0.2–2.0 μg/mL.

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References and notes

1. Smitinand, T. *Thai Plant Names*; Prachachon: Bangkok, 2001; p 152.
2. Veesommai, U.; Kavduengtain, P. *Wild Trees in Thailand*; HN Group: Bangkok, 2004; pp 249–252.
3. Kitanov, G. M.; Assenov, I.; The Van, D. *Pharmazie* **1988**, *43*, H12–H13.
4. Aderson, E. F. *Econ. Bot.* **1986**, *40*, 442–450.
5. Grosvenor, P. W.; Gothard, P. K.; William, M. C.; Supriono, A.; Gray, D. O. *J. Ethnopharmacol.* **1995**, *45*, 75–95.
6. (a) Kijjoa, A.; Jose, M.; Gonzales, T. G.; Pinto, M. M. M.; Damas, A. M.; Mondranondra, I. O.; Silva, A. M.; Herz, W. *Phytochemistry* **1998**, *49*, 2159–2162; (b) Nguyen, L. H. D.; Harrison, L. J. *Phytochemistry* **1998**, *50*, 471–476; (c) Sia, G. L.; Bennett, G. J.; Harrison, L. J.; Sim, K. Y. *Phytochemistry* **1995**, *38*, 1521–1528.
7. Bennett, G. J.; Harrison, L. J.; Sia, G. L.; Sim, K. Y. *Phytochemistry* **1993**, *32*, 1245–1251.
8. Boonsri, S.; Karalai, C.; Ponglimanont, C.; Kanjana-opas, A.; Chantrapromma, K. *Phytochemistry* **2006**, *67*, 723–727.
9. Rukachaisirikul, V.; Kamkaew, M.; Sukavisit, D.; Phongpaichit, S.; Sawangchote, P.; Taylor, W. C. *J. Nat. Prod.* **2003**, *66*, 1531–1535.
10. Seo, E.-K.; Kim, N.-C.; Wani, M. C.; Wall, M. E.; Navarro, H. A.; Burgess, J. P.; Kawanishi, K.; Kardono, L. B. S.; Riswan, S.; Rose, W. C.; Fairchild, C. R.; Farnsworth, N. R.; Kinghorn, A. D. *J. Nat. Prod.* **2002**, *65*, 299–305.
11. Chang, C.-H.; Lin, C.-C.; Kawata, Y.; Hattori, M.; Namba, T. *Phytochemistry* **1989**, *28*, 2823–2826.
12. Pattalung, P. N.; Thongtheeraparp, W.; Wiriyachitra, P.; Taylor, W. C. *Planta Med.* **1994**, *60*, 365–368.
13. Wu, T.-S.; Lin, D.-M.; Shi, L.-S.; Damu, A. G.; Kuo, P.-C.; Kuo, Y.-H. *Chem. Pharm. Bull.* **2003**, *51*, 948–950.
14. Botta, B.; Delle Monache, F.; Delle Monache, G.; Marini Bettolo, G. B.; Oguakwa, J. U. *Phytochemistry* **1983**, *22*, 539–542.
15. Deachathai, S.; Mahabusarakam, W.; Phongpaichit, S.; Taylor, W. C.; Zhang, Y. J.; Yang, C. R. *Phytochemistry* **2006**, *67*, 464–469.
16. Mahabusarakam, W.; Wiriyachitra, P.; Taylor, W. C. *J. Nat. Prod.* **1987**, *50*, 474–478.
17. Dutta, P. K.; Sen, A. K.; Sarkar, K. K.; Banerji, N. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **1987**, *26B*, 281–282.
18. Kobayashi, M.; Mahmud, T.; Yoshioka, N.; Shibuya, H.; Kitagawa, I. *Chem. Pharm. Bull.* **1997**, *45*, 1615–1619.
19. Gunasekera, S. P.; Selliah, S.; Sultanbawa, M. U. S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1539–1544.
20. Delle Monache, F.; Ferrari, F.; Marini-Bettolo, G. B.; Maxfield, P.; Cerrini, S.; Fedeli, W.; Gavuzzo, E.; Vaciago, A. *Gazz. Chim. Ital.* **1979**, *109*, 301–310.
21. Goncalves, M. L. S.; Mors, W. B. *Phytochemistry* **1981**, *20*, 1947–1950.
22. Ritchie, E.; Taylor, W. C. *Tetrahedron Lett.* **1964**, *23*, 1431–1436.
23. Kalidhar, S. B. *Phytochemistry* **1989**, *28*, 2455–2458.
24. Cohen, P. A.; Towers, G. H. N. *Phytochemistry* **1995**, *40*, 911–915.
25. Delle Monache, F.; Botta, B.; Nicoletti, M.; De Barros Coelho, J. S.; Lyra, F. D.; De Andrade Lyra, F. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 484–488.
26. Botta, B.; Delle Monache, G.; Delle Monache, F.; Marini Bettolo, G. B.; Menichini, F. *Phytochemistry* **1986**, *25*, 1217–1219.
27. Rocha, L.; Marston, A.; Kaplan, M. A. C.; Stoeckli-Evans, H.; Thull, U.; Testa, B.; Hostettmann, K. *Phytochemistry* **1994**, *36*, 1381–1385.
28. King, F. E.; King, T. J.; Manning, L. C. *J. Chem. Soc.* **1953**, 3932–3937.
29. Bruker. *APEX2 Version 1.27, SAINT and SADABS*; Bruker AXS: Madison, WI, USA, 2005.
30. Sheldrick, G. M. *SHELXTL Version 5.1*; Bruker AXS: Madison, WI, USA, 1998.
31. Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
32. Skehan, P.; Storeng, R.; Scudiero, D.; Monks, A.; McMahon, J.; Vistica, D.; Warren, J. T.; Bokesch, H.; Kenney, S.; Boyd, M. R. *J. Natl. Cancer Inst.* **1990**, *82*, 1107–1112.

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2,3-Dihydro-7-hydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one

Sompong Boonsri, Suchada Chantrapromma, Hoong-Kun Fun, Chatchanok Karalai, Akkharawit Kanjana-opas and Shazia Anjum

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2,3-Dihydro-7-hydroxy-3-[(4-methoxyphenyl)-methylene]-4*H*-1-benzopyran-4-one

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.106
Data-to-parameter ratio = 13.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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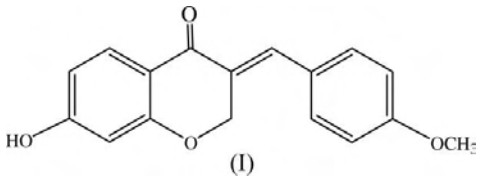
The title compound, $C_{17}H_{14}O_4$, a homoisoflavanoid, was isolated from the twigs and stems of *Caesalpinia digyna* Rottler. The pyran ring adopts an envelope conformation. The symmetry-related molecules are linked *via* O—H···O and C—H···O intermolecular hydrogen bonds to form a molecular network.

Comment

Caesalpinia digyna Rottler, locally known in Thailand as 'kamchai', belongs to the family Leguminosae-Caesalpinioideae (Smitinand, 2001). The genus *Caesalpinia* occurs mainly in the tropics and subtropics (Kinoshita *et al.*, 2005). Several members of the species *Caesalpinia* have been used traditionally for a wide variety of ethnomedical properties (Anonymous, 1992). We have isolated the title compound, (I), bonducellin (Fig. 1), for the first time from the twigs and stems of *C. digyna*, which were collected from Songkhla province in the southern part of Thailand. Compound (I) was previously isolated from *Caesalpinia pulcherrima* (Srinivas *et al.*, 2003). Our antimicrobial activity testing shows that (I) exhibits antimicrobial activities against BS (*Bacillus subsitilis*). In our continuing search for bioactive compounds from Thai medicinal plants (Chantrapromma *et al.*, 2003, 2004, 2005; Boonnak *et al.*, 2005; Fun *et al.*, 2005; Ng *et al.*, 2005; Pakhathirathien *et al.*, 2005; Teh *et al.*, 2005), we have determined the structure of (I) by X-ray analysis in order to establish its relative stereochemistry.



(I)

In the benzopyran-4-one (C1–C9/O1) ring system, the pyran ring (C1/C6–C9/O1) is in an envelope form, with

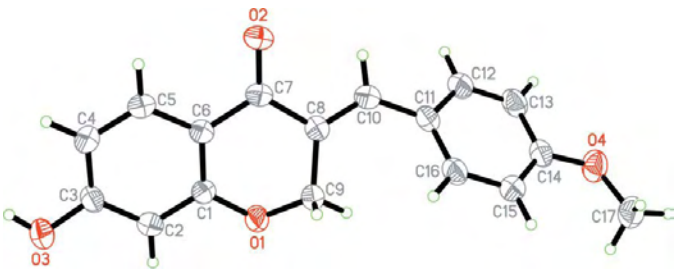


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

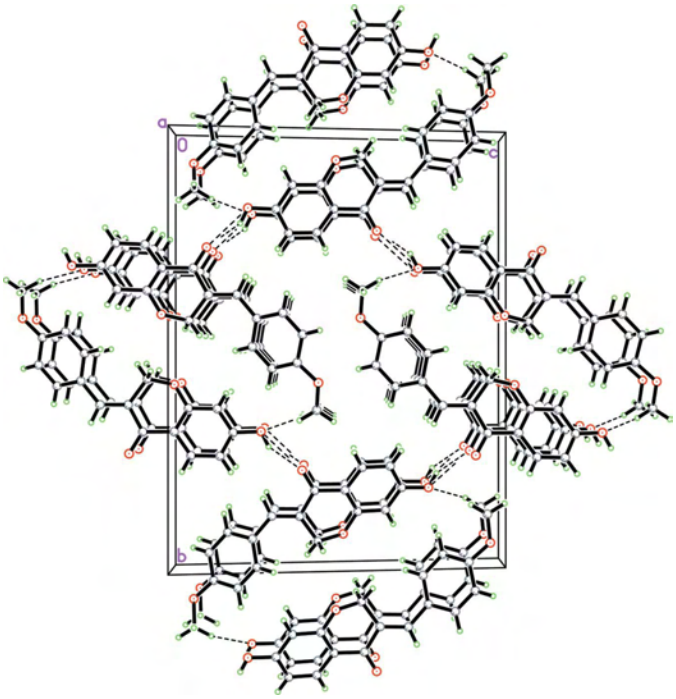


Figure 2
The crystal packing of (I), viewed down the *a* axis, showing the molecular network. Hydrogen bonds are shown as dashed lines.

puckering parameter (Cremer & Pople, 1975) Q = 0.377 (2) Å, θ = 118.9 (3)° and φ = 127.0 (3)°. The deviation of the puckered C9 atom from the C1/C6–C8/O1 plane is 0.519 (2) Å. The (4-methoxyphenyl)methylene substituent (C10–C17/O4) is attached to the pyran ring at atom C8, the torsion angle C7—C8—C10—C11 of 175.48 (18)° indicating an (+)-anti-periplanar conformation (Fig. 1). The dihedral angle between the O1/C1–C8 and C11–C16 planes is 54.15 (4)°. The methoxy group attached at atom C14 is slightly twisted away from the benzene ring [C17—O4—C14—C13 = 168.63 (17)° and C17—O4—C14—C15 = −10.9 (3)°]. All bond lengths and angles in (I) show normal values (Allen *et al.*, 1987). Selected bond lengths and angles are given in Table 1.

In the crystal packing, atom O2 is involved in an intermolecular O—H···O hydrogen bond and intramolecular C—H···O weak interaction, while atoms O4 and O3 are involved in weak C—H···O interactions (Table 2). These hydrogen bonds link the symmetry-related molecules to form a molecular network (Fig. 2).

Experimental

Air-dried twigs and stems of *C. digyna* were extracted with CH_2Cl_2 (3 × 15 l) at room temperature. The residue obtained after evaporation of the solvent was separated by quick column chromatography (QCC) over silica gel and eluted with an acetone–hexane gradient system to give twelve fractions (F1–F12). Fraction F7 (1.25 g) was re-chromatographed on a silica gel column with 5% EtOAc/CH_2Cl_2 to afford nine subfractions (F7A–F7I). Compound (I) was obtained from subfraction F7D. Crystals of (I) suitable for single-crystal X-ray diffraction studies were obtained as colorless needles by recrystallization from $CHCl_3$–CH_3OH (4:1 *v*/*v*) after several days (m.p. 488–490 K).

Crystal data

$C_{17}H_{14}O_4$
M_r = 282.28
Monoclinic, $P2_1/c$
a = 3.9591 (11) Å
b = 20.939 (5) Å
c = 16.209 (4) Å
β = 99.844 (7)°
V = 1323.9 (6) Å^3
Z = 4
D_x = 1.416 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2593 reflections
θ = 1.6–26.0°
μ = 0.10 mm^{-1}
T = 297 (2) K
Needle, colorless
0.55 × 0.05 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.994, T_{max} = 0.996
13570 measured reflections
2593 independent reflections
1997 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 26.0°
$h = -4 \rightarrow 4$
$k = -25 \rightarrow 25$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.106
S = 1.08
2593 reflections
192 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.4026P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.364 (2)	O4—C14	1.364 (2)
O1—C9	1.444 (2)	O4—C17	1.429 (2)
O2—C7	1.236 (2)	C8—C10	1.340 (2)
O3—C3	1.351 (2)	C10—C11	1.460 (2)
C1—O1—C9	116.08 (13)	C10—C8—C9	124.45 (16)
C14—O4—C17	118.30 (15)	C7—C8—C9	115.68 (14)
O1—C1—C2	116.48 (15)	C8—C10—C11	130.10 (17)
O1—C1—C6	122.26 (15)	C16—C11—C12	117.16 (16)
O3—C3—C2	116.57 (16)	C16—C11—C10	123.33 (16)
O3—C3—C4	123.04 (16)	O4—C14—C13	115.61 (16)
O2—C7—C8	122.30 (16)	O4—C14—C15	124.56 (17)
C6—C7—C8	116.01 (14)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2^{i}	0.82	1.94	2.686 (2)	151
C10—H10···O2	0.93	2.47	2.826 (2)	103
C13—H13···O4^{ii}	0.93	2.59	3.506 (3)	168
C17—H17*B*···O3^{iii}	0.96	2.49	3.398 (2)	158

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+2, -y, -z+2$; (iii) $-x+1, -y, -z+1$.

H atoms were placed in calculated positions, with an O—H distance of 0.82 Å and C—H distances in the range 0.93–0.97 Å. The U_{iso} values were constrained to be 1.5U_{eq} of the carrier atom for hydroxy and methyl H atoms, and 1.2U_{eq} for the remaining H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Anonymous (1992). *The Wealth of India*, Vol. 3, pp. 14–16. New Delhi: CSIR.
Boonnak, N., Chantrapromma, S., Fun, H.-K., Anjum Ali, S., Rahman, A. A. & Karalai, C. (2005). *Acta Cryst.* E**61**, o410–o412.
Chantrapromma, K., Saewan, N., Fun, H.-K., Chantrapromma, S. & Rahman, A. A. (2004). *Acta Cryst.* E**60**, o312–o314.
Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Rahman, A. A. (2005). *Acta Cryst.* E**61**, o2136–o2138.
Chantrapromma, S., Fun, H.-K., Razak, I. A., Laphookhieo, S. & Karalai, C. (2003). *Acta Cryst.* E**59**, o1864–o1866.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Fun, H.-K., Razak, I. A., Boonnak, N., Laphookhieo, S. & Chantrapromma, S. (2005). *Acta Cryst.* E**61**, o3086–o3088.
Kinoshita, T., Haga, Y., Narimatsu, S., Shimada, M. & Goda, Y. (2005). *Chem. Pharm. Bull.* **53**, 717–720.
Ng, S. L., Razak, I. A., Fun, H.-K., Boonsri, S., Chantrapromma, S. & Prawat, U. (2005). *Acta Cryst.* E**61**, o3234–o3236.
Pakhathirathien, C., Chantrapromma, S., Fun, H.-K., Anjum, S., Rahman, A. & Karalai, C. (2005). *Acta Cryst.* E**61**, o2942–o2944.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Smitinand, T. (2001). *Thai Plant Names*, pp. 93. Bangkok: Prachachon Publisher.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Srinivas, K. V. N. S., Rao, Y. K., Mahender, I., Das, B., Krisna, K. V. S. R., Kishore, K. H. & Murty, U. S. N. (2003). *Phytochemistry*, **63**, 789–793.
Teh, J. B.-J., Razak, I. A., Fun, H.-K., Boonnak, N., Chantrapromma, S. & Karalai, C. (2005). *Acta Cryst.* E**61**, o3653–o3655.

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1,6,7-Trihydroxy-3-methoxy-2,8-bis(3-methyl-2-butenyl)-9*H*-xanthen-9-one chloroform solvate

Nawong Boonnak, Suchada Chantrapromma, Hoong-Kun Fun and Chatchanok Karalai

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1,6,7-Trihydroxy-3-methoxy-2,8-bis(3-methyl-2-butenyl)-9*H*-xanthen-9-one chloroform solvate

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Key indicators

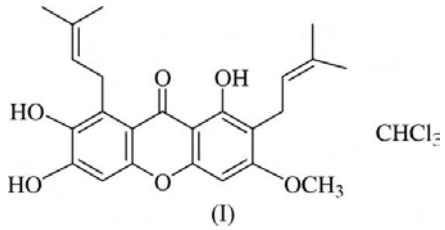
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.063
wR factor = 0.218
Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{24}H_{26}O_6\cdot CHCl_3$, which we named prunifloxanthone A, was isolated for the first time from the roots of *Cratoxylum formosum* ssp. *pruniflorum* and has never been isolated from any other natural resources as yet. The xanthone ring systems of the molecules are stacked along the *a* axis, with significant π–π interactions. In addition, O—H···O hydrogen bonds link glide-related molecules into a chain along [201].

Comment

We have previously reported the crystal structures of the compounds 5,9,10-trihydroxy-2,2-dimethyl-12-(3-methylbut-2-enyl)-2H,6*H*-pyrano[3,2-*b*]xanthen-6-one methanol solvate (Chantrapromma *et al.*, 2005) and 3-(3,7-dimethylocta-2,6-dienyloxy)-1,8-dihydroxy-6-methyl-9,10-anthraquinone (Boonnak *et al.*, 2005) isolated from the bark of *Cratoxylum formosum* ssp. *pruniflorum* or 'Tuikhon' in Thai, a medicinal plant growing in the northeastern part of Thailand. Xanthones are the main components of this plant. The title compound, (I), prunifloxanthone A, is a new xanthone which was for the first time isolated from *C. pruniflorum* and has never been isolated from any other natural resources as yet. Compound (I) is found to exhibit antioxidant activity. The present single-crystal structure determination of (I) is a part of our ongoing studies on the biological activities of Thai medicinal plants (Chantrapromma *et al.*, 2003, 2004, 2005; Boonnak *et al.*, 2005; Fun *et al.*, 2005). The structure–activity relationships (SAR) of these compounds will be further studied.



(I)

The bond lengths and angles in (I) (Table 1) show normal values (Allen *et al.*, 1987) and are comparable to those reported in a closely related structure (Chantrapromma *et al.*, 2005). The xanthone ring system is approximately planar (r.m.s. deviation 0.044 Å), with a maximim deviation of 0.093 (3) Å for atom C7. The methoxy group attached at atom C3 is almost coplanar with the xanthone ring system with a C19—O4—C3—C4 torsion angle of 2.8 (4)°. One of the 3-methylbut-2-enyl substituents is attached to the xanthone ring system at C2, with C1—C2—C20—C21 = 91.1 (4)°, indicating a (+)-anticlinal conformation (Fig. 1). The other 3-methylbut-

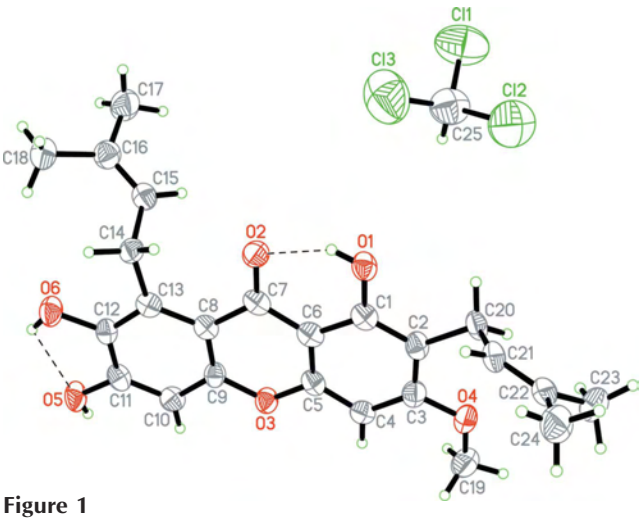


Figure 1
The structure of (I), showing 80% probability displacement ellipsoids and the atomic numbering. Dashed lines indicate O—H···O hydrogen bonds.

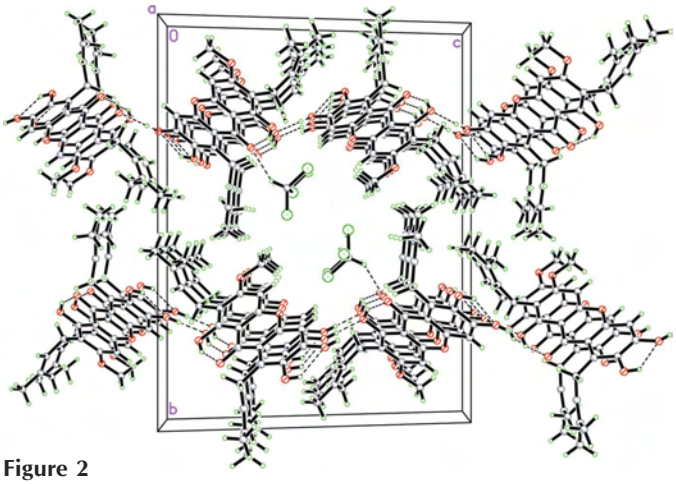


Figure 2
The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

2-enyl group is attached at C13, with C12—C13—C14—C15 = −95.4 (3)°, indicating a (−)-anticlinal conformation (Fig. 1).

The O1—H1···O2 and O6—H6···O5 intramolecular hydrogen bonds (Table 2) generate *S*(6) and *S*(5) ring motifs, respectively (Bernstein, *et al.*, 1995). In addition, a weak C14—H14*A*···O6 interaction generates an *S*(5) ring motif and a C14—H14*B*···O2 interaction generates an *S*(6) ring motif.

The xanthone ring systems of the molecules are stacked along the *a* axis in such a way that the centroids of the C1–C6 and C8–C13 benzene rings are 3.557 (2) Å apart, indicating significant π–π interactions (Fig. 2). In addition, glide-related molecules are linked into a chain along [201] *via* O5—H5···O1^{i} hydrogen bonds (symmetry code in Table 2). The chloroform molecule is linked to the xanthone derivative *via* a C—H···O hydrogen bond (Table 2).

Experimental

Air-dried roots of *C. formosum* ssp. *pruniflorum* (4 kg) were ground and extracted with hexane and CH_2Cl_2 (2 × 20 l for each solvent) for 5 d at room temperature. The residue obtained after evaporation of the solvent was subjected to quick column chromatography (QCC) over silica gel and eluted with a gradient of EtOAc–hexane to afford ten fractions (F1–F10). Fraction F7 was separated by QCC and eluted with a gradient of acetone–hexane to afford seven fractions (7A–7G). Fraction 7C was further purified by column chromatography with 80% CH_2Cl_2–hexane to give four fractions (7CA–7CD). Fraction 7CA was recrystallized from $CHCl_3$–CH_3OH (7:3 *v*/*v*) to give yellow needle-shaped single crystals of (I) after several days (m.p. 395–397 K).

Crystal data

$C_{24}H_{26}O_6{\cdot}CHCl_3$
M_r = 529.82
Monoclinic, $P2_1/c$
a = 5.9059 (1) Å
b = 23.3103 (3) Å
c = 18.4042 (2) Å
β = 103.438 (1)°
V = 2464.31 (6) Å^3
Z = 4
D_x = 1.428 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4316 reflections
θ = 1.4–26.0°
μ = 0.41 mm^{-1}
T = 100.0 (1) K
Block, yellow
0.37 × 0.22 × 0.13 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.897, T_{max} = 0.948
38758 measured reflections
4316 independent reflections
3713 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.0°
$h = -7 \rightarrow 7$
$k = -27 \rightarrow 27$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.218
S = 1.08
4316 reflections
315 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1248P)^2 + 5.5318P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C25	1.753 (5)	O4—C3	1.364 (4)
Cl2—C25	1.746 (4)	O4—C19	1.424 (4)
Cl3—C25	1.758 (5)	O5—C11	1.356 (4)
O1—C1	1.365 (4)	O6—C12	1.372 (4)
O2—C7	1.257 (4)	C15—C16	1.323 (5)
O3—C5	1.364 (4)	C21—C22	1.326 (5)
O3—C9	1.383 (4)		
O3—C5—C4	116.0 (3)	O3—C9—C8	123.4 (3)
C4—C5—C6	123.5 (3)	C16—C15—C14	126.1 (3)
C5—C6—C1	116.4 (3)	C15—C16—C18	123.0 (3)
C5—C6—C7	121.7 (3)	C17—C16—C18	115.1 (3)
C9—C8—C7	118.0 (3)	C22—C21—C20	128.6 (3)
C13—C8—C7	123.7 (3)	C21—C22—C23	124.4 (3)
O3—C9—C10	113.6 (3)	C24—C22—C23	114.8 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.82	1.77	2.505 (3)	149
O5—H5···O1^{i}	0.82	1.88	2.695 (3)	176
O6—H6···O5	0.82	2.18	2.643 (3)	116
C14—H14*A*···O6	0.97	2.36	2.769 (4)	105
C14—H14*B*···O2	0.97	2.31	2.825 (4)	112
C25—H25···O2^{ii}	0.98	2.42	3.256 (5)	142

Symmetry codes: (i) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x+1, y, z$.

H atoms were placed in calculated positions with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.98 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atoms for hydroxy and methyl H atoms, and $1.2U_{eq}$ for the remaining H atoms. A rotating group model was used for the hydroxy and methyl H atoms. The data were collected with an Oxford Cyrosystem Cobra low-temperature attachment.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chamg N.-L. (1995). *Angew. Chem. Int. Ed. Eng1.* **34**, 1555–1573.
Boonnak, N., Chantrapromma, S., Fun, H.-K., Anjum, S., Ali, S., Atta-ur-Rahman & Karalai, C. (2005). *Acta Cryst.* E**61**, o410–o412.
Bruker (2005). *APEX2* (Version 1.27), *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chantrapromma, K., Saewan, N., Fun, H.-K., Chantrapromma, S. & Rahman, A. A. (2004). *Acta Cryst.* E**60**, o312–o314.
Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Atta-ur-Rahman (2005). *Acta Cryst.* E**61**, o2136–o2138.
Chantrapromma, S., Fun, H.-K., Razak, I. A., Laphookhieo, S. & Karalai, C. (2003). *Acta Cryst.* E**59**, o1864–o1866.
Fun, H.-K., Razak, I. A., Boonnak, N., Laphookhieo, S. & Chantrapromma, S. (2005). *Acta Cryst.* E**61**, o3086–o3088.
Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

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12-(1,1-Dimethyl-2-propenyl)-5,9,10-trihydroxy-2,2-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one

Hoong-Kun Fun, Shea-Lin Ng, Ibrahim Abdul Razak, Nawong Boonnak and Suchada Chantrapromma

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12-(1,1-Dimethyl-2-propenyl)-5,9,10-trihydroxy-2,2-dimethyl-2*H*,6*H*-pyrano-[3,2-*b*]xanthen-6-one

Hoong-Kun Fun,[a]* Shea-Lin Ng,[a] Ibrahim Abdul Razak,[a] Nawong Boonnak[b] and Suchada Chantrapromma[b]*

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.145
Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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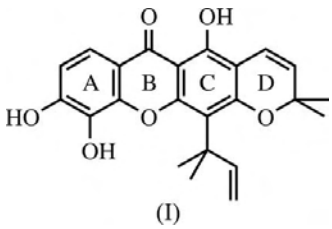
In the title compound, $C_{23}H_{22}O_6$, the xanthene ring system is essentially planar and the chromene ring is in a screw-boat conformation. Position 1 of the 1,1-dimethyl-2-propenyl substituent is coplanar with the attached ring. O—H···O intramolecular hydrogen bonds are observed in the structure. The molecules form centrosymmetric hydrogen-bonded dimers *via* weak intermolecular C—H···O interactions. The molecules are linked by intermolecular O—H···O hydrogen bonds to form a one-dimensional chain along [010].

Comment

We have previously reported the crystal structures of a xanthone and a modified rotenoid containing the chromene ring, *viz* 5,9,10-trihydroxy-2,2-dimethyl-12-(3-methylbut-2-enyl)-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one methanol solvate (Chantrapromma, Boonnak *et al.*, 2005) and 7a-*O*-methyldeguelol (Chantrapromma, Fun *et al.*, 2005). The title compound, (I), is another xanthone containing a chromene ring; since it also crystallized in the centrosymmetric space group $P2_1/c$, this indicates that (I) had been produced by non-enzymatic cyclization of a side chain (Chantrapromma, Boonnak *et al.*, 2005; Chantrapromma, Fun *et al.*, 2005).



(I)

Compound (I), macluraxanthone, was isolated from the bark of *Cratoxylum formosum* ssp. *prunifolum*, a shrub that was collected from Nhongkhai province in the northeastern part of Thailand. In our continuing search for bioactive compounds obtained from Thai medicinal plants (Chantrapromma *et al.*, 2004; Chantrapromma, Boonnak *et al.*, 2005; Chantrapromma, Fun *et al.*, 2005; Boonnak *et al.*, 2005; Fun *et al.*, 2005; Boonsri *et al.*, 2005), we have investigated *C. formosum* ssp. *pruniflorum*. Compound (I) has been reported previously (Monache *et al.*, 1981; Menache *et al.*, 1983; Goh *et al.*, 1992), but its X-ray crystal structure has not yet been reported.

The molecular structure of (I) is shown in Fig. 1. The bond distances and angles show normal values (Allen *et al.*, 1987) and are comparable to those in related structures (Chantrapromma & Boonnak *et al.*, 2005; Ravikumar *et al.*, 1987; Doriguetto *et al.*, 2001).

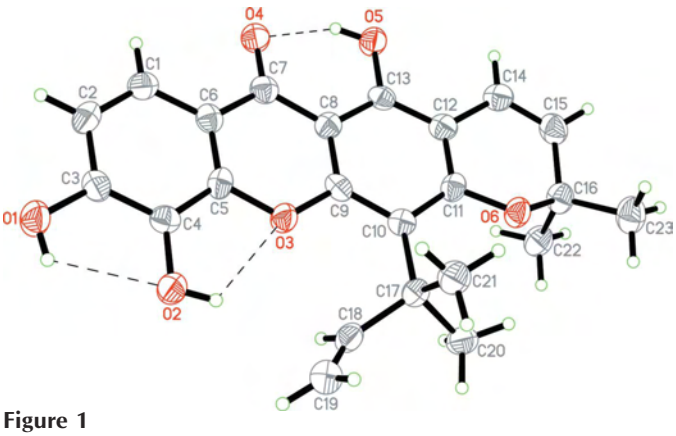


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. The dashed lines indicate hydrogen bonds.

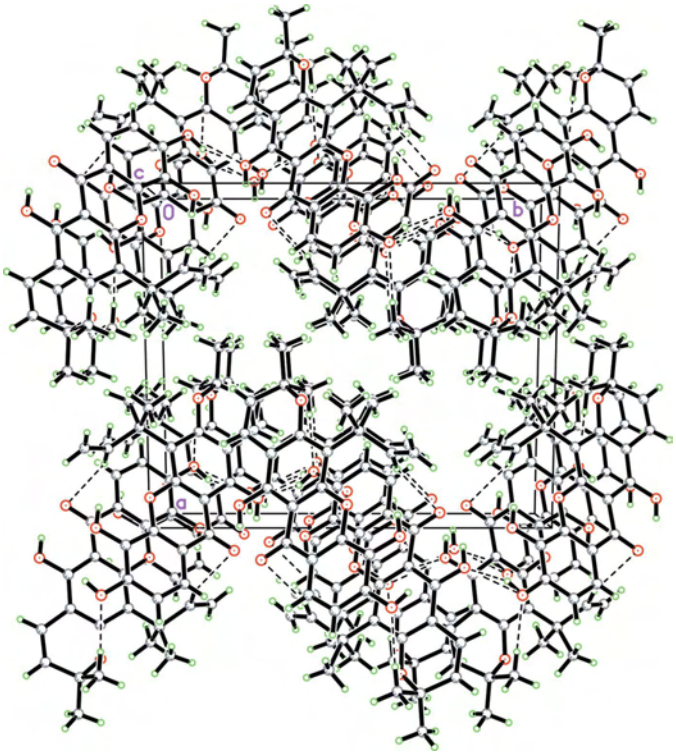


Figure 2
The crystal packing of (I), viewed down the *c* axis. Hydrogen bonds are shown as dashed lines.

The xanthene ring system (C1–C13/O3) is almost planar, with all atoms lying within 0.066 (2) Å of the mean plane. The three individual rings of xanthene are each essentially planar, the largest deviations from the ring planes being 0.010 (2), 0.033 (2) and 0.022 (2) Å for atoms C5, C6 and C9, C10 of rings *A*, *B*, and *C*, respectively. The dihedral angle between rings *A* and *B* is 2.60 (9)°, rings *B* and *C* form a dihedral angle of 5.73 (9)°, and the dihedral angle between rings *C* and *A* is 7.77 (9)°. The chromene ring, *D*, adopts a screw-boat conformation (Cremer & Pople, 1975), with puckering parameters Q = 0.348 (2) Å, θ = 64.0 (3)° and φ_2 = 326.7 (4)°. The three hydroxyl groups are each coplanar with the attached rings. Atom C17 of the 1,1-dimethyl-2-propenyl substituent is coplanar with ring *C*; the torsion angle C8—C9—C10—C17 is 176.93 (18)°.

In the crystal structure, there are intermolecular O1—H1O1···O5($-x, \frac{1}{2}+y, -\frac{1}{2}-z$), C18—H18*A*···O4($-x, 2-y, -z$) and C23—H23*A*···O1($-x, 2-y, -z$) hydrogen bonds (Table 1). The molecules are linked by O—H···O intermolecular hydrogen bonds to form infinite chains along the *b* axis (Fig. 2). These chains form layers approximately parallel to the *bc* plane and are interconnected by the C—H···O interactions.

Experimental

Air-dried barks of *C. formosum* ssp. *prunifolum* (4 kg) were ground and extracted with hexane and CH_2Cl_2 (2 × 20 l for each solvent) for 5 d at room temperature. The residue obtained after evaporation of the solvent was subjected to quick column chromatography over silica gel and eluted with a gradient of EtOAc–hexane to afford 10 fractions (F1–F10). Fraction F3 was separated by column chromatography and eluted with 10% acetone-hexane to afford four fractions (3A–3D). Fraction 3C was recrystallized from $CHCl_3$—CH_3OH (4:1 *v*/*v*) to yield, after several days, yellow needle-shaped crystals of (I), suitable for single-crystal X-ray diffraction (m.p. 456–457 K).

Crystal data

$C_{23}H_{22}O_6$
M_r = 394.41
Monoclinic, $P2_1/c$
a = 14.0220 (8) Å
b = 16.1568 (8) Å
c = 8.4157 (4) Å
β = 104.423 (4)°
V = 1846.49 (17) Å^3
Z = 4
D_x = 1.419 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4452 reflections
θ = 2.0–28.0°
μ = 0.10 mm^{-1}
T = 100.0 (1) K
Needle, yellow
0.46 × 0.08 × 0.04 mm

Data collection

Bruker SMART APEX-2 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.990, T_{max} = 0.996
16825 measured reflections
4452 independent reflections
2789 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 28.0°
$h = -18 \rightarrow 18$
$k = -21 \rightarrow 20$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.145
S = 1.05
4452 reflections
266 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O2	0.82	2.30	2.735 (2)	114
O1—H1O1···O5^{i}	0.82	1.97	2.720 (2)	153
O2—H1O2···O3	0.82	2.32	2.737 (2)	112
O5—H1O5···O4	0.82	1.77	2.509 (2)	150
C18—H18*A*···O4^{ii}	0.93	2.56	3.387 (3)	149
C20—H20*B*···O6	0.96	2.25	2.792 (3)	115
C23—H23*A*···O1^{ii}	0.96	2.56	3.492 (3)	164

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z-\frac{1}{2}$; (ii) $-x, -y+2, -z$.

H atoms were placed in calculated positions, with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.96 Å. The U_{iso}(H) values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxyl and methyl H atoms, and $1.2U_{eq}$ for the remaining H atoms.

Data collection and cell refinement: *APEX2* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); structure solution: *SHELXTL* (Sheldrick, 1998); structure refinement: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Boonnak, N., Chantrapromma, S., Fun, H.-K., Anjum, S., Ali, S., Rahman, A. U. & Karalai, C. (2005). *Acta Cryst.* E**61**, o410–o412.

Boonsri, S., Chantrapromma, S., Fun, H.-K., Karalai, C., Kanjana-opas, A. & Anjum, S. (2005). *Acta Cryst.* E**61**, o3930–o3932.

Bruker (2005). *APEX2* (Version 1.27), *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chantrapromma, K., Saewan, N., Fun, H.-K., Chantrapromma, S. & Rahman, A. A. (2004). *Acta Cryst.* E**60**, o312–o314.

Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Rahman, A. A. (2005). *Acta Cryst.* E**61**, o2136–o2138.

Chantrapromma, S., Fun, H.-K., Pullaput, Y., Wongtap, H., Dejmanee, S. & Chantrapromma, K. (2005). *Acta Cryst.* E**61**, o2340–o2342.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Doriguetto, A. C., Santos, M. H., Ellena, J. A. & Nagem, T. J. (2001). *Acta Cryst.* C**57**, 1095–1097.

Fun, H. K., Razak, I. A., Boonnak, N., Laphookhieo, S. & Chantrapromma, S. (2005). *Acta Cryst.* E**61**, o3086–o3088.

Goh, S. H., Jantan, I., Gray, A. I. & Waterman, P. G. (1992). *Phytochemistry,* **31**, 1383–1386.

Menache, G. D., Monache, F. D., Bettolo, G. B. M. & de Lima, R. A. (1983). *J. Nat. Prod.* **46**, 655–659.

Monache, F. D., Botta, B., Nicoletti, M., de B. Coelho, J. S., de A. Lyra, F. D. (1981). *J. Chem. Soc. Perkin Trans 2*, pp. 484–488.

Ravikumar, K., Rajan, S. S. & Padmanabhan, V. M. (1987). *Acta Cryst.* C**43**, 553–555.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

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1,6-Dihydroxy-3,7-dimethoxy-2,8-bis(3-methyl-2-butenyl)-9*H*-xanthen-9-one

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1,6-Dihydroxy-3,7-dimethoxy-2,8-bis(3-methyl-2-butenyl)-9*H*-xanthen-9-one

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Received 13 December 2005
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Key indicators

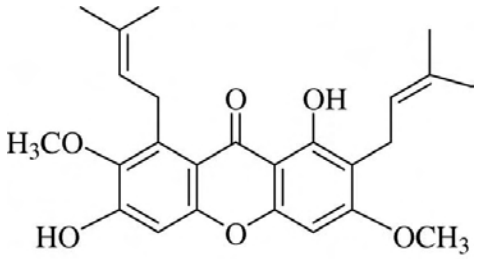
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.140
Data-to-parameter ratio = 19.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{25}H_{28}O_6$, β-mangostin, is a xanthone which was isolated from *Cratoxylum formosum* ssp. *pruniforum*. O—H···O and C—H···O intramolecular hydrogen bonds are observed in the molecular structure. In the crystal packing, inversion-related molecules are stacked along the *a* axis with C—H···π and π–π interactions.

Comment

In our search for bioactive compounds from medicinal plants, we have investigated *Cratoxylum formosum* ssp. *pruniflorum*, which has been used for traditional medicine in Southeast Asia (Usher *et al.*, 1984). The main components of this plant are xanthones and anthraquinones. We have previously reported the crystal structures of an anthraquinone and xanthones which were isolated from this plant, *viz* 3-*O*-(geranyl)anthraquinone (Boonnak, Chantrapromma, Fun, Anjum *et al.*, 2005), xanthone V_1 (Chantrapromma *et al.*, 2005), prunifloxanthone A (Boonnak, Chantrapromma, Fun & Karalai, 2005) and macluraxanthone (Fun *et al.*, 2006). The title compound, (I), β-mangostin, is another xanthone which is a secondary metabolite occurring in this plant. It has previously been isolated from *Garcinia mangostana* (Asai *et al.*, 1995) and *Cratoxylum cochinchinense* (Nguyen & Harrison, 1999). Compound (I) has exhibited cytotoxicity against human leukemia HL 60 cells (Matsumoto *et al.*, 2003) and has antiproliferative effects against human colon cancer DLD-1 cells (Matsumoto *et al.*, 2005).



(I)

The present single-crystal structure determination of (I) is part of our ongoing search for bioactive compounds from Thai medicinal plants (Chantrapromma *et al.*, 2003, 2004, 2005; Boonnak, Chantrapromma, Fun, Anjum *et al.*, 2005; Boonnak, Chantrapromma, Fun & Karalai, 2005; Fun *et al.*, 2005, 2006). The structure-activity relationship (SAR) of xanthone derivatives will be investigated further.

The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The

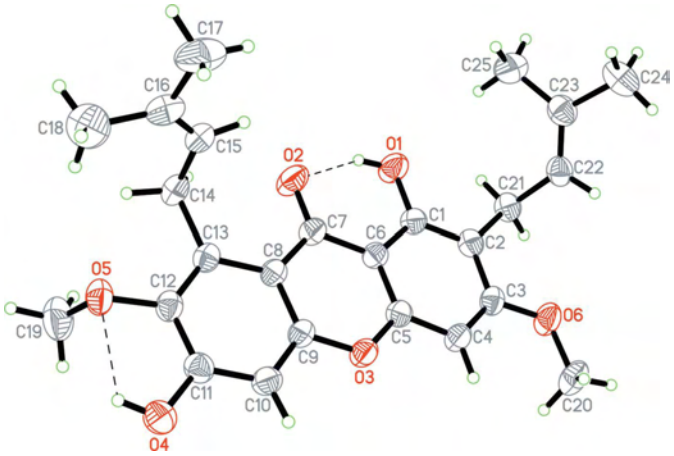


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. Dashed lines indicate hydrogen bonds.

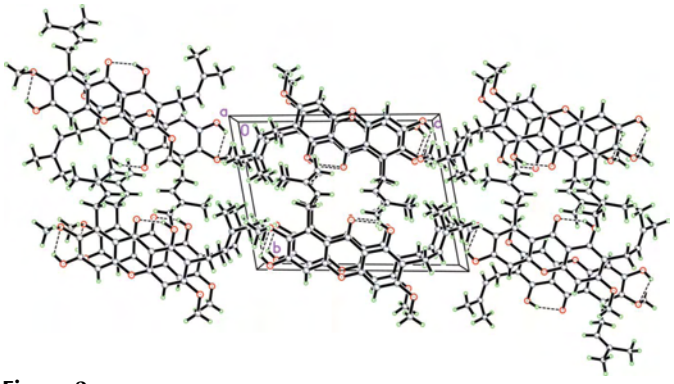


Figure 2
The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

bond distances and angles show normal values (Allen *et al.*, 1987) and are comparable with those in closely related structures (Chantrapromma *et al.*, 2005; Fun *et al.*, 2006).

The xanthene ring system of (I) (C1–C13/O3) is almost planar, with all atoms lying within 0.088 (1) Å of the mean plane. The dihedral angle between the two benzene rings of xanthene is 3.97 (5)°. The two hydroxyl groups are each coplanar with the attached rings. The methoxy group attached at atom C3 is coplanar with the xanthene ring system, with a C20—O6—C3—C2 torsion angle of 179.94 (11)°, while the other methoxy group attached at atom C12 is twisted away, with a C19–O5–C12–C11 torsion angle of −94.83 (13)°, indicating a (−)-anticlinal conformation (Fig. 1).

The two 3-methylbut-2-enyl substituents are attached to the xanthene ring system at C2 and C13; the torsion angles C1—C2—C21—C22 and C12—C13—C14—C15 are 100.42 (13) and 98.57 (12)°, respectively, both indicating a (+)-anticlinal conformation (Fig. 1). The attachment of the two 3-methylbut-2-enyl substituents is different from that observed in prunifloxanthone A (Boonnak, Chantrapromma, Fun & Karalai, 2005), in which one of them is in a (+)-anticlinal conformation and the other in a (−)-anticlinal conformation. This is due to the attachment of a methoxy group at atom C12 in (I) compared with a hydroxyl group attached at the same position in prunifloxanthone A. We expect that these differences would affect the bioactivities of these compounds.

O1—H1O1···O2 and O4—H1O4···O5 intramolecular hydrogen bonds generate $S(6)$ and $S(5)$ ring motifs, respectively (Bernstein *et al.*, 1995). There are also intramolecular C—H···O interactions present: C14—H14*A*···O2 generates an $S(6)$ ring motif, C14—H14*B*···O5 generates an $S(5)$ ring motif and C21—H21*B*···O1 generates an $S(5)$ ring motif (Table 2). The crystal structure is stabilized by C—H···π interactions involving the C8–C13 benzene ring (centroid *Cg*1). The xanthene ring systems of inversion-related molecules are stacked in such a way that the centroids of the O3/C5–C9 ring at (x, y, z) and the C1–C6 benzene ring at ($1-x$, $-y$, $1-z$) are 3.5697 (6) Å apart, indicating significant π–π interaction (Fig. 2).

Experimental

Air-dried roots of *C. formosum* ssp. *pruniflorum* (4 kg) were ground and extracted with hexane and CH_2Cl_2 (2 × 20 l for each solvent) for 5 d at room temperature. The residue obtained after evaporation of the solvent was subjected to quick column chromatography over silica gel and eluted with a gradient of EtOAc–hexane to afford ten fractions (F1–F10). Fraction F2 was separated by column chromatography (CC) and eluted with 100% CH_2Cl_2 to afford four fractions (2A–2D). Fraction 2A was further purified by CC with 30% EtOAc–hexane to give compound (I). Compound (I) was recrystallized from $CHCl_3$–CH_3OH (4:1 *v*/*v*) to yield, after several days, yellow needle-shaped single crystals (m.p. 445–447 K).

Crystal data

$C_{25}H_{28}O_6$
M_r = 424.27
Triclinic, $P\overline{1}$
a = 7.8938 (1) Å
b = 10.1976 (1) Å
c = 13.7937 (2) Å
α = 79.311 (1)°
β = 80.926 (1)°
γ = 87.850 (1)°
V = 1077.40 (2) Å^3
Z = 2
D_x = 1.309 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5720 reflections
θ = 1.5–29.0°
μ = 0.09 mm^{-1}
T = 100.0 (1) K
Block, yellow
0.50 × 0.28 × 0.23 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.969, T_{max} = 0.979
16706 measured reflections
5720 independent reflections
4623 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 29.0°
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.140
S = 1.06
5720 reflections
291 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0749P)^2 + 0.1769P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3489 (13)	O5—C19	1.4348 (18)
O2—C7	1.2488 (13)	O6—C3	1.3602 (13)
O3—C5	1.3663 (13)	O6—C20	1.4217 (16)
O3—C9	1.3670 (12)	C15—C16	1.3274 (18)
O4—C11	1.3566 (14)	C22—C23	1.3316 (18)
O5—C12	1.3881 (13)		
C12—O5—C19	112.64 (10)	C3—O6—C20	118.14 (10)
O1—C1—C2—C3	−178.93 (10)	C19—O5—C12—C13	87.73 (14)
C20—O6—C3—C4	−0.80 (18)	O4—C11—C12—C13	177.68 (11)
C21—C2—C3—C4	179.16 (10)	C11—C12—C13—C14	−168.74 (10)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···O2	0.82	1.82	2.5558 (13)	148
O4—H1O4···O5	0.85 (2)	2.21 (2)	2.6994 (14)	117 (2)
C14—H14*A*···O2	0.97	2.27	2.8283 (15)	116
C14—H14*B*···O5	0.97	2.43	2.8573 (15)	106
C18—H18*A*···O5	0.96	2.59	3.413 (2)	144
C21—H21*B*···O1	0.97	2.40	2.8103 (15)	105
C20—H20*C*···*Cg*1^{i}	0.96	2.84	3.6661 (16)	144
C21—H21*A*···*Cg*1^{ii}	0.97	2.84	3.5627 (13)	132

Symmetry codes: (i) $-x+2, -y, -z+1$; (ii) $-x+1, -y, -z+1$.

Atom H1O4 was located in a difference map and refined isotropically. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with O—H = 0.82 Å and C—H = 0.93–0.97 Å. The U_{iso}(H) values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxyl and methyl H atoms, and $1.2U_{eq}$ for the remaining H atoms.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Asai, F., Tosa, H., Tanaka, T. & Iinuma M. (1995). *Phytochemistry*, **39**, 943–944.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Boonnak, N., Chantrapromma, S., Fun, H.-K., Anjum, S., Ali, S., Atta-ur-Rahman & Karalai, C. (2005). *Acta Cryst.* E**61**, o410–o412.
Boonnak, N., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst.* E**61**, o4376–o4378.
Bruker (2005). *APEX2* (Version 1.27), *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chantrapromma, K., Saewan, N., Fun, H.-K., Chantrapromma, S. & Rahman, A. A. (2004). *Acta Cryst.* E**60**, o312–o314.
Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Atta-ur-Rahman (2005). *Acta Cryst.* E**61**, o2136–o2138.
Chantrapromma, S., Fun, H.-K., Razak, I. A., Laphookhieo, S. & Karalai, C. (2003). *Acta Cryst.* E**59**, o1864–o1866.
Fun, H.-K., Ng, S.-L., Razak, I. A., Boonnak, N. & Chantrapromma, S. (2006). *Acta Cryst.* E**62**, o130–o132.
Fun, H.-K., Razak, I. A., Boonnak, N., Laphookhieo, S. & Chantrapromma, S. (2005). *Acta Cryst.* E**61**, o3086–o3088.
Matsumoto, K., Akao, Y., Kobayashi, E., Ohguchi, K., Ito, T., Tanaka, T., Iinuma, M. & Nozawa, Y. (2003). *J. Nat. Prod.* **66**, 1124–1127.
Matsumoto, K., Akao, Y., Ohguchi, K., Ito, T., Tanaka, T., Iinuma, M. & Nozawa, Y. (2005). *Bioorg. Med. Chem.* **13**, 6064–6069.
Nguyen, L. H. D. & Harrison, L. J. (1999). *Phytochemistry*, **50**, 471–476.
Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Usher, G. (1984). *A Dictionary of Plants*, p.782. Delhi: CBS Publishers and Contributors.

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2,3-Dihydro-7,8-dihydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one

Suchada Chantrapromma, Sompong Boonsri, Hoong-Kun Fun, Shazia Anjum and Akkharawit Kanjana-opas

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2,3-Dihydro-7,8-dihydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one

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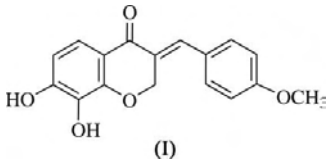
The title compound, also known as intricatinol, $C_{17}H_{14}O_5$, is a homoisoflavanoid that was isolated for the first time from the twigs and stems of *Caesalpinia digyna* Rottler. The pyran ring is in an envelope form. O—H···O intramolecular hydrogen bonds are observed. Symmetry-related molecules are linked *via* O—H···O intermolecular interactions to form infinite one-dimensional chains. These chains are interconnected to form a three-dimensional molecular network.

Comment

Caesalpinia digyna Rottler, known in Thai as kamchai, belongs to the Leguminosae-Caesalpinioideae family (Smitinand, 2001). Several members of the species *Caesalpinia* have exhibited inhibitory (Reddy *et al.*, 2003), antitumor (Gupta *et al.*, 2004), antiflammatory (Rao *et al.*, 2005), antimalarial (Linn *et al.*, 2005) and antiviral activities (Jiang *et al.*, 2002).



(I)

In a previous study, we have reported the crystal structure and activity of bonducellin, a homoisoflavanoid isolated from *C. digyna* (Boonsri *et al.*, 2005). Our further investigation of the chemical components of this plant has led to the isolation of the title compound, (I). The crystal structure of (I) was determined in order to relate the biological activity to the structural properties, which will be further investigated. The title compound, intricatinol, was previously isolated from *Hoffmanosseggia intricata* (Wall *et al.*, 1989) but we have isolated (I) (Fig. 1) for the first time from the twigs and stems of *C. digyna*. Our studies of the antimicrobial activity of (I) have shown that it is active against *Bacillus subsitilis* and *Staphylococcus aureus*.

The bond distances and angles in (I) (Fig. 1 and Table 1) show normal values (Allen *et al.*, 1987) and are comparable to those observed in 2,3-dihydro-7-hydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one (Boonsri *et al.*, 2005). In the structure, the pyran ring (C1/C6–C9/O1) is in an envelope form with puckering parameters $Q = 0.299\ (2)$ Å, $\theta = 61.9\ (4)^\circ$ and $\varphi = 319.0\ (3)^\circ$. The flap atom C9 has the maximum deviation of 0.199 (2) Å. The (4-methoxyphenyl)methylene substituent (C10–C17/O5) is twisted away from the benzopyran-4-one plane, the dihedral angle between the C1–C6 and C11–C16 benzene planes being 34.88 (7)°. The C7—C8—C10—C11 torsion angle is −177.21 (15)°, indicating a (−)-anti-periplanar conformation (Fig. 1). Owing to the

Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.110
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

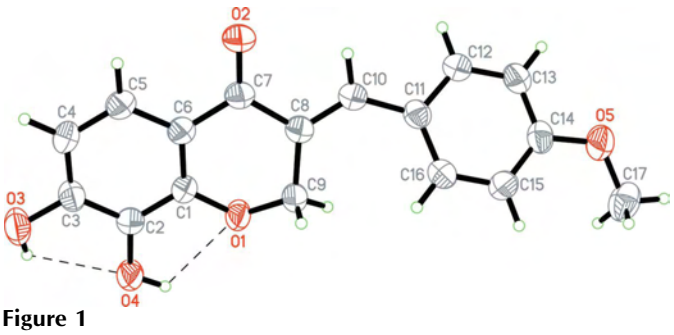


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. Hydrogen bonds are shown as dashed lines.

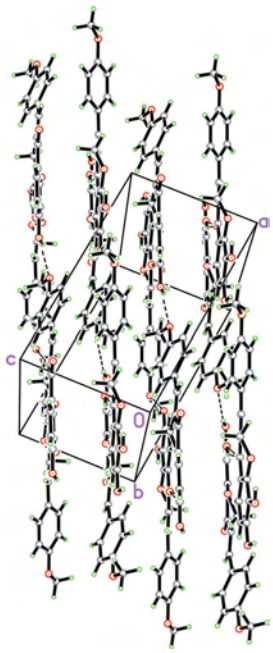


Figure 2
The crystal packing of (I), showing the packing of one-dimensional chains. Hydrogen bonds are shown as dashed lines.

steric effect between the benzopyran-4-one (C1–C9/O1–O4) and 4-methoxyphenyl (C11–C17/O5) systems, the Csp^1 angle at C10 is widened to 132.27°. The methoxy group attached at atom C14 is slightly twisted from the benzene ring [C17—O5—C14—C13 = 172.68 (15)° and C17—O5—C14—C15 = −8.6 (2)°]. Selected bond distances and angles are given in Table 1. The two hydroxy groups are involved in intramolecular hydrogen bonds.

In the crystal packing, atoms O3 and O4 are involved in both intramolecular and intermolecular O—H···O hydrogen bonds, while atom O2 is involved in an intramolecular C—H···O weak interaction (Table 2). Symmetry-related molecules are linked *via* O—H···O intermolecular interactions to form infinite one-dimensional chains along the *b* axis. These chains are linked together to form a three-dimensional molecular network (Fig. 2).

Experimental

Air-dried twigs and stems of *C. digyna* from Songkhla province in the southern part of Thailand were extracted with CH_2Cl_2 (15 l × 3) at room temperature. The CH_2Cl_2 extract (14.52 g) was fractionated by quick column chromatography (QCC) with an acetone–hexane gradient system to give 12 fractions (F1–F12). Fraction F10 (1.32 g) was rechromatographed on a silica gel column with 5% acetone/$CHCl_3$ to afford seven subfractions (F10*A*–F10*G*). Subfraction F10*E* was recrystallized from CH_2Cl_2/CH_3OH (4:1 *v*/*v*), yielding yellow single crystals of (I) after several days (m.p. 457–459 K).

Crystal data

$C_{17}H_{14}O_5$
M_r = 298.28
Monoclinic, $P2_1/c$
a = 12.886 (3) Å
b = 13.896 (3) Å
c = 7.680 (2) Å
β = 95.905 (4)°
V = 1367.9 (5) Å^3
Z = 4
D_x = 1.448 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2699 reflections
θ = 1.6–26.0°
μ = 0.11 mm^{-1}
T = 297 (2) K
Needle, yellow
0.51 × 0.11 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.947, T_{max} = 0.989
7637 measured reflections
2687 independent reflections
2291 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 26.0°
$h = -15 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.110
S = 1.05
2687 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.3706P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0049 (9)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3610 (18)	O4—C2	1.3654 (18)
O1—C9	1.4332 (19)	O5—C14	1.3725 (19)
O2—C7	1.2280 (18)	C8—C10	1.338 (2)
O3—C3	1.3589 (18)		
C1—O1—C9	117.30 (12)	C8—C10—C11	132.27 (15)
C14—O5—C17	118.42 (14)		
C7—C8—C10—C11	−177.21 (15)	C17—O5—C14—C15	−8.6 (2)
C17—O5—C14—C13	172.68 (15)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O4	0.82	2.27	2.706 (2)	113
O3—H3*A*···O5^{i}	0.82	2.13	2.802 (2)	138
O4—H4*A*···O1	0.82	2.35	2.762 (2)	112
O4—H4*A*···O2^{ii}	0.82	2.06	2.796 (2)	148
C10—H10···O2	0.93	2.34	2.755 (2)	107

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

H atoms were placed in calculated positions, with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.96 Å. The U_{iso} values were constrained to be 1.5U_{eq} of the carrier atom for hydroxy and methyl H atoms and 1.2U_{eq} for the remaining H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Boonsri, B., Chantrapromma, S., Fun, H. K., KaraLai, C., Kanjana-opas, A. & Anjum, S. (2005). *Acta Cryst.* E**61**, o3930–o3932.

Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Gupta, M., Mazumder, U. K., Kumar, R. S., Sivakumar, T. & Vamsi, M. L. M. (2004). *J. Pharmacol. Sci.* **94**, 177–184.

Jiang, R.-W., Ma, S.-C., He, Z.-D., Huang, X.-S., But, P. P.-H., Wang, H., Chan, S.-P., Ooi, V. E.-C., Xu, H.-X. & Mak, T. C. W. (2002). *Bioorg. Med. Chem.* **10**, 2161–2170.

Linn, T. Z., Awale, S., Tezuka, Y., Banskota, A. H., Kalauni, S. K., Attamini, F., Ueda, J., Asih, P. B. S., Syafruddin, D., Tanaka, K. & Kadota, S. (2005). *J. Nat. Prod.* **68**, 706–710.

Rao, Y. K., Fang, S.-H. & Tzeng, Y.-M. (2005). *J. Ethnopharmacol.* **100**, 249–253.

Reddy, N. V. L., Ravikanth, V., Lakshmi, J. V. V. N. S., Murty, S. U. & Venkateswarlu, Y. (2003). *Fitoterapia*, **74**, 600–602.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Smitinand, T. (2001). *Thai Plants Names*, pp. 93. Bangkok: Prachachon Publisher.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Wall, M. E., Wani, M. C., Manikumar, G., Taylor, H. & McGivney, R. (1989). *J. Nat. Prod.* **52**, 774–778.

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4-(1,1-Dimethylprop-2-enyl)-1,3,5,6-tetrahydroxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one monohydrate

Nawong Boonnak, Suchada Chantrapromma and Hoong-Kun Fun

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Structure Reports Online
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4-(1,1-Dimethylprop-2-enyl)-1,3,5,6-tetrahydroxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one monohydrate

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Accepted 18 April 2006

The title compound, $C_{23}H_{24}O_6\cdot H_2O$, a xanthone compound, was isolated from *Cratoxylum formosum* ssp. *pruniflorum*. The three rings in the molecule are coplanar. The 3-methylbut-2-enyl and 1,1-dimethylprop-2-enyl side chains are axially attached to the benzene ring. There are intra- and intermolecular O—H···O and C—H···O interactions. The crystal structure is stabilized by these intermolecular interactions as well by C—H···π interactions.

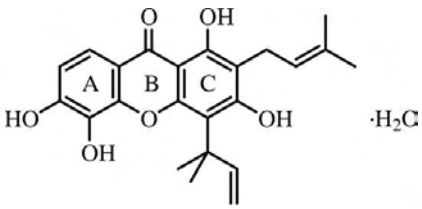
Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.152
Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Cratoxylum is a small genus belonging to the Guttiferae family and is found mainly in southeast Asia (Robson, 1974). Some species of this genus have been used for the treatment of diuretic and stomachic symptons, for tonic effects (Kitanov *et al.*, 1988), and for diarrhea and flatulence (Aderson 1986). These plants produce various types of secondary metabolites, including xanthones (Kijjoa *et al.*, 1998), triterpenoids (Nguyen & Harrison, 1998; Bennett *et al.*, 1993) and flavonoids (Kitanov *et al.*, 1988). In our previous studies, we have reported a number of crystal structures of xanthone and anthraquinone from *C. formosum* ssp. *pruniflorum*, a medicinal plant growing in the northeastern part of Thailand (Boonnak, Chantrapromma, Fun, Anjum *et al.*, 2005; Boonnak, Chantrapromma, Fun & Karalai, 2005; Chantrapromma *et al.*, 2005). As a continuation of our study on this genus, the compound known as gerontoxanthone was isolated. We report here the structure of gerontoxanthone monohydrate, (I).



(I)

In (I), the xanthone skeleton (rings *A*, *B* and *C*) is almost planar (Fig. 1). Selected bond lengths and angles are given in Table 1. The bond distances and bond angles show normal values (Allen *et al.*, 1987), comparable to those observed in some closely related compounds (Boonnak, Chantrapromma, Fun & Karalai 2005; Chantrapromma *et al.*, 2005). The maximum deviation from planarity in the essentially planar skeleton (C1–C13/O3) is 0.015 (2) Å for atom C7. The 3-methylbut-2-enyl (C14–C18) side chain is axially attached to the benzene ring *C* and a C1—C2—C14—C15 torsion angle of

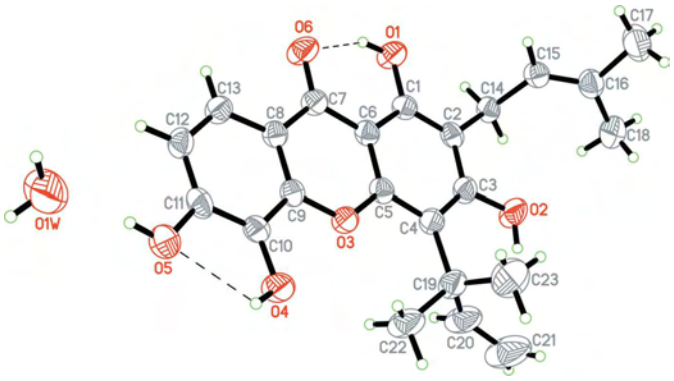


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines indicate intramolecular hydrogen bonds.

90.6 (2)°, indicating a (+)-synclinal conformation, and the 1,1-dimethylprop-2-enyl (C19–C23) substituent is axially attached to ring *C* and a C3—C4—C19—C20 torsion angle of −52.6 (3)°, indicating a (−)-synclinal conformation.

Intramolecular and intermolecular O—H···O and C—H···O interactions are observed (Table 2). The water molecule and all hydroxy O atoms are involved in hydrogen bonds. The O1—H1···O6 and O4—H4···O5 intramolecular hydrogen bonds generate $R_1^1(6)$ and $R_1^1(5)$ motifs, respectively (Bernstein *et al.*, 1995). There is a weak intramolecular C—H···O interaction (C23—H23*C*···O2), which generates an $R_1^1(6)$ ring motif. There is also a C—H···*Cg* interaction between one of the methyl groups of the 3-methylbut-2-enyl side chain and the centroid *Cg*1 of ring *A*. The molecules are linked together to form a three-dimensional network (Fig. 2).

Experimental

Air-dried bark of *C. formosum* ssp. *prunforum* (4 kg) was ground and extracted with hexane and CH_2Cl_2 (20 l for each solvent) over a period of 5 d at room temperature. The residue obtained after evaporation of the solvent was subjected to quick column chromatography over silica gel and eluted with a gradient of ethyl acetate–hexane to afford 10 fractions (F1–F10). Fraction F5 was separated by column chromatography (CC) with 10% acetone–hexane to afford six fractions (5*A*–5*F*). Fraction 5*D* was purified by CC with 15% acetone–hexane to give three fractions (5*D*1–5*D*3). Fraction 5*D*2 was recrystallized from $CHCl_3$–CH_3OH (4:1 *v*/*v*) to give yellow plate-shaped single crystals of (I) after several days (m.p. 453–454 K).

Crystal data

$C_{23}H_{24}O_6{\cdot}H_2O$
M_r = 414.44
Monoclinic, $P2_1/c$
a = 10.0244 (6) Å
b = 19.7901 (11) Å
c = 11.7645 (5) Å
β = 116.217 (4)°
V = 2093.8 (2) Å^3
Z = 4
D_x = 1.315 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 297 (2) K
Plate, yellow
0.46 × 0.20 × 0.06 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.749, T_{max} = 0.994
11308 measured reflections
4101 independent reflections
3319 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 26.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.152
S = 1.11
4101 reflections
288 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.7399P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.353 (2)	O5—C11	1.357 (2)
O2—C3	1.359 (2)	O6—C7	1.260 (2)
O3—C9	1.364 (2)	C15—C16	1.319 (3)
O3—C5	1.366 (2)	C20—C21	1.318 (4)
O4—C10	1.352 (2)		
C16—C15—C14	127.52 (19)	C21—C20—C19	127.9 (3)
C18—C16—C17	114.5 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O6	0.82	1.81	2.553 (2)	149
O4—H4···O1^{i}	0.82	2.04	2.805 (2)	156
O4—H4···O5	0.82	2.29	2.710 (2)	112
O5—H5···O1*W*	0.82	1.86	2.674 (3)	170
O1*W*—H2*W*1···O6^{ii}	0.83 (3)	1.97 (2)	2.797 (3)	172 (5)
C14—H14*B*···O4^{iii}	0.97	2.50	3.364 (3)	148
C23—H23*C*···O2	0.96	2.57	3.167 (5)	121
C17—H17*C*···*Cg*1^{iv}	0.96	2.94	3.595 (3)	129

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z$; (iii) $x+1, y, z$; (iv) $x+1, -y+\frac{1}{2}, z-\frac{1}{2}$.

H atoms of the water molecule and that attached to O2 were located in difference maps. Restraints [O1*W*—H1*W*1 = O1*W*—H1*W*2 = 0.82 (1) Å] were applied to yield an ideal water molecule configuration. The remaining H atoms were placed in calculated positions, with an O—H distance of 0.82 Å and C—H distances in the range 0.93–0.97 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxy and methyl H atoms and $1.2U_{eq}$ for the remaining H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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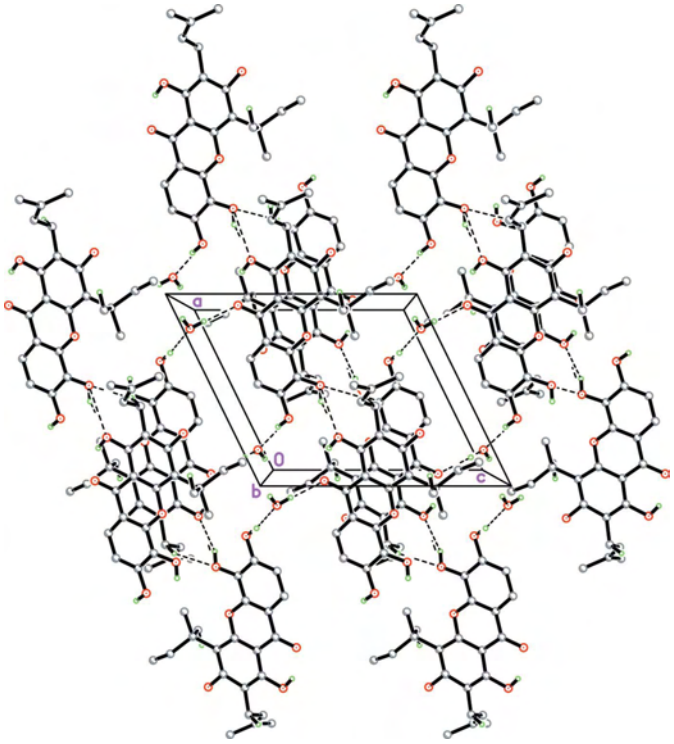

Figure 2
A view of the molecular packing down the *b* axis. H atoms have been omitted unless they are involved in hydrogen bonds (dashed lines).

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References

Aderson, E. F. (1986). *Econ. Bot.* **40**, 442–450.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bennett, G. J., Harrison, L. J., Sia, G. L. & Sim, K. Y. (1993). *Phytochemistry*, **32**, 1245–1251.
Bernstein, J., Davis, R. E., Shimoni, L. & Chamg, N.-L. (1995). *Angew. Chem. Int. Ed. Engl*. **34**, 1555–1573.
Boonnak, N., Chantrapromma, S., Fun, H.-K., Anjum Ali, S., Rahman, A. A. & Karalai, C. (2005). *Acta Cryst.* E**61**, o410–o412.
Boonnak, N., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst.* E**61**, o4376–o4378.
Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Rahman, A. A. (2005). *Acta Cryst.* E**61**, o2136–o2138.
Kijjoa, A., Jose, M., Gonzales, T. G., Pinto, M. M. M., Damas, A. M., Mondranondra, I. O., Silva, A. M. & Herz, W. (1998). *Phytochemistry*, **49**, 2159–2162.
Kitanov, G. M., Assenov, I. & The Van, D. (1988). *Pharmazie*, **43**, H12–H13.
Nguyen, L. H. D. & Harrison, L. J. (1998). *Phytochemistry*, **50**, 471–476.
Robson, N. K. B. (1974). *Flora Malesiana Ser. I*, **8**, 1.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

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3,6,9-Trimethyl-2,3-dihydrobenzo[*de*]chromene-7,8-dione

Hoong-Kun Fun, Sompong Boonsri, Suchada Chantrapromma, Nawong Boonnak and Chatchanok Karalai

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3,6,9-Trimethyl-2,3-dihydrobenzo[*de*]-chromene-7,8-dione

Hoong-Kun Fun,[a]* Sompong Boonsri,[b] Suchada Chantrapromma,[b]‡ Nawong Boonnak[b] and Chatchanok Karalai[b]

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The title sesquiterpene *ortho*-naphthoquinone compound, $C_{15}H_{14}O_3$, was isolated from *Thespesia populnea*. There are four independent molecules (*A*, *B*, *C* and *D*) in the asymmetric unit. The conformations of molecules *A* and *B* differ from those observed for *C* and *D*. In all four molecules, the pyran ring adopts an envelope conformation, with the methylene C atom as the flap atom. The molecules are arranged in layers parallel to the (100) plane, and are interconnected into a three-dimensional network by C—H···O interactions.

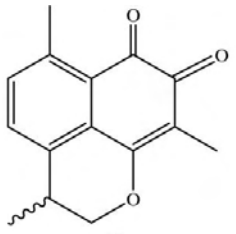
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.061
wR factor = 0.166
Data-to-parameter ratio = 10.8

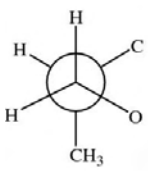
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

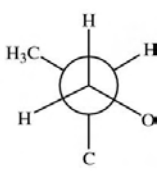
Thespesia populnea, or Po-ta-lae in Thai, is a plant in the *Malvaceae* with mainly tropical and subtropical worldwide distribution. The heartwood of *T. populnea* is a rich source of sesquiterpenoid quinines (Milbrodt *et al.*, 1997). The title compound, (I), also known as mansonone E (Marini Bettolo *et al.*, 1965; Tanaka *et al.*, 1966; Kim *et al.*, 1996), was isolated from the heartwood of *T. populnea* which was collected from Suratthani province in the southern part of Thailand. As part of our ongoing studies on the structure and biological activities of natural products from medicinal plants (Boonnak *et al.*, 2005; Chantrapromma *et al.*, 2005; Chantrapromma, Boonnak *et al.*, 2006; Chantrapromma, Boonsri *et al.*, 2006; Chantrapromma, Fun *et al.*, 2006; Fun *et al.*, 2005), we have undertaken the X-ray crystal structure determination of (I). The results of our biological activity investigation of (I) show strong cytotoxic activity and moderate antibacterial activity against *B. substilis*.



(I)



(II*a*)



(II*b*)

Compound (I) crystallizes with four independent molecules (*A*, *B*, *C* and *D*) per asymmetric unit (Fig. 1). The dimensions

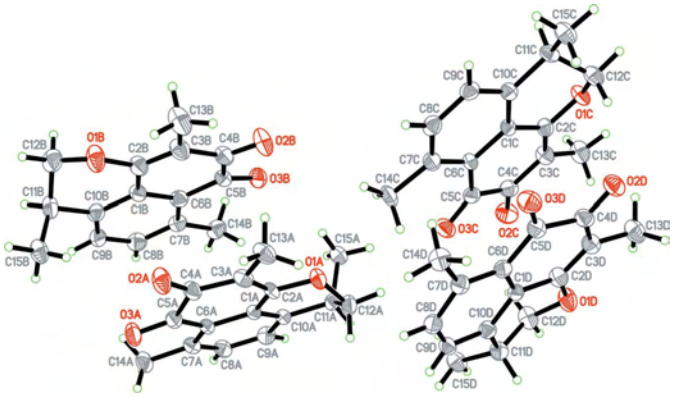


Figure 1
The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering scheme.

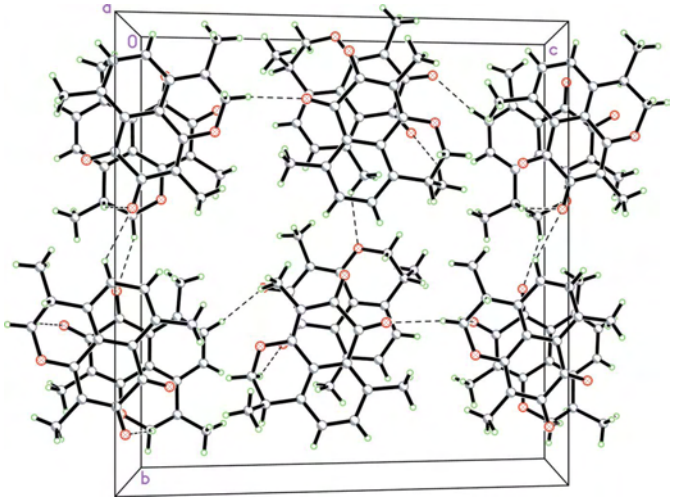


Figure 2
The crystal packing of (I), viewed approximately along the *a* axis. Hydrogen bonds are shown as dashed lines.

of all four molecules are very similar, except for slight deviations in the bond angles subtended at C11 (Table 1), with bond lengths and angles within normal ranges (Allen *et al.*, 1987). The conformations of molecules *A* and *B* are similar, the methylene and methyl groups in the pyran rings being on opposite sides of the mean plane through the molecule, while molecules *C* and *D* have similar conformations with these groups on the same side of the plane. The projections of the groups attached at C11 and C12, viewed along the C12—C11 bond, are shown in (II*a*) for molecules *A* and *B*, and (II*b*) for *C* and *D*.

The naphthoquinone ring system (C1–C10) is essentially planar, with atom C4 deviating by a maximum of 0.090 (4), 0.101 (4), 0.073 (4) and 0.075 (4) Å for molecules *A*, *B*, *C* and *D*, respectively. The pyran ring adopts an envelope conformations in all four molecules, with atom C12 displaced from the C1/C2/C10/C11/O1 plane by 0.640 (5), 0.640 (7) 0.636 (5) and 0.596 (6)Å for molecules *A*, *B*, *C* and *D*, respectively. The puckering parameters (Cremer & Pople, 1975) are Q = 0.468 (4) Å, θ = 57.2 (5) and φ = 293.8 (5)° for molecule *A*, Q = 0.469 (5) Å, θ = 56.9 (6) and φ = 292.7 (6)° for molecule *B*, Q = 0.465 (4) Å, θ = 123.0 (5) and φ = 115.1 (6)° for molecule *C*, and Q = 0.434 (4) Å, θ = 122.5 (5) and φ = 123.1 (6)° for molecule *D*. In molecules *A* and *B*, the methyl group at atom C11 is axially attached, while in *C* and *D* it is equatorially attached. Molecules *A*, *B* and *C*, *D* are related by conformational enantiomerism.

In the crystal structure, the molecules are stacked in layers parallel to the (100) plane. The molecules in a layer and in adjacent layers are linked through C—H···O intermolecular hydrogen bonds (Table 2), forming a three-dimensional network (Fig. 2).

Experimental

Air-dried heartwood of *T. populnea* (2.1 kg) was extracted with CH_2Cl_2 over a period of 5 d at room temperature. The CH_2Cl_2 extract (20 ml) was evaporated under reduced pressure, yielding an orange–brown gum (37.5 g), which was subjected to silica-gel column chromatography, affording eight fractions (F1–F8). Fraction F1 was subjected to repeated column chromatography, affording the title compound, (I). Single crystals of (I) were obtained after several days by recrystallization from MeOH–CH_2Cl_2 (3:7 *v*/*v*) (m.p. 381–383 K).

Crystal data

$C_{15}H_{14}O_3$
M_r = 242.26
Monoclinic, $P2_1$
a = 7.1615 (1) Å
b = 18.6558 (3) Å
c = 18.0323 (3) Å
β = 98.216 (1)°
V = 2384.45 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100.0 (1) K
0.32 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.971, T_{max} = 0.991
30798 measured reflections
7133 independent reflections
4478 reflections with $I > 2\sigma(I)$
R_{int} = 0.080

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.166
S = 1.01
7133 reflections
661 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C2*A*	1.354 (5)	O1*C*—C2*C*	1.351 (5)
O1*A*—C12*A*	1.450 (5)	O1*C*—C12*C*	1.448 (5)
O2*A*—C4*A*	1.221 (5)	O2*C*—C4*C*	1.227 (5)
O3*A*—C5*A*	1.204 (5)	O3*C*—C5*C*	1.214 (5)
O1*B*—C2*B*	1.347 (5)	O1*D*—C2*D*	1.359 (5)
O1*B*—C12*B*	1.452 (6)	O1*D*—C12*D*	1.448 (5)
O2*B*—C4*B*	1.226 (5)	O2*D*—C4*D*	1.227 (5)
O3*B*—C5*B*	1.207 (5)	O3*D*—C5*D*	1.211 (5)
C12*A*—C11*A*—C15*A*	112.7 (4)	C12*C*—C11*C*—C15*C*	108.9 (3)
C12*B*—C11*B*—C15*B*	113.6 (4)	C12*D*—C11*D*—C15*D*	108.0 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9C—H9CA···O2C^{i}	0.93	2.45	3.185 (5)	136
C8D—H8DA···O2B^{ii}	0.93	2.43	3.352 (5)	169
C11D—H11D···O2C^{ii}	0.98	2.55	3.449 (5)	152
C12A—H12A···O3B^{ii}	0.97	2.43	3.248 (5)	142
C12C—H12E···O3A^{iii}	0.97	2.43	3.368 (5)	162
C12C—H12F···O2D	0.97	2.43	3.349 (5)	158
C12D—H12G···O3D^{iv}	0.97	2.46	3.343 (5)	151
C12D—H12H···O2C	0.97	2.51	3.358 (6)	146
C14B—H14F···O1B^{v}	0.96	2.56	3.273 (5)	131
C15A—H15B···O3B	0.96	2.52	3.410 (5)	154

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+2$; (ii) $x+1, y, z$; (iii) $x, y, z+1$; (iv) $-x+2, y+\frac{1}{2}, -z+2$; (v) $-x, y+\frac{1}{2}, -z+1$.

H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å. The U_{iso} values were set equal to $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. A rotating-group model was used for the methyl groups. In the absence of significant anomalous scattering effects, Friedel pairs were averaged.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Boonnak, N., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst.* E**61**, o4376–o4378.
Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chantrapromma, S., Boonsri, S., Fun, H.-K., Anjum, S. & Kanjana-opas, A. (2006). *Acta Cryst.* E**62**, o1254–o1256.
Chantrapromma, S., Boonnak, N., Fun, H.-K. & Karalai, C. (2006). *Acta Cryst.* E**62**, o360–o362.
Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Atta-ur-Rahman (2005). *Acta Cryst.* E**61**, o2136–o2138.
Chantrapromma, S., Fun, H.-K., Koysomboon, S. & Chantrapromma, K. (2006). *Acta Cryst.* E**62**, o1984–o1986.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Fun, H.-K., Razak, I. A., Boonnak, N., Laphookhieo, S. & Chantrapromma, S. (2005). *Acta Cryst.* E**61**, o3086–o3088.
Kim, J.-H., Kim, W.-G., Koshino, H., Jung, J. & Yoo, I.-D. (1996). *Phytochemistry*, **43**, 425–430.
Marini Bettolo, G. B., Casinovi, C. G. & Galeffi, C. (1965). *Tetrahedron Lett.* **52**, 4875–4864.
Milbrodt, M., Konig, W. A. & Hausen, B. M. (1997). *Phytochemistry*, **45**, 1523–1525.
Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tanaka, N., Yasue, M. & Imamura, H. (1966). *Tetrahedron Lett.* **24**, 2767–2773.

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7-Hydroxy-3,6,9-trimethyl-2,3,5,6-tetrahydronaphtho[1,8-*b*,*c*]pyran-4,8-dione

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7-Hydroxy-3,6,9-trimethyl-2,3,5,6-tetrahydronaphtho[1,8-*b*,*c*]pyran-4,8-dione

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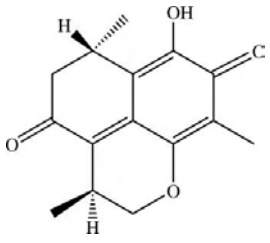
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.113; data-to-parameter ratio = 10.3.

The title sesquiterpenoid quinone compound, $C_{15}H_{16}O_4$, was isolated from *Thespesia populnea*. There are two independent molecules (*A* and *B*) with identical conformations in the asymmetric unit. In both molecules, the dihydropyran rings adopt envelope conformations, with the methylene C as the flap atom, whereas the cyclohenene rings are in screw-boat conformations. Intramolecular O—H···O hydrogen bonds generate S(5) ring motifs in both molecules. The molecules are linked into chains along the *a* axis through weak C—H···O intermolecular interactions. The crystal structure is stabilized by intramolecular O—H···O hydrogen bonds, and weak C—H···O intra- and intermolecular interactions. C—H···π interactions involving the cyclohexadiene ring are observed in the crystal structure.

Related literature

For details of the sources and biological activities of related sesquiterpenes, see Tiew *et al.* (2002); Duh *et al.* (2004); Wang *et al.* (2004); Silva *et al.* (2006). For related literature on hydrogen-bond motifs, see Bernstein *et al.* (1995), and on values of bond lengths and angles, see Allen *et al.* (1987). For a related structure, see Fun *et al.* (2007). For related literature, see: Cremer & Pople (1975); Milbrodt *et al.* (1997).



Experimental

Crystal data

$C_{15}H_{16}O_4$
M_r = 260.28
Orthorhombic, $P2_12_12_1$
a = 8.5390 (4) Å
b = 10.0913 (5) Å
c = 30.3769 (14) Å
V = 2617.6 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 100.0 (1) K
0.51 × 0.19 × 0.11 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.953, T_{max} = 0.990
28942 measured reflections
3593 independent reflections
3004 reflections with $I > 2\sigma(I)$
R_{int} = 0.067

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.113
S = 1.02
3593 reflections
349 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3*A*—H3*AA*···O2*A*	0.82	2.28	2.703 (2)	112
O3*A*—H3*AA*···O2*B*	0.82	1.98	2.760 (2)	159
O3*B*—H3*BA*···O2*A*	0.82	2.05	2.829 (2)	158
O3*B*—H3*BA*···O2*B*	0.82	2.24	2.693 (3)	115
C7*A*—H7*AA*···O3*A*	0.98	2.51	2.865 (3)	101
C7*B*—H7*BA*···O3*B*	0.98	2.50	2.854 (3)	101
C12*A*—H12*A*···O4*B*^{i}	0.97	2.50	3.452 (3)	168
C12*B*—H12*D*···O4*B*^{ii}	0.97	2.44	3.281 (3)	145
C14*A*—H14*A*···O1*A*	0.96	2.43	2.853 (3)	106
C12*A*—H12*B*···*Cg*1^{iii}	0.97	2.78	3.657 (3)	151
C13*A*—H13*B*···*Cg*1^{iv}	0.97	2.67	3.387 (3)	132

Symmetry codes: (i) $-x+\frac{3}{2}, -y+2, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{5}{2}, -z+1$; (iii) $x+\frac{3}{2}, -y-\frac{1}{2}, -z$; (iv) $x+\frac{5}{2}, -y-\frac{1}{2}, -z$. *Cg*1 is the centroid of C1*B*–C6*B*.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2300).

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Duh, C.-Y., Chien, S.-C., Song, P.-Y., Wang, S.-K., El-Gamal, A. A. H. & Dai, C.-F. (2004). *J. Nat. Prod.* **65**, 1853–1856.

Fun, H.-K., Boonsri, S., Chantrapromma, S., Boonnak, N. & Karalai, C. (2007). *Acta Cryst.* E**63**, o2127–o2129.

Milbrodt, M., Konig, W. A. & Hausen, B. M. (1997). *Phytochemistry*, **45**, 1523–1525.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Silva, G. H., Teles, H. L., Zanardi, L. M., Young, M. C. M., Eberlin, M. N., hadad, R., Pfenning, L. H., Costa-Neto, C. M., Castro-Gamboa, I., Bolzani, V. S. & Araujo, A. R. (2006). *Phytochemistry*, **67**, 1964–1969.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Tiew, P., Puntumchai, A., Kokpol, U. & Chavasiri, W. (2002). *Phytochemistry*, **60**, 773–776.

Wang, D., Xia, M.-Y., Cui, Z., Tashiro, S., Onodera, S. & Ikejima, T. (2004). *Biol. Pharm. Bull.* **27**, 1025–1030.

supplementary materials

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7-Hydroxy-3,6,9-trimethyl-2,3,5,6-tetrahydronaphtho[1,8-*b*,*c*]pyran-4,8-dione

S. Chantrapromma, S. Boonsri, H.-K. Fun and C. Karalai

Comment

The heartwood of *Thespesia populnea* is a rich source of highly oxidized sesquiterpenes containing a cadinane skeleton (Milbrodt *et al.*, 1997). Some possess significant pharmacological effects such as cytotoxicity (Tiew *et al.*, 2002; Duh *et al.*, 2004; Wang *et al.*, 2004) and antifungal activity (Silva *et al.*, 2006). Previously we reported the stucture of mansonone E, a sesquiterpene isolated from *T. populnea* (Fun *et al.*, 2007). In continuation of our study of bioactive compounds from *T. populnea*, (Po-ta-lea in Thai) a plant in the *malvaceae*, we report the structure of the title compound, (I) isolated from the heartwood of *T. populnea* collected from the Suratthani province in Thailand. Biological activity tests show that (I) is inactive against bacteria and shows an IC_{50} > 5 µg/ml) against MCF-7 (breast), Hela (cervical), HT-29 (colon) and KB (oral cavity) cancer cell lines.

Compound (I) crystallizes with two conformationally similar independent molecules (A and B) per asymmetric unit (Fig. 1). The bond lengths and angles in (I) are normal (Allen *et al.*, 1987) and comparable to those in a related structure (Fun *et al.*, 2007). In both molecules, the cyclohexadiene rings (C1—C6) are essentially planar with maximum deviations of -0.037 (3) for C1A and 0.036 (3) Å for atom C4B. The dihydropyran rings adopt envelope conformations, with atom C12 displaced from the C1/C2/C10/C11/O1 plane by -0.340 (3)Å and -0.315 (3) Å for A and B, respectively. The puckering parameters (Cremer & Pople, 1975) are Q = 0.473 (3) Å, θ = 122.7 (3)° and φ = 121.6 (3)° for A and Q = 0.439 (2) Å, θ = 124.0 (3)° and φ = 119.3 (4)° for B. Both the cycloxene rings adopt screw boat conformations with puckering parameters Q = 0.434 (3) Å, θ = 57.4 (4)° and φ = 150.4 (4)° for A and Q = 0.416 (2) Å, θ = 54.1 (4)° and φ = 154.9 (4)° for B. In both molecules, the methyl group at C3 lies in the cyclohexadiene ring plane whereas the C7 and C11 methyl groups are axial to the cyclohexene and dihydropyran rings (Fig. 1).

In the crystal intramolecular O3A—H3AA···O2A and O3B—H3BA···O2B hydrogen bonds generate S(5) ring motifs with S(10) motifs formed by O3A—H3AA···O2B and O3B—H3BA···O2A interactions (Bernstein *et al.*, 1995). These link the two molecules into dimers which form chains along a through weak intermolecular C—H···O interactions (Fig. 2, Table 1). The crystal is further stabilized by C—H···π interactions; Cg_1 is the centroid of C1B–C6B (Table 1).

Experimental

Air-dried heartwood of *T. populnea* (2.1 kg) was extracted with CH_2Cl_2 over a period of 5 d at room temperature. The CH_2Cl_2 extract was evaporated under reduced pressure to yield a orange-brown gum (37.5 g), which was subjected to silica gel column chromatography using CH_2Cl_2 as eluent to afford 8 fractions (F1—F8). Fraction F7 was subjected to repeated column chromatography with acetone-CH_2Cl_2 as eluents for gradient elution to afford the title compound (I). Purple needle-shaped single crystals of (I) were obtained by recrystallization from MeOH-CH_2Cl_2 (3:7 v/v) after several days (m.p. 532–534 K).

Refinement

In the absence of significant anomalous scattering effects, 2730 Friedel pairs were averaged. All H atoms were positioned geometrically and allowed to ride on their parent atoms, with an O—H distance of 0.82 Å and C—H distances in the range 0.93–0.96 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. A rotating group model was used for the methyl groups.

Figures

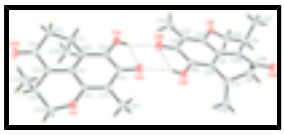


Fig. 1. The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering scheme. Hydrogen bonds are shown as dashed lines.

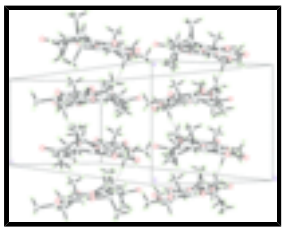


Fig. 2. The crystal packing of (I). Hydrogen bonds are shown as dashed lines.

7-Hydroxy-3,6,9-trimethyl-2,3,5,6-tetrahydronaphtho[1,8-b,c]pyran-4,8-dione

Crystal data

$C_{15}H_{16}O_4$	$D_x = 1.321$ Mg m^{-3}
$M_r = 260.28$	Melting point: 532-534 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 3593 reflections
$a = 8.5390$ (4) Å	$\theta = 1.3$–28.0^o
$b = 10.0913$ (5) Å	$\mu = 0.10$ mm^{-1}
$c = 30.3769$ (14) Å	$T = 100.0$ (1) K
$V = 2617.6$ (2) Å^3	Needle, purple
$Z = 8$	0.51 × 0.19 × 0.11 mm
$F_{000} = 1104$	

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	3593 independent reflections
Radiation source: fine-focus sealed tube	3004 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.067$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{max} = 28.0^o$
$T = 297$(3) K	$\theta_{min} = 1.3^o$
ω scans	$h = -11 \rightarrow 11$

Absorption correction: multi-scan (SADABS; Bruker, 2005)
T_{min} = 0.953, T_{max} = 0.990
28942 measured reflections

k = −12→13
l = −39→40

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.113
S = 1.03
3593 reflections
349 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: none

Special details

Experimental. The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.7493 (2)	0.62788 (16)	0.10729 (5)	0.0247 (4)
O2A	0.8398 (2)	0.77230 (17)	0.25156 (6)	0.0279 (4)
O3A	0.7968 (2)	0.52747 (17)	0.28561 (5)	0.0277 (4)
H3AA	0.7890	0.5996	0.2979	0.042*
O4A	0.7326 (3)	0.13687 (19)	0.12509 (6)	0.0436 (6)
C1A	0.7573 (3)	0.4667 (2)	0.16700 (7)	0.0194 (5)
C2A	0.7636 (3)	0.6047 (2)	0.15122 (7)	0.0198 (5)
C3A	0.7918 (3)	0.7077 (2)	0.17842 (8)	0.0214 (5)
C4A	0.8115 (3)	0.6818 (2)	0.22519 (8)	0.0212 (5)
C5A	0.7907 (3)	0.5448 (2)	0.24131 (7)	0.0217 (5)
C6A	0.7665 (3)	0.4418 (2)	0.21395 (7)	0.0201 (5)

C7A	0.7381 (3)	0.3024 (2)	0.23054 (8)	0.0244 (5)
H7AA	0.7908	0.2922	0.2590	0.029*
C8A	0.8087 (3)	0.2023 (3)	0.19815 (8)	0.0296 (6)
H8AA	0.9220	0.2079	0.1995	0.035*
H8AB	0.7787	0.1135	0.2070	0.035*
C9A	0.7560 (3)	0.2260 (3)	0.15131 (8)	0.0286 (6)
C10A	0.7422 (3)	0.3664 (2)	0.13727 (8)	0.0207 (5)
C11A	0.7211 (3)	0.3933 (2)	0.08885 (8)	0.0228 (5)
H11A	0.6446	0.3301	0.0771	0.027*
C12A	0.6554 (3)	0.5315 (3)	0.08381 (8)	0.0262 (5)
H12A	0.6522	0.5547	0.0528	0.031*
H12B	0.5490	0.5335	0.0950	0.031*
C13A	0.8749 (3)	0.3761 (3)	0.06367 (8)	0.0304 (6)
H13A	0.9186	0.2906	0.0701	0.046*
H13B	0.9473	0.4439	0.0725	0.046*
H13C	0.8553	0.3830	0.0326	0.046*
C14A	0.7978 (3)	0.8499 (2)	0.16384 (8)	0.0265 (5)
H14A	0.7826	0.8545	0.1326	0.040*
H14B	0.8979	0.8870	0.1712	0.040*
H14C	0.7166	0.8991	0.1784	0.040*
C15A	0.5626 (3)	0.2783 (3)	0.23716 (9)	0.0338 (6)
H15A	0.5210	0.3443	0.2567	0.051*
H15B	0.5468	0.1919	0.2497	0.051*
H15C	0.5100	0.2835	0.2093	0.051*
O1B	0.7010 (2)	0.87759 (16)	0.49008 (5)	0.0273 (4)
O2B	0.7770 (3)	0.73126 (18)	0.34594 (6)	0.0386 (5)
O3B	0.8073 (2)	0.97874 (18)	0.31392 (5)	0.0291 (4)
H3BA	0.8132	0.9062	0.3019	0.044*
O4B	0.7987 (2)	1.36536 (17)	0.47624 (6)	0.0274 (4)
C1B	0.7519 (3)	1.0400 (2)	0.43210 (7)	0.0189 (5)
C2B	0.7216 (3)	0.9027 (2)	0.44669 (8)	0.0218 (5)
C3B	0.7241 (3)	0.7987 (2)	0.41856 (8)	0.0254 (5)
C4B	0.7622 (3)	0.8228 (2)	0.37285 (8)	0.0258 (6)
C5B	0.7823 (3)	0.9617 (2)	0.35765 (7)	0.0226 (5)
C6B	0.7778 (3)	1.0649 (2)	0.38527 (8)	0.0194 (5)
C7B	0.7933 (3)	1.2061 (2)	0.36968 (8)	0.0217 (5)
H7BA	0.8575	1.2062	0.3429	0.026*
C8B	0.8782 (3)	1.2897 (2)	0.40482 (7)	0.0237 (5)
H8BA	0.9876	1.2640	0.4057	0.028*
H8BB	0.8733	1.3824	0.3965	0.028*
C9B	0.8086 (3)	1.2736 (2)	0.44997 (8)	0.0219 (5)
C10B	0.7607 (3)	1.1374 (2)	0.46290 (8)	0.0200 (5)
C11B	0.7364 (3)	1.1094 (2)	0.51100 (8)	0.0219 (5)
H11B	0.6778	1.1837	0.5237	0.026*
C12B	0.6393 (3)	0.9857 (2)	0.51640 (8)	0.0260 (5)
H12C	0.6384	0.9598	0.5472	0.031*
H12D	0.5323	1.0038	0.5076	0.031*
C13B	0.8948 (3)	1.1007 (3)	0.53461 (8)	0.0304 (6)
H13D	0.9493	1.1834	0.5316	0.046*

H13E	0.9562	1.0311	0.5217	0.046*
H13F	0.8780	1.0821	0.5652	0.046*
C14B	0.6971 (5)	0.6582 (3)	0.43310 (9)	0.0420 (8)
H14D	0.6267	0.6574	0.4577	0.063*
H14E	0.7950	0.6190	0.4415	0.063*
H14F	0.6522	0.6085	0.4093	0.063*
C15B	0.6336 (3)	1.2662 (3)	0.35835 (8)	0.0275 (6)
H15E	0.5832	1.2127	0.3364	0.041*
H15F	0.6479	1.3544	0.3472	0.041*
H15G	0.5697	1.2691	0.3843	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0370 (9)	0.0204 (8)	0.0166 (8)	−0.0034 (7)	−0.0031 (7)	−0.0001 (7)
O2A	0.0407 (10)	0.0216 (9)	0.0213 (9)	−0.0030 (8)	0.0021 (8)	−0.0051 (8)
O3A	0.0459 (10)	0.0225 (9)	0.0149 (8)	−0.0034 (8)	0.0008 (8)	−0.0041 (7)
O4A	0.0871 (17)	0.0196 (9)	0.0242 (10)	−0.0047 (11)	−0.0080 (10)	−0.0051 (8)
C1A	0.0231 (11)	0.0168 (11)	0.0181 (11)	−0.0006 (9)	0.0002 (9)	0.0006 (10)
C2A	0.0243 (11)	0.0196 (12)	0.0155 (11)	−0.0007 (9)	0.0016 (9)	0.0005 (9)
C3A	0.0256 (11)	0.0185 (12)	0.0202 (11)	0.0008 (9)	0.0028 (10)	−0.0009 (10)
C4A	0.0243 (11)	0.0190 (12)	0.0202 (12)	−0.0009 (9)	0.0026 (10)	−0.0043 (10)
C5A	0.0261 (11)	0.0240 (13)	0.0149 (11)	−0.0023 (10)	−0.0001 (9)	−0.0004 (10)
C6A	0.0249 (11)	0.0193 (12)	0.0161 (11)	−0.0001 (9)	0.0004 (9)	0.0002 (9)
C7A	0.0370 (13)	0.0195 (12)	0.0168 (11)	−0.0015 (10)	−0.0030 (10)	0.0011 (10)
C8A	0.0482 (15)	0.0182 (12)	0.0224 (13)	0.0002 (11)	−0.0051 (12)	0.0003 (11)
C9A	0.0430 (14)	0.0206 (13)	0.0221 (12)	−0.0006 (11)	−0.0015 (11)	−0.0017 (11)
C10A	0.0256 (11)	0.0187 (12)	0.0177 (11)	−0.0019 (10)	−0.0007 (9)	0.0003 (10)
C11A	0.0298 (12)	0.0216 (12)	0.0169 (11)	−0.0048 (10)	−0.0011 (9)	−0.0057 (10)
C12A	0.0316 (12)	0.0283 (13)	0.0187 (12)	−0.0018 (11)	−0.0053 (10)	−0.0009 (11)
C13A	0.0345 (14)	0.0336 (15)	0.0230 (13)	−0.0043 (12)	0.0038 (10)	−0.0080 (12)
C14A	0.0380 (13)	0.0191 (12)	0.0225 (12)	−0.0003 (10)	0.0037 (11)	−0.0004 (11)
C15A	0.0403 (14)	0.0339 (16)	0.0272 (14)	−0.0122 (12)	0.0014 (11)	0.0032 (13)
O1B	0.0467 (10)	0.0195 (9)	0.0158 (8)	0.0016 (8)	0.0045 (8)	0.0000 (7)
O2B	0.0733 (14)	0.0223 (10)	0.0201 (9)	−0.0025 (10)	0.0051 (10)	−0.0060 (8)
O3B	0.0487 (11)	0.0227 (9)	0.0158 (8)	−0.0002 (9)	0.0033 (8)	−0.0037 (7)
O4B	0.0365 (9)	0.0221 (9)	0.0234 (9)	−0.0015 (8)	−0.0008 (8)	−0.0042 (8)
C1B	0.0210 (10)	0.0197 (11)	0.0160 (11)	−0.0007 (9)	0.0009 (8)	0.0000 (10)
C2B	0.0282 (12)	0.0201 (12)	0.0171 (11)	0.0023 (10)	0.0028 (9)	0.0020 (9)
C3B	0.0376 (13)	0.0188 (12)	0.0199 (12)	0.0016 (11)	0.0019 (11)	0.0002 (10)
C4B	0.0390 (14)	0.0212 (13)	0.0172 (12)	−0.0009 (10)	−0.0006 (10)	−0.0024 (10)
C5B	0.0305 (12)	0.0231 (12)	0.0143 (11)	−0.0003 (10)	−0.0003 (9)	0.0015 (10)
C6B	0.0246 (11)	0.0175 (11)	0.0160 (11)	0.0014 (9)	0.0002 (9)	0.0014 (9)
C7B	0.0300 (12)	0.0185 (12)	0.0167 (11)	−0.0016 (10)	0.0038 (10)	0.0011 (10)
C8B	0.0296 (12)	0.0212 (12)	0.0203 (12)	−0.0028 (10)	0.0028 (10)	−0.0001 (10)
C9B	0.0245 (11)	0.0209 (12)	0.0204 (11)	−0.0001 (10)	−0.0010 (9)	−0.0005 (10)
C10B	0.0224 (11)	0.0198 (11)	0.0179 (11)	0.0028 (9)	−0.0011 (9)	0.0008 (10)
C11B	0.0285 (12)	0.0221 (12)	0.0149 (11)	0.0048 (10)	−0.0012 (9)	−0.0032 (10)

C12B	0.0373 (13)	0.0248 (13)	0.0159 (11)	0.0015 (11)	0.0045 (10)	−0.0011 (10)
C13B	0.0361 (14)	0.0360 (16)	0.0190 (12)	0.0061 (12)	−0.0038 (10)	−0.0023 (12)
C14B	0.081 (2)	0.0204 (14)	0.0248 (14)	−0.0058 (15)	0.0088 (15)	0.0020 (12)
C15B	0.0340 (13)	0.0257 (14)	0.0229 (13)	0.0004 (11)	−0.0028 (10)	0.0045 (11)

Geometric parameters (Å, °)

O1A—C2A	1.360 (3)	O1B—C2B	1.353 (3)
O1A—C12A	1.448 (3)	O1B—C12B	1.451 (3)
O2A—C4A	1.239 (3)	O2B—C4B	1.240 (3)
O3A—C5A	1.358 (3)	O3B—C5B	1.356 (3)
O3A—H3AA	0.8200	O3B—H3BA	0.8200
O4A—C9A	1.218 (3)	O4B—C9B	1.225 (3)
C1A—C10A	1.363 (3)	C1B—C10B	1.359 (3)
C1A—C6A	1.450 (3)	C1B—C6B	1.461 (3)
C1A—C2A	1.474 (3)	C1B—C2B	1.478 (3)
C2A—C3A	1.349 (3)	C2B—C3B	1.353 (3)
C3A—C4A	1.454 (3)	C3B—C4B	1.447 (3)
C3A—C14A	1.503 (3)	C3B—C14B	1.503 (4)
C4A—C5A	1.477 (3)	C4B—C5B	1.485 (3)
C5A—C6A	1.347 (3)	C5B—C6B	1.338 (3)
C6A—C7A	1.514 (3)	C6B—C7B	1.508 (3)
C7A—C15A	1.532 (4)	C7B—C15B	1.531 (3)
C7A—C8A	1.533 (4)	C7B—C8B	1.541 (3)
C7A—H7AA	0.9800	C7B—H7BA	0.9800
C8A—C9A	1.512 (3)	C8B—C9B	1.503 (3)
C8A—H8AA	0.9700	C8B—H8BA	0.9700
C8A—H8AB	0.9700	C8B—H8BB	0.9700
C9A—C10A	1.485 (3)	C9B—C10B	1.487 (3)
C10A—C11A	1.506 (3)	C10B—C11B	1.503 (3)
C11A—C12A	1.511 (3)	C11B—C12B	1.508 (3)
C11A—C13A	1.530 (3)	C11B—C13B	1.533 (3)
C11A—H11A	0.9800	C11B—H11B	0.9800
C12A—H12A	0.9700	C12B—H12C	0.9700
C12A—H12B	0.9700	C12B—H12D	0.9700
C13A—H13A	0.9600	C13B—H13D	0.9600
C13A—H13B	0.9600	C13B—H13E	0.9600
C13A—H13C	0.9600	C13B—H13F	0.9600
C14A—H14A	0.9600	C14B—H14D	0.9600
C14A—H14B	0.9600	C14B—H14E	0.9600
C14A—H14C	0.9600	C14B—H14F	0.9600
C15A—H15A	0.9600	C15B—H15E	0.9600
C15A—H15B	0.9600	C15B—H15F	0.9600
C15A—H15C	0.9600	C15B—H15G	0.9600
C2A—O1A—C12A	114.68 (18)	C2B—O1B—C12B	116.32 (18)
C5A—O3A—H3AA	109.5	C5B—O3B—H3BA	109.5
C10A—C1A—C6A	121.9 (2)	C10B—C1B—C6B	122.5 (2)
C10A—C1A—C2A	119.3 (2)	C10B—C1B—C2B	118.8 (2)
C6A—C1A—C2A	118.8 (2)	C6B—C1B—C2B	118.7 (2)

C3A—C2A—O1A	119.0 (2)	C3B—C2B—O1B	118.2 (2)
C3A—C2A—C1A	122.3 (2)	C3B—C2B—C1B	122.3 (2)
O1A—C2A—C1A	118.56 (19)	O1B—C2B—C1B	119.3 (2)
C2A—C3A—C4A	118.7 (2)	C2B—C3B—C4B	118.7 (2)
C2A—C3A—C14A	124.1 (2)	C2B—C3B—C14B	122.9 (2)
C4A—C3A—C14A	117.1 (2)	C4B—C3B—C14B	118.4 (2)
O2A—C4A—C3A	121.4 (2)	O2B—C4B—C3B	122.0 (2)
O2A—C4A—C5A	119.9 (2)	O2B—C4B—C5B	119.1 (2)
C3A—C4A—C5A	118.6 (2)	C3B—C4B—C5B	118.9 (2)
C6A—C5A—O3A	121.2 (2)	C6B—C5B—O3B	121.3 (2)
C6A—C5A—C4A	122.4 (2)	C6B—C5B—C4B	122.4 (2)
O3A—C5A—C4A	116.4 (2)	O3B—C5B—C4B	116.3 (2)
C5A—C6A—C1A	118.8 (2)	C5B—C6B—C1B	118.7 (2)
C5A—C6A—C7A	122.4 (2)	C5B—C6B—C7B	122.4 (2)
C1A—C6A—C7A	118.7 (2)	C1B—C6B—C7B	118.8 (2)
C6A—C7A—C15A	110.3 (2)	C6B—C7B—C15B	111.5 (2)
C6A—C7A—C8A	109.6 (2)	C6B—C7B—C8B	109.93 (19)
C15A—C7A—C8A	111.4 (2)	C15B—C7B—C8B	111.0 (2)
C6A—C7A—H7AA	108.5	C6B—C7B—H7BA	108.1
C15A—C7A—H7AA	108.5	C15B—C7B—H7BA	108.1
C8A—C7A—H7AA	108.5	C8B—C7B—H7BA	108.1
C9A—C8A—C7A	112.5 (2)	C9B—C8B—C7B	112.8 (2)
C9A—C8A—H8AA	109.1	C9B—C8B—H8BA	109.0
C7A—C8A—H8AA	109.1	C7B—C8B—H8BA	109.0
C9A—C8A—H8AB	109.1	C9B—C8B—H8BB	109.0
C7A—C8A—H8AB	109.1	C7B—C8B—H8BB	109.0
H8AA—C8A—H8AB	107.8	H8BA—C8B—H8BB	107.8
O4A—C9A—C10A	120.3 (2)	O4B—C9B—C10B	120.5 (2)
O4A—C9A—C8A	123.2 (2)	O4B—C9B—C8B	122.7 (2)
C10A—C9A—C8A	116.4 (2)	C10B—C9B—C8B	116.7 (2)
C1A—C10A—C9A	120.7 (2)	C1B—C10B—C9B	120.1 (2)
C1A—C10A—C11A	121.6 (2)	C1B—C10B—C11B	121.7 (2)
C9A—C10A—C11A	117.5 (2)	C9B—C10B—C11B	117.9 (2)
C10A—C11A—C12A	108.0 (2)	C10B—C11B—C12B	109.7 (2)
C10A—C11A—C13A	111.4 (2)	C10B—C11B—C13B	110.1 (2)
C12A—C11A—C13A	111.9 (2)	C12B—C11B—C13B	112.7 (2)
C10A—C11A—H11A	108.5	C10B—C11B—H11B	108.1
C12A—C11A—H11A	108.5	C12B—C11B—H11B	108.1
C13A—C11A—H11A	108.5	C13B—C11B—H11B	108.1
O1A—C12A—C11A	111.35 (19)	O1B—C12B—C11B	111.3 (2)
O1A—C12A—H12A	109.4	O1B—C12B—H12C	109.4
C11A—C12A—H12A	109.4	C11B—C12B—H12C	109.4
O1A—C12A—H12B	109.4	O1B—C12B—H12D	109.4
C11A—C12A—H12B	109.4	C11B—C12B—H12D	109.4
H12A—C12A—H12B	108.0	H12C—C12B—H12D	108.0
C11A—C13A—H13A	109.5	C11B—C13B—H13D	109.5
C11A—C13A—H13B	109.5	C11B—C13B—H13E	109.5
H13A—C13A—H13B	109.5	H13D—C13B—H13E	109.5
C11A—C13A—H13C	109.5	C11B—C13B—H13F	109.5

H13A—C13A—H13C	109.5	H13D—C13B—H13F	109.5
H13B—C13A—H13C	109.5	H13E—C13B—H13F	109.5
C3A—C14A—H14A	109.5	C3B—C14B—H14D	109.5
C3A—C14A—H14B	109.5	C3B—C14B—H14E	109.5
H14A—C14A—H14B	109.5	H14D—C14B—H14E	109.5
C3A—C14A—H14C	109.5	C3B—C14B—H14F	109.5
H14A—C14A—H14C	109.5	H14D—C14B—H14F	109.5
H14B—C14A—H14C	109.5	H14E—C14B—H14F	109.5
C7A—C15A—H15A	109.5	C7B—C15B—H15E	109.5
C7A—C15A—H15B	109.5	C7B—C15B—H15F	109.5
H15A—C15A—H15B	109.5	H15E—C15B—H15F	109.5
C7A—C15A—H15C	109.5	C7B—C15B—H15G	109.5
H15A—C15A—H15C	109.5	H15E—C15B—H15G	109.5
H15B—C15A—H15C	109.5	H15F—C15B—H15G	109.5
C12A—O1A—C2A—C3A	−154.1 (2)	C12B—O1B—C2B—C3B	−156.9 (2)
C12A—O1A—C2A—C1A	29.6 (3)	C12B—O1B—C2B—C1B	27.5 (3)
C10A—C1A—C2A—C3A	−174.2 (2)	C10B—C1B—C2B—C3B	−174.4 (2)
C6A—C1A—C2A—C3A	6.2 (3)	C6B—C1B—C2B—C3B	3.1 (4)
C10A—C1A—C2A—O1A	2.0 (3)	C10B—C1B—C2B—O1B	1.0 (3)
C6A—C1A—C2A—O1A	−177.67 (19)	C6B—C1B—C2B—O1B	178.5 (2)
O1A—C2A—C3A—C4A	−178.3 (2)	O1B—C2B—C3B—C4B	−173.7 (2)
C1A—C2A—C3A—C4A	−2.1 (4)	C1B—C2B—C3B—C4B	1.8 (4)
O1A—C2A—C3A—C14A	4.5 (4)	O1B—C2B—C3B—C14B	3.2 (4)
C1A—C2A—C3A—C14A	−179.4 (2)	C1B—C2B—C3B—C14B	178.6 (3)
C2A—C3A—C4A—O2A	179.0 (2)	C2B—C3B—C4B—O2B	175.0 (3)
C14A—C3A—C4A—O2A	−3.6 (4)	C14B—C3B—C4B—O2B	−1.9 (4)
C2A—C3A—C4A—C5A	−3.5 (3)	C2B—C3B—C4B—C5B	−5.7 (4)
C14A—C3A—C4A—C5A	174.0 (2)	C14B—C3B—C4B—C5B	177.3 (3)
O2A—C4A—C5A—C6A	−177.1 (2)	O2B—C4B—C5B—C6B	−175.7 (3)
C3A—C4A—C5A—C6A	5.4 (4)	C3B—C4B—C5B—C6B	5.0 (4)
O2A—C4A—C5A—O3A	3.1 (3)	O2B—C4B—C5B—O3B	3.6 (4)
C3A—C4A—C5A—O3A	−174.5 (2)	C3B—C4B—C5B—O3B	−175.6 (2)
O3A—C5A—C6A—C1A	178.5 (2)	O3B—C5B—C6B—C1B	−179.4 (2)
C4A—C5A—C6A—C1A	−1.3 (4)	C4B—C5B—C6B—C1B	−0.1 (4)
O3A—C5A—C6A—C7A	2.6 (4)	O3B—C5B—C6B—C7B	2.6 (4)
C4A—C5A—C6A—C7A	−177.3 (2)	C4B—C5B—C6B—C7B	−178.1 (2)
C10A—C1A—C6A—C5A	176.1 (2)	C10B—C1B—C6B—C5B	173.5 (2)
C2A—C1A—C6A—C5A	−4.3 (3)	C2B—C1B—C6B—C5B	−3.9 (3)
C10A—C1A—C6A—C7A	−7.8 (3)	C10B—C1B—C6B—C7B	−8.5 (3)
C2A—C1A—C6A—C7A	171.9 (2)	C2B—C1B—C6B—C7B	174.2 (2)
C5A—C6A—C7A—C15A	90.4 (3)	C5B—C6B—C7B—C15B	89.7 (3)
C1A—C6A—C7A—C15A	−85.6 (3)	C1B—C6B—C7B—C15B	−88.3 (3)
C5A—C6A—C7A—C8A	−146.6 (2)	C5B—C6B—C7B—C8B	−146.8 (2)
C1A—C6A—C7A—C8A	37.4 (3)	C1B—C6B—C7B—C8B	35.2 (3)
C6A—C7A—C8A—C9A	−51.6 (3)	C6B—C7B—C8B—C9B	−50.2 (3)
C15A—C7A—C8A—C9A	70.8 (3)	C15B—C7B—C8B—C9B	73.6 (3)
C7A—C8A—C9A—O4A	−144.8 (3)	C7B—C8B—C9B—O4B	−143.4 (2)
C7A—C8A—C9A—C10A	38.7 (3)	C7B—C8B—C9B—C10B	40.5 (3)
C6A—C1A—C10A—C9A	−8.3 (4)	C6B—C1B—C10B—C9B	−4.2 (3)

C2A—C1A—C10A—C9A	172.1 (2)	C2B—C1B—C10B—C9B	173.1 (2)
C6A—C1A—C10A—C11A	175.6 (2)	C6B—C1B—C10B—C11B	−178.9 (2)
C2A—C1A—C10A—C11A	−4.1 (4)	C2B—C1B—C10B—C11B	−1.6 (3)
O4A—C9A—C10A—C1A	175.4 (3)	O4B—C9B—C10B—C1B	171.1 (2)
C8A—C9A—C10A—C1A	−8.0 (4)	C8B—C9B—C10B—C1B	−12.7 (3)
O4A—C9A—C10A—C11A	−8.3 (4)	O4B—C9B—C10B—C11B	−14.0 (3)
C8A—C9A—C10A—C11A	168.3 (2)	C8B—C9B—C10B—C11B	162.2 (2)
C1A—C10A—C11A—C12A	−22.9 (3)	C1B—C10B—C11B—C12B	−23.9 (3)
C9A—C10A—C11A—C12A	160.8 (2)	C9B—C10B—C11B—C12B	161.3 (2)
C1A—C10A—C11A—C13A	100.4 (3)	C1B—C10B—C11B—C13B	100.7 (3)
C9A—C10A—C11A—C13A	−75.9 (3)	C9B—C10B—C11B—C13B	−74.1 (3)
C2A—O1A—C12A—C11A	−58.4 (3)	C2B—O1B—C12B—C11B	−53.8 (3)
C10A—C11A—C12A—O1A	52.5 (3)	C10B—C11B—C12B—O1B	49.7 (3)
C13A—C11A—C12A—O1A	−70.5 (3)	C13B—C11B—C12B—O1B	−73.4 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3A—H3AA···O2A	0.82	2.28	2.703 (2)	112
O3A—H3AA···O2B	0.82	1.98	2.760 (2)	159
O3B—H3BA···O2A	0.82	2.05	2.829 (2)	158
O3B—H3BA···O2B	0.82	2.24	2.693 (3)	115
C7A—H7AA···O3A	0.98	2.51	2.865 (3)	101
C7B—H7BA···O3B	0.98	2.50	2.854 (3)	101
C12A—H12A···O4B^{i}	0.97	2.50	3.452 (3)	168
C12B—H12D···O4B^{ii}	0.97	2.44	3.281 (3)	145
C14A—H14A···O1A	0.96	2.43	2.853 (3)	106
C12A—H12B···Cg1^{iii}	0.97	2.78	3.657 (3)	151
C13A—H13B···Cg1^{iv}	0.97	2.67	3.387 (3)	132

Symmetry codes: (i) −*x*+3/2, −*y*+2, *z*−1/2; (ii) *x*−1/2, −*y*+5/2, −*z*+1; (iii) *x*+3/2, −*y*−1/2, −*z*; (iv) *x*+5/2, −*y*−1/2, −*z*.

Fig. 1

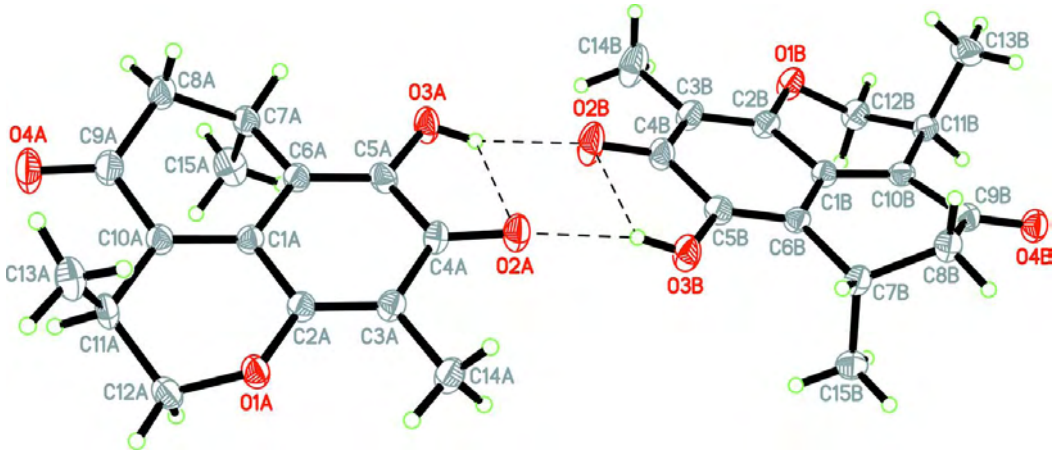
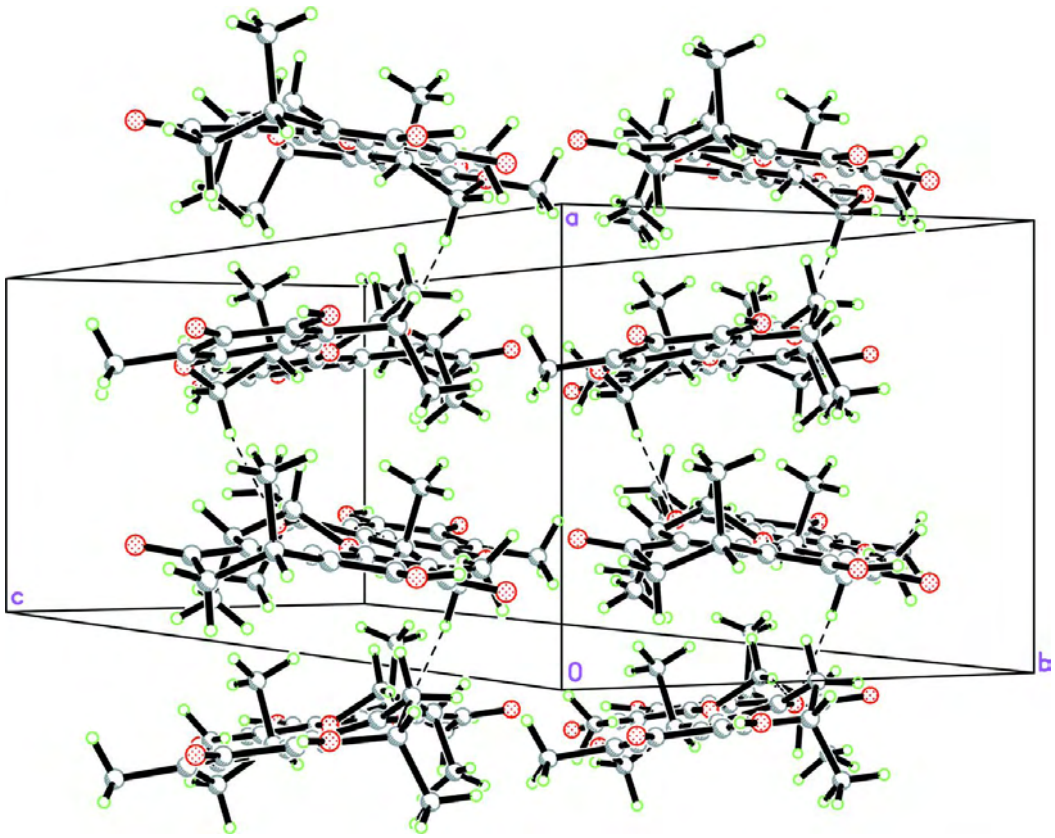


Fig. 2



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Gerontoxanthone I methanol solvate

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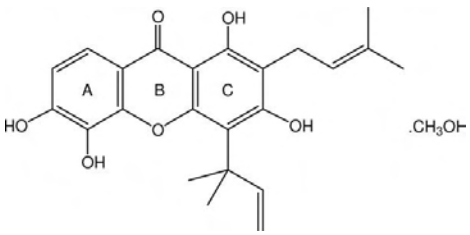
Key indicators: single-crystal X-ray study; T = 297 K; mean σ(C–C) = 0.002 Å; R factor = 0.048; wR factor = 0.141; data-to-parameter ratio = 13.0.

A methanol solvate of gerontoxanthone I [systematic name: 4-(1,1-dimethylprop-2-enyl)-1,3,5,6-tetrahydroxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one methanol solvate], $C_{23}H_{24}O_6\cdot CH_3OH$, is reported. Gerontoxanthone I was isolated from the roots of *Cratoxylum formosum* ssp. *pruniflorum*. The three rings in the structure are essentially coplanar. The 3-methylbut-2-enyl side chain is equatorially attached to the benzene ring, whereas the 1-methylbut-2-enyl substituent is bisectionally attached to the benzene ring. Intramolecular O—H···O hydrogen bonds generate S(5) and S(6) ring motifs. In the crystal structure, intermolecular O—H···O hydrogen bonds and C—H···O interactions connect the molecules of gerontoxanthone I into chains along the [100] direction. The crystal structure is stabilized by intra- and intermolecular O—H···O hydrogen bonds, weak C—H···O intra- and intermolecular interactions, and C—H···π interactions.

Related literature

For related literature on hydrogen-bond motifs, see: Bernstein *et al.* (1995). For related literature on values of bond lengths, see: Allen *et al.* (1987). For related structures, see, for example: Boonnak *et al.* (2005); Boonnak, Chantrapromma & Fun (2006); Boonnak, Karalai *et al.* (2006); Chantrapromma *et al.* (2005, 2006); Fun *et al.* (2006). For related literature on bioactivities of xanthones, see, for example: Aderson (1986); Boonnak, Karalai *et al.* (2006); Kitanov *et al.* (1988).



Experimental

Crystal data

$C_{23}H_{24}O_6\cdot CH_4O$
M_r = 428.46
Monoclinic, $P2_1/c$
a = 10.0411 (8) Å
b = 20.1500 (16) Å
c = 12.1807 (7) Å
β = 117.534 (5)°
V = 2185.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 297 (2) K
0.55 × 0.29 × 0.19 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.950, T_{max} = 0.982
11274 measured reflections
3834 independent reflections
3429 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.141
S = 1.05
3834 reflections
296 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C1–C6 benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O7^{i}	0.85 (3)	1.79 (3)	2.632 (2)	170 (3)
O2—H1O2···O1	0.82	2.29	2.7117 (19)	113
O2—H1O2···O4^{ii}	0.82	2.03	2.7995 (19)	155
O4—H1O4···O3	0.82	1.81	2.5505 (18)	149
O7—H1O7···O3	0.83 (2)	1.954 (19)	2.755 (2)	161 (4)
C18—H18*B*···O6	0.96	2.25	2.638 (2)	103
C19—H19*A*···O2^{iii}	0.97	2.54	3.378 (2)	145
C19—H19*A*···O4	0.97	2.50	2.8451 (19)	101
C22—H22*B*···*Cg*1^{iv}	0.96	3.10	3.705 (2)	123

Symmetry codes: (i) $x-1, y, z-1$; (ii) $x-1, y, z$; (iii) $x+1, y, z$; (iv) $x+1, -y-\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2198).

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References

Aderson, E. F. (1986). *Econ. Bot.* **40**, 442–450.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Boonnak, N., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst.* E**61**, o4376–o4378.
Boonnak, N., Chantrapromma, S. & Fun, H.-K. (2006). *Acta Cryst.* E**62**, o2034–o2036.
Boonnak, N., Karalai, C., Chantrapromma, S., Ponglimanont, C., Fun, H.-K., Kanjana-Opas, A. & Laphookhieo, S. (2006). *Tetrahedron*, **62**, 8850–8859.
Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Atta-ur-Rahman (2005). *Acta Cryst.* E**61**, o2136–o2138.
Chantrapromma, S., Boonnak, N., Fun, H.-K. & Karalai, C. (2006). *Acta Cryst.* E**62**, o360–o362.
Fun, H.-K., Ng, S.-L., Razak, I. A., Boonnak, N. & Chantrapromma, S. (2006). *Acta Cryst.* E**62**, o130–o132.
Kitanov, G. M., Assenov, I. & The Van, D. (1988). *Pharmazie*, **43**, H12–H13.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

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Gerontoxanthone I methanol solvate

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Comment

Some species of plants in the genus *Cratoxylum* have been used for the treatment of diuretic, stomachic, and tonic effects (Kitanov *et al.*, 1988), as well as for diarrhea and flatulence (Aderson, 1986). In our ongoing research of bioactive compounds from medicinal plants, the title compound, gerontoxanthone I, was isolated from a dichloromethane extract of the roots of *Cratoxylum formosum* ssp. *pruniflorum*, collected from Nhongkai Province in the northeasthern part of Thailand. As the title compound showed strong antibacterial and cytotoxic activities (Boonnak, Karalai, *et al.*, 2006), its X-ray crystal structure was determined in order to gain more information for further SAR (Structure and Activity Relationship) analysis. In our previous studies, we have reported the crystal structures of xanthone and anthraquinone compounds from the roots and barks of this plant (Boonnak *et al.*, 2005; Boonnak, Chantrapromma & Fun, 2006; Boonnak, Karalai *et al.*, 2006; Chantrapromma *et al.*, 2005; 2006; Fun *et al.*, 2006). We report here the crystal structure of the methanol solvate of gerontoxanthone I.

In the title compound (Fig. 1), the xanthone skeleton (rings A, B and C) is essentially planar, the maximum deviation from planarity being 0.043 (2) Å for atom C3. The O2—H2A···O1 and O4—H4A···O3 hydrogen bonds generate S(5) and S(6) ring motifs, respectively (Bernstein *et al.*, 1995) and help to stabilize the planarity of the structure. There are also weak intramolecular C—H···O interactions; C18—H18B···O6 and C19—H19A···O4 generate S(6) and S(5) ring motifs respectively (Table 1).

The orientation of the 3-methylbut-2-enyl [C19–C23] side chain with respect to the benzene ring *C* is indicated by the torsion angle of C13—C12—C19—C20 = −93.25 (17)°, [90.6 (2)° in the monohydrate compound (Boonnak, Chantrapromma & Fun, 2006)], indicating a (-)-synclinal conformation (Fig. 1). The 1,1-dimethylprop-2-enyl [C14–C18] substituent is attached to the benzene ring at C10 with the torsion angle C9—C10—C14—C15 of −137.06 (17)° [−52.6 (3)° in Boonnak, Chantrapromma & Fun, 2006], indicating a (-)-anticlinal conformation. Bond distances and angles in the title compound are in normal ranges (Allen *et al.*, 1987) and comparable to those reported in the gerontoxanthone I monohydrate (Boonnak, Chantrapromma & Fun, 2006) and other closely related structures (Boonnak *et al.*, 2005; Boonnak, Karalai *et al.*, 2006; Chantrapromma *et al.*, 2005; 2006; Fun *et al.*, 2006). The methanol solvent molecule is also involved in hydrogen bonds (Table 1).

In the crystal packing (Fig. 2), the gerontoxanthone I molecules are linked together into chains along the *a* axis by the intermolecular O2—H1O2···O4 hydrogen bond (symmetry code: −1 + *x*, *y*, *z*) and weak C19—H19A···O2 interaction (symmetry code: 1 + *x*, *y*, *z*) (Table 1) and are further linked to the methanol molecules by O1—H1O1···O7 (symmetry code: −1 + *x*, *y*, −1 + *z*) and O7—H1O7···O3 (symmetry code: 1 − *x*, 1 − *y*, 1 − *z*) hydrogen bonds (Table 1). This packing is different from the three dimensional crystal packing of the monohydrate compound (Boonnak, Chantrapromma & Fun, 2006). The crystal structure is stabilized by intra- and intermolecular O—H···O hydrogen bonds, weak C—H···O intra- and intramolecular interactions (Table 1). In addition, the molecular packing is further stabilized by a C—H···π interaction between one of the methyl groups of the 3-methylbut-2-enyl side chain and the centroid of the C1–C6 benzene ring (Cg_1) (Table 1).

Experimental

Air-dried roots of *Cratoxylum formosum* ssp. *pruniflorum* (5.30 kg) were ground and extracted with CH_2Cl_2 (2x20 l for 2x5 days) at room temperature. The residue obtained after evaporation of the solvent was subjected to quick column chromatography (QCC) on silica gel, using hexane as first eluent and then increasing polarity with EtOAc and acetone, to afford 8 fractions (F1–F8). Fraction F3 was separated by CC with 10% acetone–hexane to give the title compound. Yellow needle-shaped single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvents from a $CHCl_3/CH_3OH$ (7:3 *v*/*v*) solution after several days (*M*.p. 452–453 K).

Refinement

H atoms of the methanol molecule and the H atoms attached to O5 and O7 were located in a difference map. The remaining H atoms were placed in calculated positions with O—H distance of 0.82 Å and C—H distances in the range 0.93–0.97 Å. The U_{iso}(H) values were constrained to be $1.5U_{eq}$(carrier atom) for hydroxyl and methyl H atoms and $1.2U_{eq}$(carrier atom) for the remaining H atoms. Owing to a large fraction of weak data at higher angles, the 2θ maximum was limited to 50°. A rotating group model was used for the methyl groups.

Figures

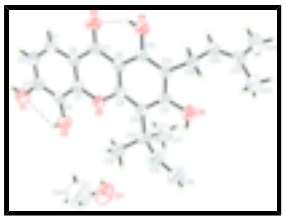


Fig. 1. The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering scheme. Hydrogen bonds are drawn as dashed lines.

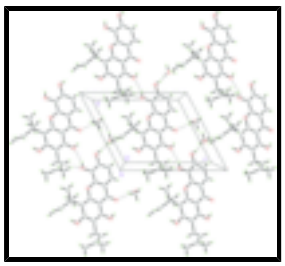


Fig. 2. The crystal packing of the title compound viewed along the *b* axis. Hydrogen bonds are drawn as dashed lines.

4-(1,1-dimethylprop-2-enyl)-1,3,5,6-tetrahydroxy-2-(3-methylbut-2-enyl)- 9*H*-xanthen-9-one methanol solvate

Crystal data

$C_{23}H_{24}O_6 \cdot CH_4O$	F_{000} = 912
M_r = 428.46	D_x = 1.302 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 452-453 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 10.0411 (8) Å	Cell parameters from 3834 reflections
b = 20.1500 (16) Å	θ = 2.3–25.0º

c = 12.1807 (7) Å	μ = 0.10 mm^{-1}
β = 117.534 (5)º	T = 297 (2) K
V = 2185.4 (3) Å^3	Needle, yellow
Z = 4	0.55 × 0.29 × 0.19 mm

Data collection

Siemens SMART CCD area-detector diffractometer	3834 independent reflections
Radiation source: fine-focus sealed tube	3429 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.018
Detector resolution: 8.33 pixels mm^{-1}	θ_{max} = 25.0º
T = 297(2) K	θ_{min} = 2.3º
ω scans	h = −11→11
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	k = −23→23
T_{min} = 0.950, T_{max} = 0.982	l = −7→14
11274 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.048	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.141	$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2 + 0.4621P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max} < 0.001$
3834 reflections	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
296 parameters	$\Delta\rho_{min}$ = −0.36 e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.16926 (13)	0.49056 (7)	0.21463 (12)	0.0639 (4)
H1O1	−0.222 (3)	0.5096 (14)	0.146 (3)	0.096*
O2	0.02703 (12)	0.42552 (7)	0.42133 (11)	0.0636 (4)
H1O2	−0.0623	0.4333	0.3972	0.095*
O3	0.48730 (12)	0.48078 (7)	0.25536 (11)	0.0570 (3)
O4	0.73927 (12)	0.42967 (6)	0.40403 (11)	0.0536 (3)
H1O4	0.6776	0.4502	0.3439	0.080*
O5	0.77233 (13)	0.30854 (7)	0.74175 (13)	0.0638 (4)
H5A	0.727 (3)	0.3031 (13)	0.789 (3)	0.100 (8)*
O6	0.30754 (11)	0.40989 (5)	0.47182 (9)	0.0449 (3)
O7	0.6422 (2)	0.53884 (12)	0.99678 (17)	0.0999 (6)
H1O7	0.595 (5)	0.525 (2)	0.9244 (17)	0.176 (18)*
C1	0.17612 (17)	0.50642 (8)	0.18518 (14)	0.0453 (4)
H1B	0.2105	0.5248	0.1329	0.054*
C2	0.02873 (17)	0.51419 (8)	0.15877 (14)	0.0472 (4)
H2A	−0.0361	0.5380	0.0889	0.057*
C3	−0.02461 (16)	0.48670 (8)	0.23586 (14)	0.0459 (4)
C4	0.07148 (16)	0.45290 (8)	0.34219 (14)	0.0434 (3)
C5	0.22065 (15)	0.44518 (7)	0.36748 (13)	0.0387 (3)
C6	0.27565 (16)	0.47090 (7)	0.29057 (13)	0.0395 (3)
C7	0.43129 (16)	0.45928 (7)	0.32226 (13)	0.0408 (3)
C8	0.51977 (15)	0.42168 (7)	0.43328 (13)	0.0385 (3)
C9	0.45495 (15)	0.39753 (7)	0.50637 (13)	0.0381 (3)
C10	0.53244 (16)	0.35998 (7)	0.61333 (14)	0.0419 (3)
C11	0.68362 (16)	0.34693 (7)	0.64363 (14)	0.0437 (4)
C12	0.75637 (15)	0.37038 (7)	0.57675 (14)	0.0407 (3)
C13	0.67322 (15)	0.40703 (7)	0.47158 (13)	0.0397 (3)
C14	0.46210 (18)	0.32904 (9)	0.69122 (16)	0.0530 (4)
C15	0.5654 (2)	0.33895 (13)	0.82710 (18)	0.0704 (6)
H15A	0.6029	0.3816	0.8514	0.084*
C16	0.6087 (3)	0.29370 (19)	0.9158 (3)	0.1141 (12)
H16A	0.5746	0.2502	0.8967	0.137*
H16B	0.6733	0.3054	0.9972	0.137*
C17	0.4329 (4)	0.25566 (12)	0.6555 (3)	0.1012 (9)
H17A	0.3985	0.2339	0.7078	0.152*
H17B	0.5242	0.2352	0.6656	0.152*
H17C	0.3577	0.2519	0.5706	0.152*
C18	0.3143 (2)	0.36078 (13)	0.67513 (19)	0.0753 (6)
H18A	0.2879	0.3426	0.7353	0.113*
H18B	0.2357	0.3516	0.5934	0.113*
H18C	0.3273	0.4079	0.6866	0.113*
C19	0.92107 (15)	0.35478 (7)	0.62011 (14)	0.0430 (4)
H19A	0.9650	0.3897	0.5924	0.052*
H19B	0.9730	0.3543	0.7099	0.052*
C20	0.94472 (16)	0.28944 (8)	0.57296 (15)	0.0456 (4)

H20A	0.9067	0.2860	0.4876	0.055*
C21	1.01301 (18)	0.23594 (8)	0.63764 (17)	0.0533 (4)
C22	1.0272 (3)	0.17404 (10)	0.5744 (2)	0.0791 (6)
H22A	0.9881	0.1823	0.4873	0.119*
H22B	0.9715	0.1387	0.5869	0.119*
H22C	1.1310	0.1616	0.6087	0.119*
C23	1.0826 (3)	0.23100 (11)	0.7756 (2)	0.0756 (6)
H23A	1.0799	0.2737	0.8096	0.113*
H23B	1.1850	0.2166	0.8077	0.113*
H23C	1.0277	0.1995	0.7981	0.113*
C24	0.6202 (7)	0.6016 (2)	0.9882 (4)	0.186 (2)
H24A	0.6362	0.6187	0.9217	0.223*
H24B	0.6890	0.6224	1.0644	0.223*
H24C	0.5190	0.6107	0.9722	0.223*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0327 (6)	0.0978 (10)	0.0607 (7)	0.0177 (6)	0.0213 (5)	0.0222 (7)
O2	0.0348 (6)	0.0987 (10)	0.0647 (8)	0.0163 (6)	0.0292 (6)	0.0302 (7)
O3	0.0383 (6)	0.0864 (9)	0.0505 (6)	0.0073 (5)	0.0240 (5)	0.0220 (6)
O4	0.0333 (5)	0.0794 (8)	0.0545 (7)	0.0092 (5)	0.0256 (5)	0.0206 (6)
O5	0.0421 (6)	0.0850 (9)	0.0676 (8)	0.0232 (6)	0.0282 (6)	0.0380 (7)
O6	0.0290 (5)	0.0620 (6)	0.0457 (6)	0.0085 (4)	0.0189 (5)	0.0151 (5)
O7	0.0808 (11)	0.1318 (17)	0.0661 (10)	0.0343 (11)	0.0160 (9)	0.0218 (10)
C1	0.0373 (8)	0.0569 (9)	0.0414 (8)	0.0024 (6)	0.0178 (6)	0.0067 (7)
C2	0.0375 (8)	0.0566 (9)	0.0416 (8)	0.0087 (6)	0.0133 (6)	0.0075 (7)
C3	0.0311 (7)	0.0554 (9)	0.0480 (8)	0.0067 (6)	0.0155 (6)	0.0009 (7)
C4	0.0327 (7)	0.0547 (9)	0.0456 (8)	0.0049 (6)	0.0204 (6)	0.0047 (6)
C5	0.0310 (7)	0.0444 (7)	0.0389 (7)	0.0032 (5)	0.0147 (6)	0.0023 (6)
C6	0.0323 (7)	0.0448 (7)	0.0401 (7)	0.0011 (6)	0.0156 (6)	0.0012 (6)
C7	0.0334 (7)	0.0508 (8)	0.0398 (7)	−0.0001 (6)	0.0183 (6)	0.0025 (6)
C8	0.0304 (7)	0.0445 (7)	0.0412 (8)	0.0006 (5)	0.0170 (6)	0.0015 (6)
C9	0.0271 (7)	0.0451 (8)	0.0427 (7)	0.0015 (5)	0.0166 (6)	0.0017 (6)
C10	0.0336 (7)	0.0479 (8)	0.0460 (8)	0.0021 (6)	0.0199 (6)	0.0076 (6)
C11	0.0353 (7)	0.0481 (8)	0.0469 (8)	0.0064 (6)	0.0184 (6)	0.0095 (6)
C12	0.0307 (7)	0.0447 (8)	0.0466 (8)	0.0029 (6)	0.0177 (6)	0.0024 (6)
C13	0.0311 (7)	0.0470 (8)	0.0442 (8)	−0.0004 (6)	0.0203 (6)	0.0012 (6)
C14	0.0413 (8)	0.0624 (10)	0.0590 (10)	0.0025 (7)	0.0262 (7)	0.0196 (8)
C15	0.0429 (9)	0.1156 (16)	0.0581 (10)	0.0101 (10)	0.0279 (8)	0.0288 (11)
C16	0.0689 (14)	0.195 (3)	0.0909 (17)	0.0497 (17)	0.0475 (13)	0.078 (2)
C17	0.125 (2)	0.0777 (15)	0.129 (2)	−0.0289 (14)	0.083 (2)	0.0060 (14)
C18	0.0423 (9)	0.1250 (18)	0.0686 (12)	0.0133 (10)	0.0340 (9)	0.0399 (12)
C19	0.0299 (7)	0.0508 (8)	0.0478 (8)	0.0040 (6)	0.0176 (6)	0.0065 (6)
C20	0.0319 (7)	0.0571 (9)	0.0484 (8)	0.0031 (6)	0.0191 (6)	0.0033 (7)
C21	0.0432 (8)	0.0526 (9)	0.0642 (10)	0.0049 (7)	0.0251 (8)	0.0062 (8)
C22	0.0806 (14)	0.0597 (11)	0.0947 (15)	0.0130 (10)	0.0385 (12)	−0.0020 (11)
C23	0.0811 (14)	0.0732 (13)	0.0703 (12)	0.0236 (11)	0.0330 (11)	0.0244 (10)

C24	0.280 (6)	0.137 (3)	0.115 (3)	0.066 (4)	0.070 (4)	−0.008 (3)

Geometric parameters (Å, °)

O1—C3	1.3547 (18)	C12—C19	1.5183 (19)
O1—H1O1	0.85 (3)	C14—C15	1.506 (3)
O2—C4	1.3529 (19)	C14—C17	1.531 (3)
O2—H1O2	0.8200	C14—C18	1.543 (2)
O3—C7	1.2617 (18)	C15—C16	1.324 (3)
O4—C13	1.3526 (17)	C15—H15A	0.9300
O4—H1O4	0.8200	C16—H16A	0.9300
O5—C11	1.3550 (18)	C16—H16B	0.9300
O5—H5A	0.89 (3)	C17—H17A	0.9600
O6—C9	1.3616 (17)	C17—H17B	0.9600
O6—C5	1.3627 (17)	C17—H17C	0.9600
O7—C24	1.279 (5)	C18—H18A	0.9600
O7—H1O7	0.831 (10)	C18—H18B	0.9600
C1—C2	1.370 (2)	C18—H18C	0.9600
C1—C6	1.405 (2)	C19—C20	1.499 (2)
C1—H1B	0.9300	C19—H19A	0.9700
C2—C3	1.393 (2)	C19—H19B	0.9700
C2—H2A	0.9300	C20—C21	1.324 (2)
C3—C4	1.385 (2)	C20—H20A	0.9300
C4—C5	1.391 (2)	C21—C23	1.496 (3)
C5—C6	1.389 (2)	C21—C22	1.507 (3)
C6—C7	1.445 (2)	C22—H22A	0.9600
C7—C8	1.443 (2)	C22—H22B	0.9600
C8—C9	1.410 (2)	C22—H22C	0.9600
C8—C13	1.4193 (19)	C23—H23A	0.9600
C9—C10	1.392 (2)	C23—H23B	0.9600
C10—C11	1.411 (2)	C23—H23C	0.9600
C10—C14	1.551 (2)	C24—H24A	0.9600
C11—C12	1.404 (2)	C24—H24B	0.9600
C12—C13	1.376 (2)	C24—H24C	0.9600
C3—O1—H1O1	109.7 (18)	C18—C14—C10	116.03 (13)
C4—O2—H1O2	109.5	C16—C15—C14	127.2 (3)
C13—O4—H1O4	109.5	C16—C15—H15A	116.4
C11—O5—H5A	108.6 (17)	C14—C15—H15A	116.4
C9—O6—C5	121.30 (11)	C15—C16—H16A	120.0
C24—O7—H1O7	104 (3)	C15—C16—H16B	120.0
C2—C1—C6	120.51 (14)	H16A—C16—H16B	120.0
C2—C1—H1B	119.7	C14—C17—H17A	109.5
C6—C1—H1B	119.7	C14—C17—H17B	109.5
C1—C2—C3	120.42 (14)	H17A—C17—H17B	109.5
C1—C2—H2A	119.8	C14—C17—H17C	109.5
C3—C2—H2A	119.8	H17A—C17—H17C	109.5
O1—C3—C4	115.40 (14)	H17B—C17—H17C	109.5
O1—C3—C2	124.11 (14)	C14—C18—H18A	109.5
C4—C3—C2	120.49 (14)	C14—C18—H18B	109.5

O2—C4—C3	123.39 (13)	H18A—C18—H18B	109.5
O2—C4—C5	118.20 (13)	C14—C18—H18C	109.5
C3—C4—C5	118.39 (14)	H18A—C18—H18C	109.5
O6—C5—C6	122.75 (12)	H18B—C18—H18C	109.5
O6—C5—C4	115.11 (12)	C20—C19—C12	112.88 (12)
C6—C5—C4	122.13 (13)	C20—C19—H19A	109.0
C5—C6—C1	118.02 (13)	C12—C19—H19A	109.0
C5—C6—C7	118.51 (13)	C20—C19—H19B	109.0
C1—C6—C7	123.47 (13)	C12—C19—H19B	109.0
O3—C7—C8	121.37 (13)	H19A—C19—H19B	107.8
O3—C7—C6	121.45 (13)	C21—C20—C19	128.13 (15)
C8—C7—C6	117.18 (12)	C21—C20—H20A	115.9
C9—C8—C13	117.94 (13)	C19—C20—H20A	115.9
C9—C8—C7	120.60 (13)	C20—C21—C23	124.55 (17)
C13—C8—C7	121.46 (13)	C20—C21—C22	121.00 (17)
O6—C9—C10	116.49 (12)	C23—C21—C22	114.45 (16)
O6—C9—C8	119.66 (12)	C21—C22—H22A	109.5
C10—C9—C8	123.84 (13)	C21—C22—H22B	109.5
C9—C10—C11	114.48 (13)	H22A—C22—H22B	109.5
C9—C10—C14	125.11 (13)	C21—C22—H22C	109.5
C11—C10—C14	120.26 (13)	H22A—C22—H22C	109.5
O5—C11—C12	113.44 (13)	H22B—C22—H22C	109.5
O5—C11—C10	121.74 (13)	C21—C23—H23A	109.5
C12—C11—C10	124.81 (13)	C21—C23—H23B	109.5
C13—C12—C11	117.79 (12)	H23A—C23—H23B	109.5
C13—C12—C19	121.96 (13)	C21—C23—H23C	109.5
C11—C12—C19	120.25 (13)	H23A—C23—H23C	109.5
O4—C13—C12	119.35 (12)	H23B—C23—H23C	109.5
O4—C13—C8	119.54 (13)	O7—C24—H24A	109.5
C12—C13—C8	121.11 (13)	O7—C24—H24B	109.5
C15—C14—C17	112.63 (19)	H24A—C24—H24B	109.5
C15—C14—C18	102.58 (16)	O7—C24—H24C	109.5
C17—C14—C18	108.52 (18)	H24A—C24—H24C	109.5
C15—C14—C10	110.00 (14)	H24B—C24—H24C	109.5
C17—C14—C10	107.19 (16)		
C6—C1—C2—C3	−0.3 (2)	C8—C9—C10—C11	−0.6 (2)
C1—C2—C3—O1	−178.16 (15)	O6—C9—C10—C14	2.9 (2)
C1—C2—C3—C4	2.0 (2)	C8—C9—C10—C14	−176.02 (14)
O1—C3—C4—O2	−0.4 (2)	C9—C10—C11—O5	−176.97 (14)
C2—C3—C4—O2	179.48 (15)	C14—C10—C11—O5	−1.3 (2)
O1—C3—C4—C5	177.91 (14)	C9—C10—C11—C12	1.9 (2)
C2—C3—C4—C5	−2.2 (2)	C14—C10—C11—C12	177.57 (15)
C9—O6—C5—C6	−0.3 (2)	O5—C11—C12—C13	176.72 (14)
C9—O6—C5—C4	178.79 (13)	C10—C11—C12—C13	−2.2 (2)
O2—C4—C5—O6	0.1 (2)	O5—C11—C12—C19	−2.8 (2)
C3—C4—C5—O6	−178.31 (13)	C10—C11—C12—C19	178.28 (14)
O2—C4—C5—C6	179.21 (14)	C11—C12—C13—O4	−179.14 (13)
C3—C4—C5—C6	0.8 (2)	C19—C12—C13—O4	0.4 (2)
O6—C5—C6—C1	179.88 (13)	C11—C12—C13—C8	1.2 (2)

C4—C5—C6—C1	0.8 (2)	C19—C12—C13—C8	−179.33 (13)
O6—C5—C6—C7	0.5 (2)	C9—C8—C13—O4	−179.69 (13)
C4—C5—C6—C7	−178.59 (13)	C7—C8—C13—O4	1.2 (2)
C2—C1—C6—C5	−1.1 (2)	C9—C8—C13—C12	0.0 (2)
C2—C1—C6—C7	178.30 (14)	C7—C8—C13—C12	−179.13 (14)
C5—C6—C7—O3	179.25 (14)	C9—C10—C14—C15	−137.06 (17)
C1—C6—C7—O3	−0.1 (2)	C11—C10—C14—C15	47.7 (2)
C5—C6—C7—C8	−0.4 (2)	C9—C10—C14—C17	100.2 (2)
C1—C6—C7—C8	−179.77 (14)	C11—C10—C14—C17	−75.0 (2)
O3—C7—C8—C9	−179.44 (14)	C9—C10—C14—C18	−21.2 (3)
C6—C7—C8—C9	0.2 (2)	C11—C10—C14—C18	163.56 (17)
O3—C7—C8—C13	−0.3 (2)	C17—C14—C15—C16	−12.2 (3)
C6—C7—C8—C13	179.32 (13)	C18—C14—C15—C16	104.3 (2)
C5—O6—C9—C10	−178.87 (13)	C10—C14—C15—C16	−131.7 (2)
C5—O6—C9—C8	0.1 (2)	C13—C12—C19—C20	−93.25 (17)
C13—C8—C9—O6	−179.22 (12)	C11—C12—C19—C20	86.25 (17)
C7—C8—C9—O6	−0.1 (2)	C12—C19—C20—C21	−115.91 (17)
C13—C8—C9—C10	−0.3 (2)	C19—C20—C21—C23	−0.3 (3)
C7—C8—C9—C10	178.84 (14)	C19—C20—C21—C22	−179.77 (16)
O6—C9—C10—C11	178.37 (13)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···O7^{i}	0.85 (3)	1.79 (3)	2.632 (2)	170 (3)
O2—H1O2···O1	0.82	2.29	2.7117 (19)	113
O2—H1O2···O4^{ii}	0.82	2.03	2.7995 (19)	155
O4—H1O4···O3	0.82	1.81	2.5505 (18)	149
O7—H1O7···O3i	0.83 (2)	1.954 (19)	2.755 (2)	161 (4)
C18—H18B···O6	0.96	2.25	2.638 (2)	103
C19—H19A···O2^{iii}	0.97	2.54	3.378 (2)	145
C19—H19A···O4	0.97	2.50	2.8451 (19)	101
C22—H22B···Cg1^{iv}	0.96	3.10	3.705 (2)	123

Symmetry codes: (i) *x*−1, *y*, *z*−1; (ii) *x*−1, *y*, *z*; i; (iii) *x*+1, *y*, *z*; (iv) *x*+1, −*y*−1/2, *z*−1/2.

Fig. 1

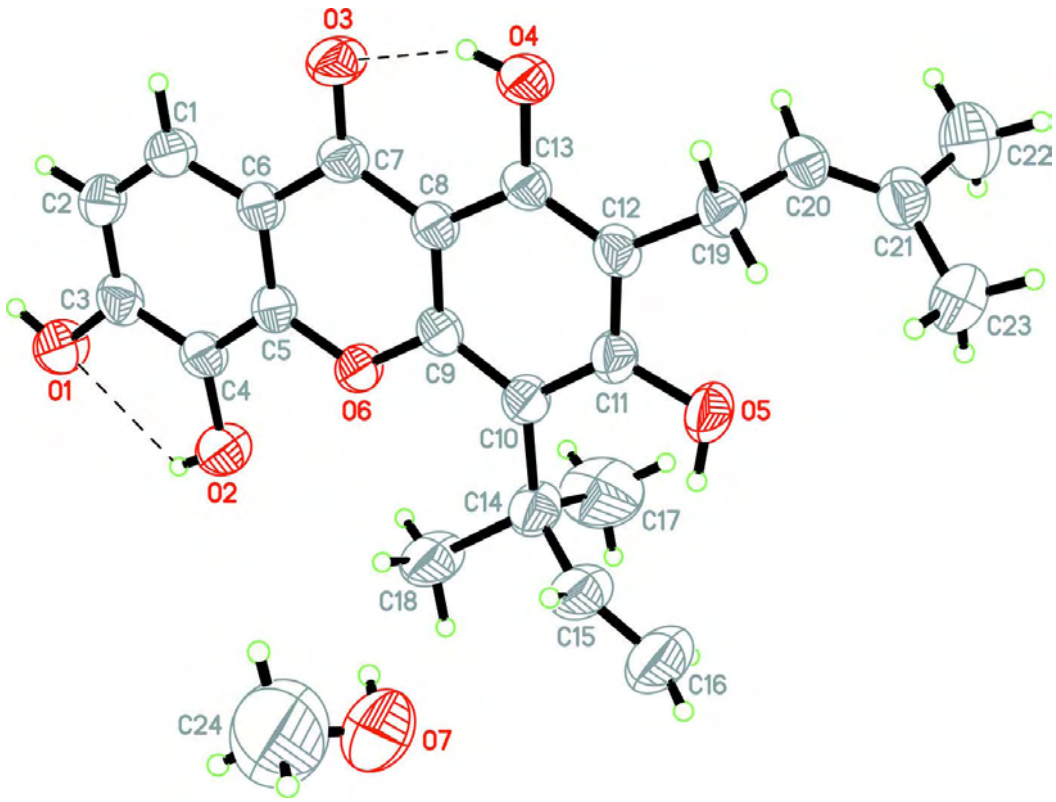
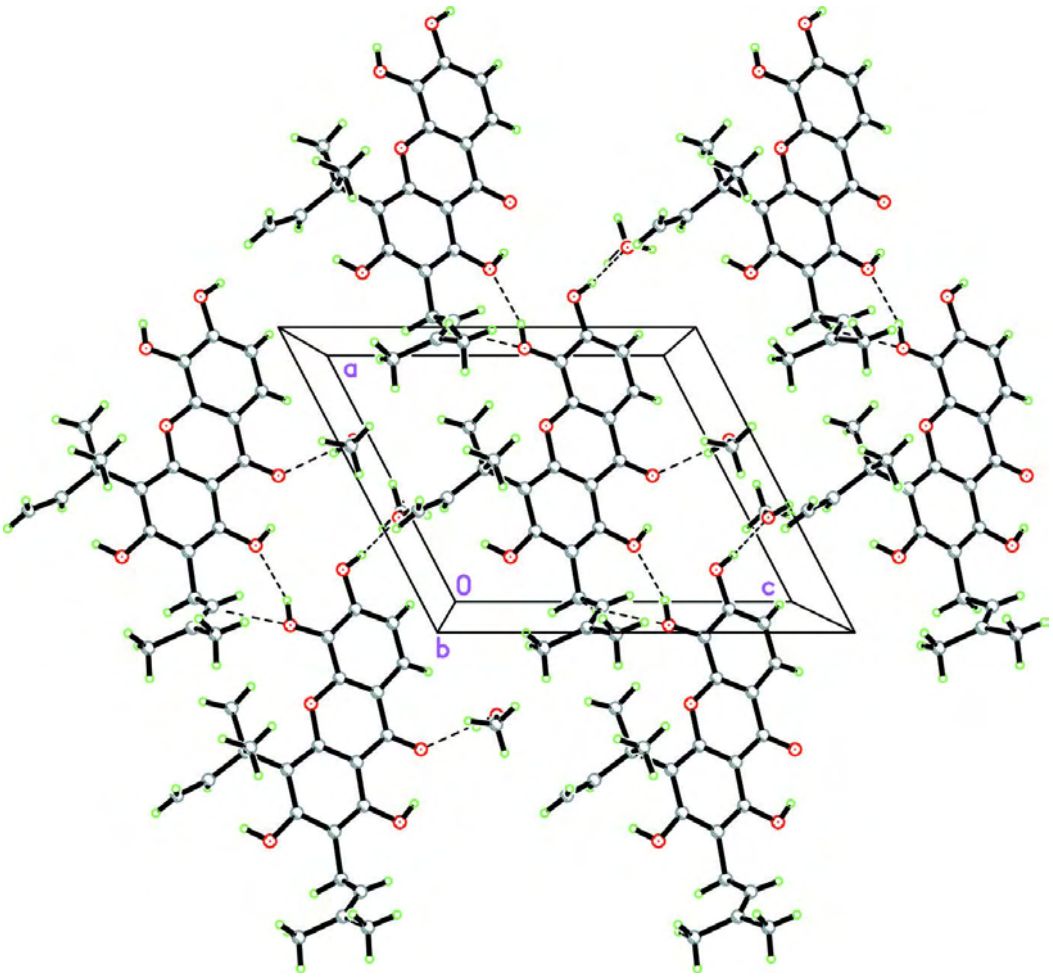


Fig. 2



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1,5,8-Trimethyl-1,2-dihydronaphtho[2,1-*b*]furan-6,7-dione

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1,5,8-Trimethyl-1,2-dihydronaphtho-[2,1-*b*]furan-6,7-dione

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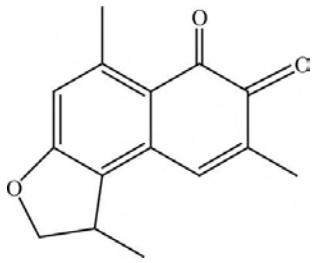
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.010 Å; R factor = 0.088; wR factor = 0.259; data-to-parameter ratio = 7.5.

The title sesquiterpene *ortho*-naphthoquinone compound, $C_{15}H_{14}O_3$, known as Mansonone D, was isolated from *Thespesia populnea*. There are two independent molecules in the asymmetric unit. In both molecules the dihydrofuran ring adopts an envelope conformation. The molecules are connected into sheets parallel to the *bc* plane by weak C—H···O interactions. The sheets are stacked along the *a* axis, with molecules of adjacent sheets linked by C—H···O hydrogen bonds, C—H···π and π–π [centroid–centroid distance = 3.579 (4) Å] interactions.

Related literature

For bond-length data, see: Allen *et al.* (1987). For ring puckering parameters, see: Cremer & Pople (1975). For related quinone structures, see: Chantrapromma *et al.* (2007); Fun *et al.* (2007); Milbrodt *et al.* (1997); Puckhaber & Stipanovic (2004).



Experimental

Crystal data

$C_{15}H_{14}O_3$
M_r = 242.26
Orthorhombic, $P2_12_12_1$
a = 7.1218 (2) Å
b = 10.2061 (2) Å
c = 32.9005 (7) Å
V = 2391.4 (1) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100.0 (1) K
0.37 × 0.16 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.966, T_{max} = 0.989
23139 measured reflections
2445 independent reflections
1873 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.088
$wR(F^2)$ = 0.259
S = 1.07
2445 reflections
325 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C3*A*/C4*A*/C9*A*–C12*A* ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1*B*—H1*BA*···O3*B*^{i}	0.97	2.47	3.413 (10)	164
C11*B*—H11*B*···O1*A*^{ii}	0.93	2.43	3.349 (8)	169
C13*B*—H13*E*···O2*A*^{iii}	0.96	2.42	3.204 (10)	138
C13*B*—H13*F*···O2*B*^{i}	0.96	2.54	3.500 (9)	174
C15*B*—H15*D*···*Cg*1^{iii}	0.96	2.87	3.539 (9)	127
C15*B*—H15*E*···*Cg*1^{iv}	0.96	2.86	3.632 (9)	138

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+\frac{3}{2}, -y+1, z-\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z$; (iv) $-x-1, y+\frac{3}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2508).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
Bruker (2005). *APEX2* (Version 1.27), *SAINT* (Version 7.12a) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
Chantrapromma, S., Boonsri, S., Fun, H.-K. & Karalai, C. (2007). *Acta Cryst.* E**63**, o2749–o2750.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Fun, H.-K., Boonsri, S., Chantrapromma, S., Boonnak, N. & Karalai, C. (2007). *Acta Cryst.* E**63**, o2127–o2129.
Milbrodt, M., Konig, W. A. & Hausen, B. M. (1997). *Phytochemistry*, **45**, 1523–1525.
Puckhaber, L. S. & Stipanovic, R. D. (2004). *J. Nat. Prod.* **67**, 1571–1573.
Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

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supplementary materials

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1,5,8-Trimethyl-1,2-dihydronaphtho[2,1-*b*]furan-6,7-dione

S. Boonsri, S. Chantrapromma, H.-K. Fun and C. Karalai

Comment

We have been investigating the chemical constituents of *Thespesia populnea*, or Po-ta-lae in Thai, a genus of *malvaceae* with basically tropical and subtropical worldwide distribution. The heartwood of this plant is a rich source of sesquiterpenoid quinines (Milbrodt *et al.*, 1997). We have previously reported the crystal structures of sesquiterpenoid quinone compounds from this plant namely 3,6,9-trimethyl-2,3-dihydrobenzo[*de*]-chromene-7,8-dione (Fun *et al.*, 2007) and 7-hydroxy-3,6,9-trimethyl-2,3,5,6-tetrahydronaphtho [1,8 − *b*,*c*]pyran-4,8-dione (Chantrapromma *et al.*, 2007). We report the crystal structure of the title compound known as Mansonone D (Puckhaber & Stipanovic, 2004) which was isolated from the heartwood of *T. populnea*, collected from the Suratthani province in the southern part of Thailand.

The title compound crystallizes with two molecules (*A* and *B*) per asymmetric unit (Fig. 1). The bond lengths and angles in the title compound are within normal ranges (Allen *et al.*, 1987) and comparable with closely related structures (Chantrapromma *et al.*, 2007; Fun *et al.*, 2007). The naphthoquinone ring system (C3–C12) is essentially planar, with atom C7A deviating by a maximum of 0.059 (7) Å in molecule *A* and atom C10B deviating by a maximum of 0.056 (7) Å in molecule *B*. The furan ring adopts an envelope conformation in both molecules, with atom C1 displaced from the C2/C3/C12/O1 plane by −0.096 (11) and −0.138 (9) Å, respectively, for molecules *A* and *B*. The puckering parameters (Cremer & Pople, 1975) are Q = 0.154 (7) Å and θ = 42 (3)° for molecule *A* and Q = 0.218 (7) Å and θ = 42.5 (19)° for molecule *B*. The methyl group at atom C2 is axially attached, as indicated by the torsion angles C13–C2–C3–C12 of 109.8 (7)° and 103.4 (7)°, respectively, in molecules *A* and *B*.

In the crystal structure (Fig. 2), the molecules are connected into sheets parallel to the *bc* plane by weak C—H···O interactions (Table 1), and the sheets are stacked along the *a* axis. In addition to C—H···O hydrogen bonds, C—H···π interactions (Table 1) involving the C3A/C4A/C9A—C12A ring (centroid *Cg*1), and π-π interactions involving the C4A—C9A and C3B/C4B/C9B—C12B rings [centroid-centroid distance is 3.579 (4) Å] are observed between the sheets.

Experimental

Air-dried heartwood of *T. populnea* was extracted with CH_2Cl_2 over a period of 5 d at room temperature. The CH_2Cl_2 extract was evaporated under reduced pressure to furnish a orange-brown residue (37.5 g) which was subjected to quick column chromatography on silica gel, eluting with CH_2Cl_2 and separated into 8 fractions (F1—F8). Fraction F7 was purified by quick column chromatography with a gradient of acetone-CH_2Cl_2 to give the title compound. Single crystals of the title compound were obtained by recrystalization from MeOH-CH_2Cl_2 (3:7 *v*/*v*) after several days (m.p. 432–434 K).

Refinement

H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. A total of 1761 Friedel pairs were merged before final

refinement as there is no large anomalous dispersion for the determination of the absolute configuration. Large anisotropic displacement parameters and difference density features indicate possible disorder in both independent molecules, but no suitable disorder model was found.

Figures

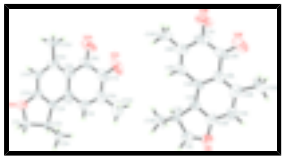


Fig. 1. The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering scheme.

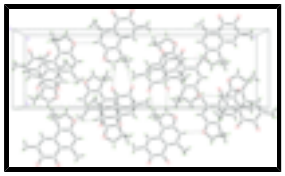


Fig. 2. The crystal packing of the title compound, viewed approximately along the *a* axis. Hydrogen bonds are shown as dashed lines.

1,5,8-Trimethyl-1,2-dihydronaphtho[2,1-*b*]furan-6,7-dione

Crystal data

$C_{15}H_{14}O_3$	D_x = 1.346 Mg m^{-3}
M_r = 242.26	Melting point: 432-434 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 2445 reflections
a = 7.1218 (2) Å	θ = 1.2–25.0º
b = 10.2061 (2) Å	μ = 0.09 mm^{-1}
c = 32.9005 (7) Å	T = 100.0 (1) K
V = 2391.4 (1) Å^3	Plate, colourless
Z = 8	0.37 × 0.16 × 0.12 mm
F_{000} = 1024	

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	2445 independent reflections
Radiation source: fine-focus sealed tube	1873 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.059
Detector resolution: 8.33 pixels mm^{-1}	θ_{max} = 25.0º
T = 100.0(1) K	θ_{min} = 1.2º
ω scans	h = −8→8
Absorption correction: multi-scan (SADABS; Bruker, 2005)	k = −11→12
T_{min} = 0.966, T_{max} = 0.989	l = −39→36
23139 measured reflections	

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.088$

$wR(F^2) = 0.259$

$S = 1.07$

2445 reflections

325 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1374P)^2 + 3.3697P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.68$ e Å^{-3}

$\Delta\rho_{min} = -0.22$ e Å^{-3}

Extinction correction: none

Special details

Experimental. The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.7860 (8)	0.1631 (5)	0.23458 (13)	0.0521 (13)
O2A	0.7413 (9)	0.7367 (6)	0.0870 (2)	0.082 (2)
O3A	0.6978 (10)	0.7477 (5)	0.1677 (2)	0.082 (2)
C1A	0.8304 (15)	0.0739 (8)	0.2016 (2)	0.067 (3)
H1AA	0.7599	−0.0068	0.2047	0.080*
H1AB	0.9632	0.0528	0.2020	0.080*
C2A	0.7783 (11)	0.1413 (6)	0.16119 (19)	0.0441 (17)
H2AA	0.8829	0.1344	0.1420	0.053*
C3A	0.7582 (10)	0.2811 (6)	0.17544 (18)	0.0384 (15)
C4A	0.7458 (10)	0.3985 (6)	0.15415 (19)	0.0374 (15)
C5A	0.7488 (10)	0.3972 (7)	0.1104 (2)	0.0480 (18)
H5AA	0.7557	0.3161	0.0976	0.058*
C6A	0.7425 (10)	0.5055 (8)	0.0863 (2)	0.0519 (19)
C7A	0.7335 (10)	0.6332 (8)	0.1061 (3)	0.058 (2)
C8A	0.7167 (11)	0.6400 (7)	0.1528 (3)	0.0567 (15)

C9A	0.7284 (9)	0.5177 (6)	0.1763 (2)	0.0428 (16)
C10A	0.7230 (10)	0.5159 (7)	0.2191 (2)	0.0491 (19)
C11A	0.7399 (10)	0.3971 (7)	0.2398 (2)	0.0479 (18)
H11A	0.7368	0.3942	0.2681	0.057*
C12A	0.7613 (11)	0.2844 (6)	0.2174 (2)	0.0439 (17)
C13A	0.6035 (12)	0.0846 (7)	0.1427 (2)	0.052 (2)
H13A	0.5734	0.1313	0.1182	0.078*
H13B	0.5015	0.0923	0.1616	0.078*
H13C	0.6240	−0.0062	0.1364	0.078*
C14A	0.7541 (12)	0.5032 (9)	0.0414 (2)	0.073 (3)
H14A	0.7541	0.4141	0.0321	0.109*
H14B	0.8677	0.5456	0.0329	0.109*
H14C	0.6480	0.5485	0.0302	0.109*
C15A	0.7062 (13)	0.6392 (8)	0.2456 (3)	0.068 (2)
H15A	0.7065	0.6145	0.2738	0.102*
H15B	0.5911	0.6838	0.2394	0.102*
H15C	0.8104	0.6963	0.2403	0.102*
O1B	0.6595 (8)	0.6338 (5)	−0.14493 (14)	0.0526 (14)
O2B	0.8305 (13)	1.2728 (5)	−0.0344 (2)	0.097 (3)
O3B	0.7238 (10)	1.2479 (5)	−0.1135 (2)	0.0796 (19)
C1B	0.6116 (12)	0.5724 (8)	−0.1074 (2)	0.061 (2)
H1BA	0.6657	0.4853	−0.1063	0.074*
H1BB	0.4762	0.5642	−0.1052	0.074*
C2B	0.6862 (10)	0.6546 (6)	−0.0722 (2)	0.0433 (17)
H2BA	0.5956	0.6582	−0.0498	0.052*
C3B	0.7019 (10)	0.7842 (6)	−0.0932 (2)	0.0398 (16)
C4B	0.7307 (10)	0.9114 (6)	−0.0810 (2)	0.0410 (16)
C5B	0.7446 (9)	0.9358 (7)	−0.0353 (2)	0.0435 (16)
H5BA	0.7309	0.8647	−0.0179	0.052*
C6B	0.7744 (10)	1.0504 (7)	−0.0194 (2)	0.0516 (19)
C7B	0.7858 (13)	1.1676 (8)	−0.0467 (3)	0.067 (2)
C8B	0.7482 (10)	1.1473 (7)	−0.0909 (3)	0.0567 (15)
C9B	0.7388 (10)	1.0164 (7)	−0.1085 (2)	0.0464 (17)
C10B	0.7339 (10)	0.9925 (8)	−0.1500 (2)	0.0517 (19)
C11B	0.7083 (11)	0.8608 (8)	−0.1639 (2)	0.0528 (19)
H11B	0.7048	0.8419	−0.1915	0.063*
C12B	0.6885 (10)	0.7611 (7)	−0.1350 (2)	0.0478 (18)
C13B	0.8766 (11)	0.6060 (7)	−0.0575 (2)	0.054 (2)
H13D	0.9099	0.6504	−0.0328	0.081*
H13E	0.9697	0.6235	−0.0779	0.081*
H13F	0.8705	0.5134	−0.0526	0.081*
C14B	0.7923 (13)	1.0738 (8)	0.0239 (2)	0.064 (2)
H14D	0.7974	0.9915	0.0380	0.097*
H14E	0.6861	1.1232	0.0333	0.097*
H14F	0.9054	1.1222	0.0291	0.097*
C15B	0.7494 (12)	1.0943 (7)	−0.1844 (3)	0.065 (2)
H15D	0.8544	1.1509	−0.1793	0.098*
H15E	0.6363	1.1454	−0.1854	0.098*
H15F	0.7670	1.0501	−0.2098	0.098*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.064 (3)	0.049 (3)	0.044 (3)	0.005 (3)	−0.012 (3)	−0.004 (2)
O2A	0.046 (3)	0.062 (4)	0.137 (6)	0.000 (3)	−0.012 (4)	0.048 (4)
O3A	0.075 (4)	0.035 (3)	0.135 (5)	0.001 (3)	0.000 (4)	−0.006 (3)
C1A	0.091 (7)	0.050 (4)	0.060 (5)	0.022 (5)	−0.028 (5)	−0.022 (4)
C2A	0.051 (4)	0.041 (4)	0.041 (3)	0.015 (4)	−0.007 (3)	−0.014 (3)
C3A	0.033 (3)	0.045 (4)	0.037 (3)	0.000 (3)	0.002 (3)	−0.012 (3)
C4A	0.032 (4)	0.034 (3)	0.046 (4)	0.001 (3)	0.005 (3)	−0.006 (3)
C5A	0.029 (3)	0.058 (5)	0.056 (4)	0.003 (3)	0.006 (4)	−0.014 (4)
C6A	0.026 (3)	0.064 (5)	0.065 (5)	0.003 (4)	0.010 (4)	0.013 (4)
C7A	0.022 (3)	0.055 (5)	0.098 (6)	0.001 (4)	−0.003 (4)	0.012 (5)
C8A	0.034 (3)	0.031 (3)	0.106 (5)	0.003 (2)	0.007 (3)	0.000 (3)
C9A	0.028 (3)	0.037 (3)	0.063 (5)	0.000 (3)	0.014 (3)	−0.010 (3)
C10A	0.029 (3)	0.044 (4)	0.074 (5)	−0.005 (3)	0.012 (4)	−0.023 (4)
C11A	0.039 (4)	0.053 (4)	0.052 (4)	−0.004 (3)	0.005 (4)	−0.020 (3)
C12A	0.044 (4)	0.041 (4)	0.047 (4)	−0.001 (4)	−0.004 (4)	−0.013 (3)
C13A	0.069 (5)	0.040 (4)	0.047 (4)	0.003 (4)	−0.016 (4)	−0.010 (3)
C14A	0.041 (4)	0.103 (7)	0.073 (5)	−0.012 (5)	0.002 (4)	0.028 (5)
C15A	0.063 (5)	0.053 (5)	0.089 (6)	0.001 (4)	0.009 (5)	−0.035 (4)
O1B	0.064 (3)	0.046 (3)	0.048 (3)	−0.007 (3)	−0.005 (3)	−0.009 (2)
O2B	0.133 (7)	0.038 (3)	0.120 (5)	−0.021 (4)	0.019 (5)	−0.004 (3)
O3B	0.072 (4)	0.044 (3)	0.123 (5)	−0.001 (3)	0.012 (4)	0.012 (3)
C1B	0.060 (5)	0.052 (5)	0.072 (5)	−0.003 (4)	0.004 (5)	−0.006 (4)
C2B	0.044 (4)	0.037 (4)	0.048 (4)	−0.009 (3)	0.005 (3)	−0.002 (3)
C3B	0.041 (4)	0.030 (3)	0.049 (4)	−0.004 (3)	0.011 (3)	0.000 (3)
C4B	0.031 (3)	0.029 (3)	0.063 (4)	0.007 (3)	−0.016 (3)	0.003 (3)
C5B	0.022 (3)	0.041 (4)	0.068 (4)	−0.004 (3)	0.002 (3)	0.012 (3)
C6B	0.033 (4)	0.047 (4)	0.075 (5)	−0.001 (3)	0.005 (4)	−0.005 (4)
C7B	0.062 (5)	0.047 (5)	0.093 (6)	−0.024 (4)	0.023 (5)	−0.020 (4)
C8B	0.034 (3)	0.031 (3)	0.106 (5)	0.003 (2)	0.007 (3)	0.000 (3)
C9B	0.032 (3)	0.048 (4)	0.059 (4)	0.004 (3)	0.006 (4)	0.008 (3)
C10B	0.023 (3)	0.075 (5)	0.058 (4)	0.004 (4)	0.002 (3)	−0.004 (4)
C11B	0.048 (4)	0.062 (5)	0.048 (4)	−0.006 (4)	−0.008 (4)	0.006 (4)
C12B	0.038 (4)	0.054 (4)	0.051 (4)	−0.001 (4)	0.001 (3)	0.000 (4)
C13B	0.053 (4)	0.043 (4)	0.067 (5)	0.007 (4)	0.003 (4)	0.024 (4)
C14B	0.063 (5)	0.046 (4)	0.084 (6)	−0.007 (4)	0.018 (5)	−0.018 (4)
C15B	0.047 (4)	0.050 (4)	0.099 (6)	0.008 (4)	0.006 (5)	0.035 (4)

Geometric parameters (Å, °)

O1A—C12A	1.372 (8)	O1B—C12B	1.355 (9)
O1A—C1A	1.451 (9)	O1B—C1B	1.427 (9)
O2A—C7A	1.231 (9)	O2B—C7B	1.191 (9)
O3A—C8A	1.211 (9)	O3B—C8B	1.280 (9)
C1A—C2A	1.543 (10)	C1B—C2B	1.525 (10)
C1A—H1AA	0.97	C1B—H1BA	0.97

C1A—H1AB	0.97	C1B—H1BB	0.97
C2A—C13A	1.501 (10)	C2B—C3B	1.497 (9)
C2A—C3A	1.508 (9)	C2B—C13B	1.522 (10)
C2A—H2AA	0.98	C2B—H2BA	0.98
C3A—C12A	1.380 (9)	C3B—C4B	1.374 (9)
C3A—C4A	1.390 (9)	C3B—C12B	1.400 (10)
C4A—C9A	1.424 (9)	C4B—C9B	1.406 (9)
C4A—C5A	1.441 (9)	C4B—C5B	1.525 (10)
C5A—C6A	1.360 (10)	C5B—C6B	1.299 (10)
C5A—H5AA	0.93	C5B—H5BA	0.93
C6A—C7A	1.458 (11)	C6B—C14B	1.449 (11)
C6A—C14A	1.479 (11)	C6B—C7B	1.498 (11)
C7A—C8A	1.543 (12)	C7B—C8B	1.492 (12)
C8A—C9A	1.471 (10)	C8B—C9B	1.459 (10)
C9A—C10A	1.410 (10)	C9B—C10B	1.386 (10)
C10A—C11A	1.396 (10)	C10B—C11B	1.431 (11)
C10A—C15A	1.535 (9)	C10B—C15B	1.540 (10)
C11A—C12A	1.376 (9)	C11B—C12B	1.400 (10)
C11A—H11A	0.93	C11B—H11B	0.93
C13A—H13A	0.96	C13B—H13D	0.96
C13A—H13B	0.96	C13B—H13E	0.96
C13A—H13C	0.96	C13B—H13F	0.96
C14A—H14A	0.96	C14B—H14D	0.96
C14A—H14B	0.96	C14B—H14E	0.96
C14A—H14C	0.96	C14B—H14F	0.96
C15A—H15A	0.96	C15B—H15D	0.96
C15A—H15B	0.96	C15B—H15E	0.96
C15A—H15C	0.96	C15B—H15F	0.96
C12A—O1A—C1A	106.6 (5)	C12B—O1B—C1B	104.4 (5)
O1A—C1A—C2A	108.2 (6)	O1B—C1B—C2B	109.4 (6)
O1A—C1A—H1AA	110.1	O1B—C1B—H1BA	109.8
C2A—C1A—H1AA	110.1	C2B—C1B—H1BA	109.8
O1A—C1A—H1AB	110.1	O1B—C1B—H1BB	109.8
C2A—C1A—H1AB	110.1	C2B—C1B—H1BB	109.8
H1AA—C1A—H1AB	108.4	H1BA—C1B—H1BB	108.2
C13A—C2A—C3A	114.3 (6)	C3B—C2B—C13B	111.6 (6)
C13A—C2A—C1A	112.1 (7)	C3B—C2B—C1B	99.3 (6)
C3A—C2A—C1A	100.2 (5)	C13B—C2B—C1B	111.8 (7)
C13A—C2A—H2AA	109.9	C3B—C2B—H2BA	111.2
C3A—C2A—H2AA	109.9	C13B—C2B—H2BA	111.2
C1A—C2A—H2AA	109.9	C1B—C2B—H2BA	111.2
C12A—C3A—C4A	118.9 (6)	C4B—C3B—C12B	117.2 (6)
C12A—C3A—C2A	109.4 (6)	C4B—C3B—C2B	135.3 (6)
C4A—C3A—C2A	131.6 (5)	C12B—C3B—C2B	107.5 (6)
C3A—C4A—C9A	119.0 (6)	C3B—C4B—C9B	122.5 (7)
C3A—C4A—C5A	119.7 (6)	C3B—C4B—C5B	116.9 (6)
C9A—C4A—C5A	121.4 (6)	C9B—C4B—C5B	120.6 (6)
C6A—C5A—C4A	125.0 (7)	C6B—C5B—C4B	123.7 (6)
C6A—C5A—H5AA	117.5	C6B—C5B—H5BA	118.2

C4A—C5A—H5AA	117.5	C4B—C5B—H5BA	118.2
C5A—C6A—C7A	117.9 (7)	C5B—C6B—C14B	124.0 (7)
C5A—C6A—C14A	124.5 (8)	C5B—C6B—C7B	119.1 (7)
C7A—C6A—C14A	117.5 (7)	C14B—C6B—C7B	116.9 (7)
O2A—C7A—C6A	122.5 (8)	O2B—C7B—C8B	120.2 (8)
O2A—C7A—C8A	118.3 (8)	O2B—C7B—C6B	122.1 (9)
C6A—C7A—C8A	119.2 (7)	C8B—C7B—C6B	117.6 (6)
O3A—C8A—C9A	124.4 (8)	O3B—C8B—C9B	119.8 (7)
O3A—C8A—C7A	116.9 (7)	O3B—C8B—C7B	118.6 (7)
C9A—C8A—C7A	118.7 (6)	C9B—C8B—C7B	121.6 (7)
C10A—C9A—C4A	120.2 (6)	C10B—C9B—C4B	120.0 (7)
C10A—C9A—C8A	122.3 (6)	C10B—C9B—C8B	123.7 (7)
C4A—C9A—C8A	117.5 (6)	C4B—C9B—C8B	116.3 (7)
C11A—C10A—C9A	119.8 (6)	C9B—C10B—C11B	118.9 (7)
C11A—C10A—C15A	116.2 (7)	C9B—C10B—C15B	127.0 (7)
C9A—C10A—C15A	124.0 (7)	C11B—C10B—C15B	114.1 (7)
C12A—C11A—C10A	118.3 (6)	C12B—C11B—C10B	118.6 (7)
C12A—C11A—H11A	120.9	C12B—C11B—H11B	120.7
C10A—C11A—H11A	120.9	C10B—C11B—H11B	120.7
O1A—C12A—C11A	123.1 (6)	O1B—C12B—C3B	114.1 (6)
O1A—C12A—C3A	113.2 (6)	O1B—C12B—C11B	123.2 (6)
C11A—C12A—C3A	123.7 (7)	C3B—C12B—C11B	122.6 (7)
C2A—C13A—H13A	109.5	C2B—C13B—H13D	109.5
C2A—C13A—H13B	109.5	C2B—C13B—H13E	109.5
H13A—C13A—H13B	109.5	H13D—C13B—H13E	109.5
C2A—C13A—H13C	109.5	C2B—C13B—H13F	109.5
H13A—C13A—H13C	109.5	H13D—C13B—H13F	109.5
H13B—C13A—H13C	109.5	H13E—C13B—H13F	109.5
C6A—C14A—H14A	109.5	C6B—C14B—H14D	109.5
C6A—C14A—H14B	109.5	C6B—C14B—H14E	109.5
H14A—C14A—H14B	109.5	H14D—C14B—H14E	109.5
C6A—C14A—H14C	109.5	C6B—C14B—H14F	109.5
H14A—C14A—H14C	109.5	H14D—C14B—H14F	109.5
H14B—C14A—H14C	109.5	H14E—C14B—H14F	109.5
C10A—C15A—H15A	109.5	C10B—C15B—H15D	109.5
C10A—C15A—H15B	109.5	C10B—C15B—H15E	109.5
H15A—C15A—H15B	109.5	H15D—C15B—H15E	109.5
C10A—C15A—H15C	109.5	C10B—C15B—H15F	109.5
H15A—C15A—H15C	109.5	H15D—C15B—H15F	109.5
H15B—C15A—H15C	109.5	H15E—C15B—H15F	109.5
C12A—O1A—C1A—C2A	−15.4 (9)	C12B—O1B—C1B—C2B	−22.2 (8)
O1A—C1A—C2A—C13A	−106.3 (7)	O1B—C1B—C2B—C3B	22.6 (8)
O1A—C1A—C2A—C3A	15.4 (9)	O1B—C1B—C2B—C13B	−95.3 (7)
C13A—C2A—C3A—C12A	109.8 (7)	C13B—C2B—C3B—C4B	−74.1 (11)
C1A—C2A—C3A—C12A	−10.3 (9)	C1B—C2B—C3B—C4B	167.9 (9)
C13A—C2A—C3A—C4A	−73.1 (10)	C13B—C2B—C3B—C12B	103.4 (7)
C1A—C2A—C3A—C4A	166.8 (8)	C1B—C2B—C3B—C12B	−14.6 (8)
C12A—C3A—C4A—C9A	−2.7 (11)	C12B—C3B—C4B—C9B	2.7 (11)
C2A—C3A—C4A—C9A	−179.7 (7)	C2B—C3B—C4B—C9B	−179.9 (7)

C12A—C3A—C4A—C5A	177.9 (6)	C12B—C3B—C4B—C5B	179.9 (6)
C2A—C3A—C4A—C5A	0.9 (13)	C2B—C3B—C4B—C5B	−2.8 (13)
C3A—C4A—C5A—C6A	−178.3 (7)	C3B—C4B—C5B—C6B	178.9 (7)
C9A—C4A—C5A—C6A	2.4 (12)	C9B—C4B—C5B—C6B	−3.9 (11)
C4A—C5A—C6A—C7A	0.6 (11)	C4B—C5B—C6B—C14B	−178.4 (7)
C4A—C5A—C6A—C14A	177.2 (7)	C4B—C5B—C6B—C7B	3.5 (11)
C5A—C6A—C7A—O2A	174.5 (7)	C5B—C6B—C7B—O2B	−172.6 (9)
C14A—C6A—C7A—O2A	−2.3 (11)	C14B—C6B—C7B—O2B	9.1 (13)
C5A—C6A—C7A—C8A	−4.6 (10)	C5B—C6B—C7B—C8B	4.3 (11)
C14A—C6A—C7A—C8A	178.6 (7)	C14B—C6B—C7B—C8B	−173.9 (7)
O2A—C7A—C8A—O3A	5.5 (12)	O2B—C7B—C8B—O3B	−15.4 (13)
C6A—C7A—C8A—O3A	−175.4 (7)	C6B—C7B—C8B—O3B	167.6 (7)
O2A—C7A—C8A—C9A	−173.3 (6)	O2B—C7B—C8B—C9B	164.7 (9)
C6A—C7A—C8A—C9A	5.8 (11)	C6B—C7B—C8B—C9B	−12.4 (11)
C3A—C4A—C9A—C10A	−0.3 (11)	C3B—C4B—C9B—C10B	−5.6 (11)
C5A—C4A—C9A—C10A	179.1 (7)	C5B—C4B—C9B—C10B	177.3 (6)
C3A—C4A—C9A—C8A	179.6 (7)	C3B—C4B—C9B—C8B	173.1 (7)
C5A—C4A—C9A—C8A	−1.0 (10)	C5B—C4B—C9B—C8B	−4.0 (10)
O3A—C8A—C9A—C10A	−1.7 (12)	O3B—C8B—C9B—C10B	10.5 (11)
C7A—C8A—C9A—C10A	177.0 (6)	C7B—C8B—C9B—C10B	−169.5 (7)
O3A—C8A—C9A—C4A	178.4 (8)	O3B—C8B—C9B—C4B	−168.1 (7)
C7A—C8A—C9A—C4A	−2.9 (10)	C7B—C8B—C9B—C4B	11.9 (10)
C4A—C9A—C10A—C11A	1.7 (11)	C4B—C9B—C10B—C11B	4.0 (11)
C8A—C9A—C10A—C11A	−178.2 (7)	C8B—C9B—C10B—C11B	−174.6 (7)
C4A—C9A—C10A—C15A	179.5 (7)	C4B—C9B—C10B—C15B	−177.3 (7)
C8A—C9A—C10A—C15A	−0.4 (11)	C8B—C9B—C10B—C15B	4.1 (12)
C9A—C10A—C11A—C12A	−0.1 (11)	C9B—C10B—C11B—C12B	0.2 (11)
C15A—C10A—C11A—C12A	−178.0 (7)	C15B—C10B—C11B—C12B	−178.6 (7)
C1A—O1A—C12A—C11A	−171.8 (8)	C1B—O1B—C12B—C3B	12.5 (8)
C1A—O1A—C12A—C3A	8.8 (9)	C1B—O1B—C12B—C11B	−169.0 (7)
C10A—C11A—C12A—O1A	177.6 (7)	C4B—C3B—C12B—O1B	−179.8 (6)
C10A—C11A—C12A—C3A	−3.2 (12)	C2B—C3B—C12B—O1B	2.2 (9)
C4A—C3A—C12A—O1A	−176.0 (6)	C4B—C3B—C12B—C11B	1.7 (11)
C2A—C3A—C12A—O1A	1.5 (9)	C2B—C3B—C12B—C11B	−176.3 (7)
C4A—C3A—C12A—C11A	4.6 (12)	C10B—C11B—C12B—O1B	178.5 (7)
C2A—C3A—C12A—C11A	−177.8 (7)	C10B—C11B—C12B—C3B	−3.1 (12)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1B—H1BA···O3B^{i}	0.97	2.47	3.413 (10)	164
C11B—H11B···O1A^{ii}	0.93	2.43	3.349 (8)	169
C13B—H13E···O2A^{iii}	0.96	2.42	3.204 (10)	138
C13B—H13F···O2B^{i}	0.96	2.54	3.500 (9)	174
C15B—H15D···Cg1^{iii}	0.96	2.87	3.539 (9)	127
C15B—H15E···Cg1^{iv}	0.96	2.86	3.632 (9)	138

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+3/2, −*y*+1, *z*−1/2; (iii) *x*+1/2, −*y*+3/2, −*z*; (iv) −*x*−1, *y*+3/2, −*z*+1/2.

Fig. 1

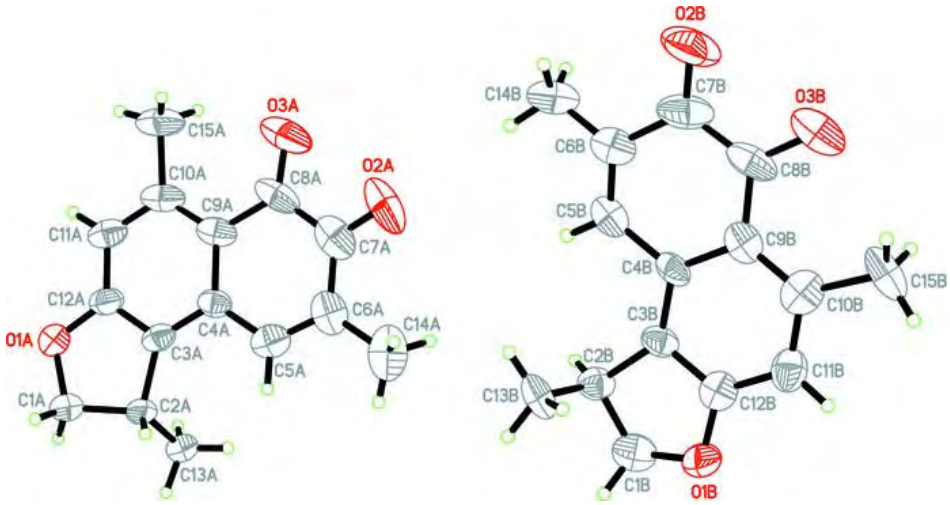
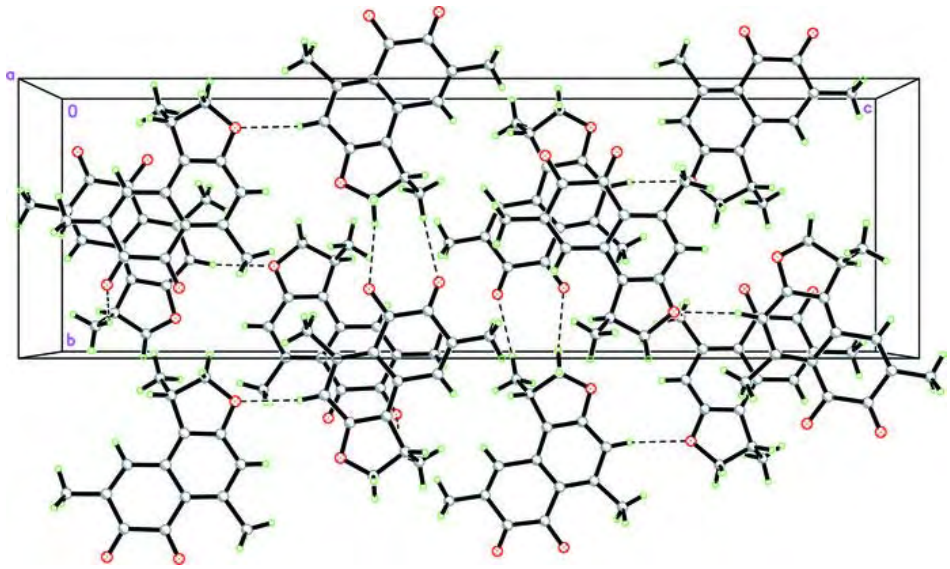


Fig. 2



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4,8-Dihydroxy-2,3-dimethoxy-1-(3-methylbut-2-enyl)-9*H*-xanthen-9-one

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4,8-Dihydroxy-2,3-dimethoxy-1-(3-methylbut-2-enyl)-9*H*-xanthen-9-one

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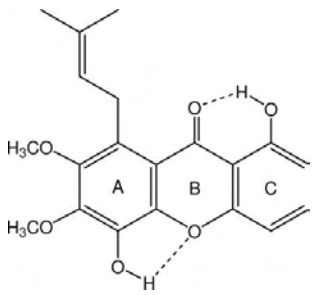
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.049; wR factor = 0.116; data-to-parameter ratio = 16.1.

The title xanthone compound, $C_{20}H_{20}O_6$, was isolated from the roots of *Cratoxylum formosum* ssp. *pruniflorum*. The xanthone ring system is essentially planar. The 3-methylbut-2-enyl substituent plane is not coplanar with the attached benzene ring, the dihedral angle being 62.59 (12) Å. The two methoxy groups are twisted away from the mean plane of the attached benzene ring. The two hydroxy groups are coplanar with the attached benzene rings and contribute to O—H···O intramolecular hydrogen bonds which generate S(5) and S(6) ring motifs. In the crystal structure, intermolecular O—H···O hydrogen bonds and weak C—H···O intermolecular interactions connect the molecules into infinite one-dimensional chains along the [201] direction. The crystal is further stabilized by C—H···π interactions.

Related literature

For related literature on hydrogen-bond motifs, see: Bernstein *et al.* (1995). For values of bond lengths, see: Allen *et al.* (1987). For related structures, see, for example: Boonnak *et al.* (2005); Boonnak, Chantrapromma & Fun (2006); Boonnak, Karalai *et al.* (2006); Chantrapromma *et al.* (2005, 2006); Fun *et al.* (2006). For related literature on the bioactivities of xanthones, see, for example: Aderson (1986); Boonnak, Karalai *et al.* (2006); Kitanov *et al.* (1988).



Experimental

Crystal data

$C_{20}H_{20}O_6$
M_r = 356.36
Monoclinic, $P2_1/c$
a = 4.3883 (2) Å
b = 32.2730 (13) Å
c = 11.8006 (5) Å
β = 92.733 (3)°
V = 1669.34 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100.0 (1) K
0.30 × 0.16 × 0.11 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.969, T_{max} = 0.989
33106 measured reflections
3837 independent reflections
2645 reflections with $I > 2\sigma(I)$
R_{int} = 0.081

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.116
S = 1.05
3837 reflections
239 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the ring C6–C11.

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1O3···O2	0.82	1.80	2.5343 (18)	148
O4—H1O4···O1	0.82	2.24	2.6782 (18)	114
O4—H1O4···O3^{i}	0.82	1.98	2.7531 (18)	158
C4—H4*A*···O2^{i}	0.93	2.51	3.375 (2)	154
C14—H14*B*···O4	0.96	2.58	3.105 (2)	115
C15—H15*C*···O5	0.96	2.48	3.024 (2)	116
C16—H16*A*···O2	0.97	2.34	2.828 (2)	111
C16—H16*B*···O6	0.97	2.35	2.806 (2)	108
C16—H16*A*···*Cg*1^{ii}	0.96	2.86	3.3671 (19)	114

Symmetry codes: (i) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-1, y, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2251).

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References

Aderson, E. F. (1986). *Econ. Bot.* **40**, 442–450.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Boonnak, N., Chantrapromma, S. & Fun, H.-K. (2006). *Acta Cryst.* E**62**, o2034–o2036.

Boonnak, N., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst.* E**61**, o4376–o4378.

Boonnak, N., Karalai, C., Chantrapromma, S., Ponglimanont, C., Fun, H.-K., Kanjana-Opas, A. & Laphookhieo, S. (2006). *Tetrahedron*, **62**, 8850–8859.

Bruker (2005). *APEX2* (Version 1.27), *SAINT* (Version 7.12a) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.

Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Atta-ur-Rahman (2005). *Acta Cryst.* E**61**, o2136–o2138.

Chantrapromma, S., Boonnak, N., Fun, H.-K. & Karalai, C. (2006). *Acta Cryst.* E**62**, o360–o362.

Fun, H.-K., Ng, S.-L., Razak, I. A., Boonnak, N. & Chantrapromma, S. (2006). *Acta Cryst.* E**62**, o130–o132.

Kitanov, G. M., Assenov, I. & The Van, D. (1988). *Pharmazie*, **43**, H12–H13.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2007). E**63**, o4903-o4904 [**doi:10.1107/S1600536807061090**]

4,8-Dihydroxy-2,3-dimethoxy-1-(3-methylbut-2-enyl)-9*H*-xanthen-9-one

N. Boonnak, S. Chantrapromma, H.-K. Fun and C. Karalai

Comment

Secondary metabolites in the plants of *Cratoxylum* genus are mainly xanthones and antraquinones. The plants in this family were used in folk medicine such as, for treatment of diuretic, stomachic, and tonic effects (Kitanov *et al.*, 1988) as well as for diarrhea and flatulence (Aderson, 1986). We have reported previously a number of crystal structures of xanthones and antraquinones isolated from *Cratoxylum formosum* ssp. *pruniflorum* (Boonnak *et al.*, 2005; Boonnak, Chantrapromma & Fun, 2006; Boonnak, Karalai *et al.*, 2006; Chantrapromma *et al.*, 2005, 2006; Fun *et al.*, 2006). The title xanthone was isolated from the methylene chloride extract of the roots of *Cratoxylum formosum* ssp. *pruniflorum* which were collected from Nhongkai province in the northeasthern part of Thailand. The single-crystal *X*-ray structural study of the title xanthone was undertaken in order to establish the structure and conformation of the various groups for further study of Structural Activity Relationships (SAR).

In the molecular structure of the title xanthone (Fig. 1), the xanthone skeleton (rings *A*, *B* and *C*) is essentially planar, the maximum deviation from planarity is 0.018 (2) Å for atom C8. The two hydroxy groups are coplanar with the attached benzene rings and contribute to O—H···O intramolecular hydrogen bonds, namely O3—H1O3···O2 and O4—H1O4···O1 hydrogen bonds which generate the S(6) and S(5) ring motifs, respectively (Bernstein *et al.*, 1995) and help to stabilize the planarity of the structure. There are also weak intramolecular C—H···O interactions; C14—H14B···O4, C15—H15C···O5 and C16—H16B···O2 generate S(6) and C16—H16A···O6 generates S(5) ring motifs (Table 1). The two methoxy groups are twisted away from the mean plane of the attached benzene ring with torsion angles C15–O6–C9–C8 = 75.3 (2)° and C14–O5–C8–C7 = −76.4 (2)°. The orientation of the 3-methylbut-2-enyl (C16–C20) side chain with respect to the benzene ring *A* is indicated by the torsion angle of C9–C10–C16–C17 = 101.62 (19)°, indicating a (+)-anticlinal conformation (Fig. 1) Bond distances and angles in the title xanthone are in normal ranges (Allen *et al.*, 1987) and are comparable to other closely related compounds (Boonnak *et al.*, 2005; Boonnak, Chantrapromma & Fun, 2006; Boonnak, Karalai *et al.*, 2006; Chantrapromma *et al.*, 2005, 2006; Fun *et al.*, 2006).

In the crystal packing (Fig. 2), the molecules are linked together by an intermolecular O4—H1O4···O3^{i} hydrogen bond and a weak C4—H4A···O2^{i} interaction [symmetry code: (i) 1 + *x*, 1/2 − *y*, 1/2 + *z*; Table 1] into infinite one dimension chains along the [2 0 1] direction. The crystal packing is further stabilized by a C—H···π interaction between the 3-methylbut-2-enyl side chain and the centroid of C6–C11 benzene ring (*Cg*1); C16—H16A···*Cg*1^{ii} [symmetry code: (ii) −1 + *x*, *y*, *z*; Table 1].

Experimental

Air-dried roots of *Cratoxylum formosum* ssp. *pruniflorum* (5.30 kg) were ground and extracted with CH_2Cl_2 (2 × 20 *L* for 2 × 5 days) at room temperature. The residue obtained after evaporation of the solvent was subjected to quick column chromatography (QCC) on silica gel using hexane as first eluent and then increasing the polarity with EtOAc and acetone, respectively, to afford 8 fractions (F1—F8). Fraction F4 was further separated by column chromatography with a gradient

of acetone–hexane to give the title xanthone. Yellow needle-shaped single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a $CHCl_3/CH_3OH$ (9:1 *v*/*v*) solvent after several days (m.p. 445–447 K).

Refinement

All H atoms were placed in calculated positions with O—H distance of 0.82 Å and C—H distances in the range 0.93–0.97 Å. The U_{iso}(H) values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxyl and methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. A rotating group model was used for the methyl groups.

Figures

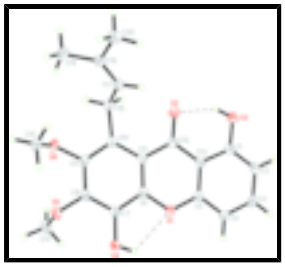


Fig. 1. The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering scheme. Hydrogen bonds were drawn as dash lines.

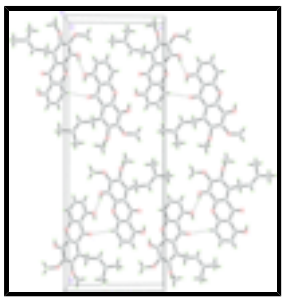


Fig. 2. The crystal packing of the title compound view along the *a* axis. Hydrogen bonds were drawn as dash lines.

4,8-Dihydroxy-2,3-dimethoxy-1-(3-methylbut-2-enyl)-9*H*-xanthen-9-one

Crystal data

$C_{20}H_{20}O_6$	F_{000} = 752
M_r = 356.36	D_x = 1.418 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 445-447 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 4.3883 (2) Å	Cell parameters from 3837 reflections
b = 32.2730 (13) Å	θ = 1.3–27.5º
c = 11.8006 (5) Å	μ = 0.11 mm^{-1}
β = 92.733 (3)º	*T* = 100.0 (1) K
V = 1669.34 (12) Å^3	Block, yellow
Z = 4	0.30 × 0.16 × 0.11 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	3837 independent reflections
Radiation source: fine-focus sealed tube	2645 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.081$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{max} = 27.5^o$
$T = 100.0(1)$ K	$\theta_{min} = 1.3^o$
ω scans	$h = -5 \rightarrow 5$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -40 \rightarrow 41$
$T_{min} = 0.969$, $T_{max} = 0.989$	$l = -15 \rightarrow 15$
33106 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H-atom parameters constrained
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.5487P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = <0.001$
3837 reflections	$\Delta\rho_{max} = 0.25$ e $Å^{-3}$
239 parameters	$\Delta\rho_{min} = -0.23$ e $Å^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. The low-temparture data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.9952 (3)	0.28976 (4)	0.51586 (10)	0.0198 (3)
O2	0.3551 (3)	0.29827 (4)	0.25288 (11)	0.0266 (3)
O3	0.4148 (3)	0.22140 (4)	0.21607 (11)	0.0278 (3)

H1O3	0.3501	0.2451	0.2069	0.042*
O4	1.1908 (3)	0.35415 (4)	0.64269 (10)	0.0209 (3)
H1O4	1.2252	0.3293	0.6508	0.031*
O5	0.9565 (3)	0.43168 (4)	0.60360 (10)	0.0218 (3)
O6	0.5256 (3)	0.44539 (4)	0.43486 (11)	0.0207 (3)
C1	0.6196 (4)	0.22059 (6)	0.30595 (16)	0.0202 (4)
C2	0.7516 (4)	0.18357 (6)	0.33817 (16)	0.0232 (4)
H2A	0.7008	0.1594	0.2989	0.028*
C3	0.9616 (4)	0.18267 (6)	0.42990 (17)	0.0249 (4)
H3A	1.0498	0.1575	0.4517	0.030*
C4	1.0432 (4)	0.21804 (6)	0.48971 (17)	0.0230 (4)
H4A	1.1848	0.2170	0.5508	0.028*
C5	0.9081 (4)	0.25509 (5)	0.45601 (15)	0.0181 (4)
C6	0.8676 (4)	0.32749 (5)	0.48741 (15)	0.0174 (4)
C7	0.9768 (4)	0.35973 (5)	0.55695 (15)	0.0178 (4)
C8	0.8589 (4)	0.39895 (5)	0.53707 (15)	0.0172 (4)
C9	0.6441 (4)	0.40591 (5)	0.44743 (15)	0.0176 (4)
C10	0.5352 (4)	0.37432 (5)	0.37673 (15)	0.0171 (4)
C11	0.6496 (4)	0.33368 (5)	0.39838 (15)	0.0171 (4)
C12	0.5527 (4)	0.29696 (6)	0.33270 (15)	0.0188 (4)
C13	0.6946 (4)	0.25778 (5)	0.36497 (15)	0.0185 (4)
C14	0.8287 (5)	0.43194 (6)	0.71306 (16)	0.0281 (5)
H14A	0.8797	0.4575	0.7511	0.042*
H14B	0.9097	0.4091	0.7572	0.042*
H14C	0.6109	0.4294	0.7043	0.042*
C15	0.7311 (4)	0.47470 (6)	0.38786 (17)	0.0228 (4)
H15A	0.6584	0.5023	0.4002	0.034*
H15B	0.7418	0.4698	0.3079	0.034*
H15C	0.9303	0.4715	0.4240	0.034*
C16	0.3001 (4)	0.38489 (6)	0.28207 (15)	0.0199 (4)
H16A	0.1430	0.3637	0.2796	0.024*
H16B	0.2040	0.4110	0.3001	0.024*
C17	0.4283 (4)	0.38831 (6)	0.16660 (15)	0.0202 (4)
H17A	0.5317	0.3652	0.1409	0.024*
C18	0.4096 (4)	0.42083 (6)	0.09720 (15)	0.0209 (4)
C19	0.2711 (5)	0.46191 (6)	0.12536 (17)	0.0296 (5)
H19A	0.2072	0.4614	0.2020	0.044*
H19B	0.0979	0.4671	0.0746	0.044*
H19C	0.4196	0.4834	0.1175	0.044*
C20	0.5276 (5)	0.41855 (6)	−0.02071 (16)	0.0302 (5)
H20A	0.6190	0.3919	−0.0318	0.045*
H20B	0.6772	0.4398	−0.0297	0.045*
H20C	0.3616	0.4224	−0.0756	0.045*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0244 (7)	0.0134 (6)	0.0212 (7)	0.0013 (5)	−0.0045 (5)	−0.0008 (5)

O2	0.0326 (8)	0.0202 (7)	0.0258 (7)	−0.0002 (6)	−0.0111 (6)	0.0006 (6)
O3	0.0376 (8)	0.0168 (7)	0.0277 (8)	−0.0012 (6)	−0.0115 (6)	−0.0010 (6)
O4	0.0266 (7)	0.0161 (6)	0.0195 (7)	−0.0003 (5)	−0.0050 (6)	−0.0002 (5)
O5	0.0315 (7)	0.0161 (7)	0.0181 (7)	−0.0037 (5)	0.0023 (6)	−0.0020 (5)
O6	0.0205 (7)	0.0145 (6)	0.0273 (7)	0.0007 (5)	0.0054 (6)	0.0026 (5)
C1	0.0220 (10)	0.0202 (10)	0.0183 (9)	−0.0032 (8)	0.0010 (8)	0.0001 (8)
C2	0.0266 (10)	0.0181 (10)	0.0247 (10)	−0.0019 (8)	−0.0002 (8)	−0.0044 (8)
C3	0.0276 (10)	0.0162 (10)	0.0309 (11)	0.0048 (8)	0.0000 (9)	0.0010 (8)
C4	0.0255 (10)	0.0189 (10)	0.0238 (10)	0.0012 (8)	−0.0065 (8)	−0.0009 (8)
C5	0.0208 (9)	0.0152 (9)	0.0183 (9)	−0.0020 (7)	0.0023 (7)	−0.0031 (7)
C6	0.0184 (9)	0.0149 (9)	0.0193 (9)	−0.0008 (7)	0.0041 (7)	0.0021 (7)
C7	0.0183 (9)	0.0201 (9)	0.0150 (9)	−0.0016 (7)	0.0008 (7)	0.0017 (7)
C8	0.0205 (9)	0.0149 (9)	0.0166 (9)	−0.0040 (7)	0.0042 (7)	−0.0011 (7)
C9	0.0175 (9)	0.0142 (9)	0.0216 (9)	0.0012 (7)	0.0062 (8)	0.0023 (7)
C10	0.0158 (9)	0.0188 (9)	0.0172 (9)	0.0001 (7)	0.0051 (7)	0.0025 (7)
C11	0.0174 (9)	0.0168 (9)	0.0174 (9)	−0.0013 (7)	0.0036 (7)	0.0006 (7)
C12	0.0194 (9)	0.0183 (9)	0.0187 (9)	−0.0022 (7)	0.0015 (8)	0.0014 (7)
C13	0.0204 (9)	0.0157 (9)	0.0194 (9)	−0.0017 (7)	0.0029 (8)	0.0009 (7)
C14	0.0401 (12)	0.0250 (11)	0.0196 (10)	−0.0017 (9)	0.0070 (9)	−0.0053 (8)
C15	0.0267 (10)	0.0173 (10)	0.0247 (10)	−0.0012 (8)	0.0039 (8)	0.0034 (8)
C16	0.0196 (9)	0.0184 (9)	0.0217 (10)	0.0018 (7)	0.0016 (8)	0.0019 (8)
C17	0.0211 (9)	0.0168 (9)	0.0226 (10)	0.0011 (8)	−0.0010 (8)	−0.0029 (8)
C18	0.0225 (10)	0.0200 (10)	0.0198 (10)	−0.0012 (8)	−0.0011 (8)	−0.0004 (8)
C19	0.0379 (12)	0.0230 (11)	0.0280 (11)	0.0061 (9)	0.0026 (9)	0.0059 (9)
C20	0.0402 (12)	0.0287 (11)	0.0217 (10)	−0.0022 (9)	0.0014 (9)	0.0027 (9)

Geometric parameters (Å, °)

O1—C5	1.368 (2)	C9—C10	1.388 (2)
O1—C6	1.375 (2)	C10—C11	1.423 (2)
O2—C12	1.250 (2)	C10—C16	1.523 (2)
O3—C1	1.357 (2)	C11—C12	1.468 (2)
O3—H1O3	0.8200	C12—C13	1.452 (2)
O4—C7	1.359 (2)	C14—H14A	0.9600
O4—H1O4	0.8200	C14—H14B	0.9600
O5—C8	1.372 (2)	C14—H14C	0.9600
O5—C14	1.433 (2)	C15—H15A	0.9600
O6—C9	1.382 (2)	C15—H15B	0.9600
O6—C15	1.436 (2)	C15—H15C	0.9600
C1—C2	1.374 (3)	C16—C17	1.503 (3)
C1—C13	1.418 (2)	C16—H16A	0.9700
C2—C3	1.388 (3)	C16—H16B	0.9700
C2—H2A	0.9300	C17—C18	1.331 (2)
C3—C4	1.380 (3)	C17—H17A	0.9300
C3—H3A	0.9300	C18—C19	1.502 (3)
C4—C5	1.384 (2)	C18—C20	1.509 (3)
C4—H4A	0.9300	C19—H19A	0.9600
C5—C13	1.394 (2)	C19—H19B	0.9600
C6—C7	1.396 (2)	C19—H19C	0.9600

C6—C11	1.401 (2)	C20—H20A	0.9600
C7—C8	1.383 (2)	C20—H20B	0.9600
C8—C9	1.401 (2)	C20—H20C	0.9600
C5—O1—C6	119.85 (13)	C13—C12—C11	117.05 (15)
C1—O3—H1O3	109.5	C5—C13—C1	117.22 (16)
C7—O4—H1O4	109.5	C5—C13—C12	121.35 (16)
C8—O5—C14	113.28 (14)	C1—C13—C12	121.42 (16)
C9—O6—C15	114.12 (13)	O5—C14—H14A	109.5
O3—C1—C2	119.20 (16)	O5—C14—H14B	109.5
O3—C1—C13	119.80 (16)	H14A—C14—H14B	109.5
C2—C1—C13	121.00 (17)	O5—C14—H14C	109.5
C1—C2—C3	119.32 (17)	H14A—C14—H14C	109.5
C1—C2—H2A	120.3	H14B—C14—H14C	109.5
C3—C2—H2A	120.3	O6—C15—H15A	109.5
C4—C3—C2	121.86 (17)	O6—C15—H15B	109.5
C4—C3—H3A	119.1	H15A—C15—H15B	109.5
C2—C3—H3A	119.1	O6—C15—H15C	109.5
C3—C4—C5	118.04 (17)	H15A—C15—H15C	109.5
C3—C4—H4A	121.0	H15B—C15—H15C	109.5
C5—C4—H4A	121.0	C17—C16—C10	114.31 (15)
O1—C5—C4	116.92 (15)	C17—C16—H16A	108.7
O1—C5—C13	120.53 (16)	C10—C16—H16A	108.7
C4—C5—C13	122.55 (16)	C17—C16—H16B	108.7
O1—C6—C7	113.09 (15)	C10—C16—H16B	108.7
O1—C6—C11	124.40 (15)	H16A—C16—H16B	107.6
C7—C6—C11	122.51 (16)	C18—C17—C16	126.92 (17)
O4—C7—C8	119.15 (15)	C18—C17—H17A	116.5
O4—C7—C6	122.98 (16)	C16—C17—H17A	116.5
C8—C7—C6	117.87 (16)	C17—C18—C19	124.98 (18)
O5—C8—C7	120.21 (15)	C17—C18—C20	120.98 (17)
O5—C8—C9	119.28 (15)	C19—C18—C20	114.03 (17)
C7—C8—C9	120.50 (16)	C18—C19—H19A	109.5
O6—C9—C10	119.73 (15)	C18—C19—H19B	109.5
O6—C9—C8	117.72 (15)	H19A—C19—H19B	109.5
C10—C9—C8	122.43 (16)	C18—C19—H19C	109.5
C9—C10—C11	117.43 (16)	H19A—C19—H19C	109.5
C9—C10—C16	118.58 (16)	H19B—C19—H19C	109.5
C11—C10—C16	123.99 (16)	C18—C20—H20A	109.5
C6—C11—C10	119.24 (16)	C18—C20—H20B	109.5
C6—C11—C12	116.80 (15)	H20A—C20—H20B	109.5
C10—C11—C12	123.96 (16)	C18—C20—H20C	109.5
O2—C12—C13	120.03 (16)	H20A—C20—H20C	109.5
O2—C12—C11	122.91 (16)	H20B—C20—H20C	109.5
O3—C1—C2—C3	179.85 (17)	O1—C6—C11—C10	−179.68 (16)
C13—C1—C2—C3	0.0 (3)	C7—C6—C11—C10	0.5 (3)
C1—C2—C3—C4	−0.3 (3)	O1—C6—C11—C12	0.4 (3)
C2—C3—C4—C5	0.2 (3)	C7—C6—C11—C12	−179.40 (17)
C6—O1—C5—C4	−179.40 (17)	C9—C10—C11—C6	−1.1 (2)

C6—O1—C5—C13	1.1 (2)	C16—C10—C11—C6	179.55 (16)
C3—C4—C5—O1	−179.31 (17)	C9—C10—C11—C12	178.79 (17)
C3—C4—C5—C13	0.1 (3)	C16—C10—C11—C12	−0.6 (3)
C5—O1—C6—C7	179.28 (16)	C6—C11—C12—O2	178.42 (17)
C5—O1—C6—C11	−0.6 (3)	C10—C11—C12—O2	−1.5 (3)
O1—C6—C7—O4	0.9 (3)	C6—C11—C12—C13	−0.8 (2)
C11—C6—C7—O4	−179.21 (16)	C10—C11—C12—C13	179.28 (17)
O1—C6—C7—C8	−178.79 (16)	O1—C5—C13—C1	178.99 (16)
C11—C6—C7—C8	1.1 (3)	C4—C5—C13—C1	−0.4 (3)
C14—O5—C8—C7	−76.4 (2)	O1—C5—C13—C12	−1.6 (3)
C14—O5—C8—C9	105.05 (19)	C4—C5—C13—C12	178.95 (18)
O4—C7—C8—O5	−0.3 (3)	O3—C1—C13—C5	−179.50 (16)
C6—C7—C8—O5	179.45 (16)	C2—C1—C13—C5	0.4 (3)
O4—C7—C8—C9	178.28 (16)	O3—C1—C13—C12	1.1 (3)
C6—C7—C8—C9	−2.0 (3)	C2—C1—C13—C12	−179.01 (18)
C15—O6—C9—C10	−108.65 (18)	O2—C12—C13—C5	−177.83 (17)
C15—O6—C9—C8	75.3 (2)	C11—C12—C13—C5	1.4 (3)
O5—C8—C9—O6	−4.1 (2)	O2—C12—C13—C1	1.5 (3)
C7—C8—C9—O6	177.37 (16)	C11—C12—C13—C1	−179.19 (17)
O5—C8—C9—C10	180.00 (16)	C9—C10—C16—C17	101.62 (19)
C7—C8—C9—C10	1.4 (3)	C11—C10—C16—C17	−79.0 (2)
O6—C9—C10—C11	−175.71 (15)	C10—C16—C17—C18	−123.3 (2)
C8—C9—C10—C11	0.2 (3)	C16—C17—C18—C19	4.2 (3)
O6—C9—C10—C16	3.7 (2)	C16—C17—C18—C20	−174.94 (17)
C8—C9—C10—C16	179.57 (16)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1O3···O2	0.82	1.80	2.5343 (18)	148
O4—H1O4···O1	0.82	2.24	2.6782 (18)	114
O4—H1O4···O3^{i}	0.82	1.98	2.7531 (18)	158
C4—H4A···O2^{i}	0.93	2.51	3.375 (2)	154
C14—H14B···O4	0.96	2.58	3.105 (2)	115
C15—H15C···O5	0.96	2.48	3.024 (2)	116
C16—H16A···O2	0.97	2.34	2.828 (2)	111
C16—H16B···O6	0.97	2.35	2.806 (2)	108
C16—H16A···Cg1^{ii}	0.96	2.86	3.3671 (19)	114

Symmetry codes: (i) *x*+1, −*y*+1/2, *z*+1/2; (ii) *x*−1, *y*, *z*.

Fig. 1

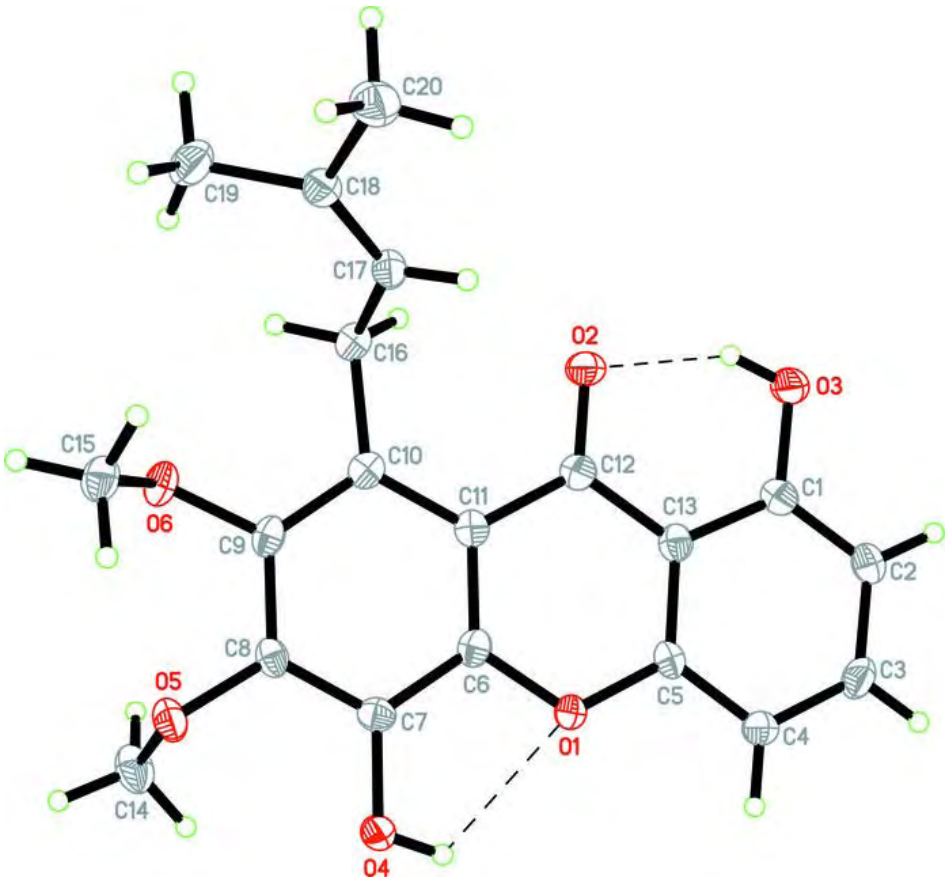
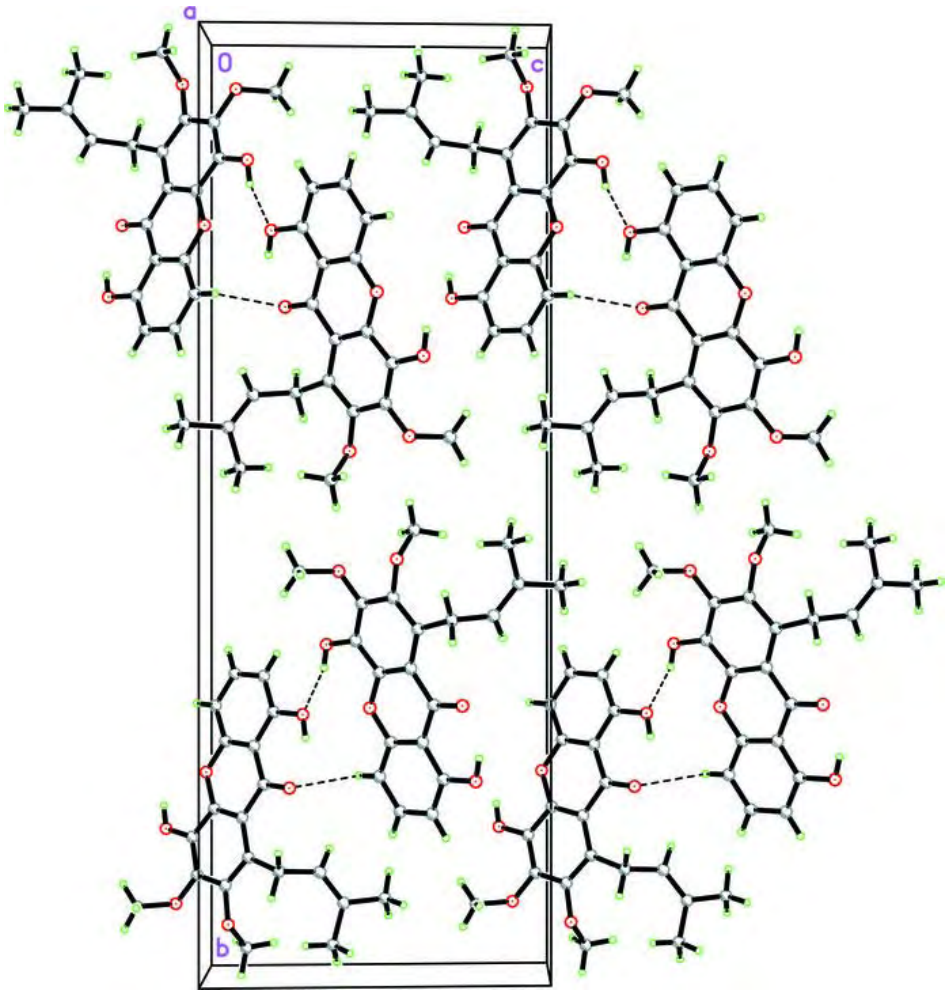


Fig. 2



Cytotoxic and Antibacterial Sesquiterpenes from *Thespesia populnea*

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Eight new sesquiterpenoids, named populene A−H (**1**−**8**), were isolated from dichloromethane extracts of the wood and dark heartwood of *Thespesia populnea*, together with 11 known compounds (**9**−**19**). Their structures were determined on the basis of spectroscopic analyses. The cytotoxic activity of isolated compounds was evaluated against four cancer cell lines: MCF-7, HeLa, HT-29, and KB. Mansonone E (**11**) and (+)-gossypol (**18**) showed significant activities. Their antibacterial properties against *Bacillus subtilis*, *Staphylococcus aureus*, and *Enterococcus faecalis* are also presented.

Thespesia populnea (L.) Soland. Ex Coor (Malvaceae) is widely distributed in Hawaii, California, Florida, Africa, the Caribbean islands, and Asia.[1] Various parts of this plant are found to possess useful medicinal properties, such as antifertility, antibacterial, anti-inflammatory, antioxidant, purgative, and hepatoprotective activities.[2] Previous chemical investigations of this species have yielded highly oxidized sesquiterpenes containing a cadinane skeleton.[1,3,4] Some of these compounds possess significant cytotoxic,[5−7] antifungal,[8] or antioxidative activities.[9]As part of our search for bioactive natural products from mangroves and tropical plants,[10−12] we now describe the isolation and structure elucidation of compounds **1**−**19** from the dark heartwood and wood of *T. populnea*. Two new compounds, populenes A and B (**1** and **2**), along with mansonone E (**11**),[5] (+)-gossypol (**18**),[13] and (+)-6,6′-methoxygossypol (**19**)[14] were purified from the wood. Six new compounds, populene C−H (**3**−**8**), were obtained from the dark heartwood, together with mansonones C,[5] D,[3] E,[5,9] G,[3] H,[9] and S[15] (**9**−**14**), 7-hydroxycadalene (**15**),[3] 7-hydroxy-2,3,5,6-tetrahydro-3,6,9-trimethylnaphtho[1,8-*b*,*c*]pyran-4,8-dione (**16**),[1,16] and thespesone (**17**).[1,3] Antibacterial and cytotoxic activities of **1**−**19** were also evaluated.

Results and Discussion

The heartwood and wood of *T. populnea* were separately extracted with dichloromethane. These extracts showed significant cytotoxicity against MCF-7, HeLa, HT-29, and KB cancer cell lines and weak antibacterial activity against *B. subtilis*. Therefore, each extract was subjected to chromatography on silica gel to give compounds **1**−**19**.

Compound **1** was obtained as a yellow gum with the molecular formula $C_{15}H_{18}O_3$ on the basis of a molecular ion at *m*/*z* 246.1262 in the HREIMS. The IR spectrum of **1** showed a OH absorption (3365 cm^{-1}), and the UV spectrum showed absorption maxima at 216, 251, 259 (sh), 279, and 289, suggesting a benzofuran chromophore.[17] The ^1H NMR data of **1** (Table 1) were characteristic of a cadinane skeleton[1,3,8] with a benzofuran moiety. Aromatic protons resonating at δ 7.02 (1H, br s) and 7.10 (1H, br s) were assigned to H-4 and H-2, respectively, and a furan proton signal at δ 7.50 (d, J = 0.9 Hz) was assigned to H-9. Signals assigned to a methine proton [δ 3.02 (dd, J = 7.8, 3.9 Hz)], two oxymethines [δ 4.01 (dd, J = 7.8, 7.8 Hz) and 4.90 (dd, J = 7.8, 0.9 Hz)], a methyl group (δ 2.48, s) and one isopropyl moiety [δ 1.16 (d, J = 7.2 Hz); 1.18 (d, J = 7.2 Hz) and 2.58 (m)] were also observed. The methyl signal at δ 2.48 was placed at C-3 because of HMBC correlations to C-2 (δ 109.3) and C-4 (δ 121.6), and the isopropyl group was placed at C-5 due to HMBC correlations of the methine H-11 at δ 2.58 with C-4a (δ 131.4), C-5 (δ 49.8), and C-6 (δ 75.7). The two oxymethine protons at δ 4.01 and 4.90 were assigned to H-6 and H-7, respectively, judging from the allylic coupling (0.9 Hz) of H-9 with H-7, which was in turn coupled to H-6 in the COSY experiment. The relative configuration at C-5, C-6, and C-7 was assigned by NOESY experiment, in which only methyl protons of the isopropyl group showed a cross-peak with H-6, indicating that H-6 was on the same side of the ring as the isopropyl group but opposite that of H-5 and H-7. The pseudo-*trans*-diaxial coupling (7.8 Hz) of H-6 with H-5 and H-7 also supported the NOESY data. Therefore, the relative configuration at H-5, H-6, and H-7 should be *trans*−*trans*. Thus, **1** was named populene A.

Compound **2** possessed the same formula as **1** by HREIMS. The similarity of the mass, IR, UV, and ^1H and ^{13}C NMR spectra (Table 1) of **1** and **2** indicated that **2** was a diastereomer of **1**. The main difference was found in the small coupling constant of H-6 (δ 4.38, dd, J = 3.3, 3.3 Hz) in **2** as compared to that in **1** (δ 4.01, t, J = 7.8 Hz). The NOESY experiment exhibited cross-peaks of H-5 and H-6 and between H-6 and H-7, suggesting their *cis* orientation. Accordingly, the structure of **2** was as indicated, and it was named populene B.

Compound **3** had the molecular formula $C_{18}H_{20}O_3$ as determined by HREIMS. The EI mass spectrum was diagnostic, showing a relatively intense $[M + 2]^+$ ion peak characteristic of *ortho*-naphthoquinones, which was not displayed by *para*- naphthoquinones.[18] The IR spectrum exhibited carbonyl absorptions at 1757 and 1698 cm^{-1}. The UV spectrum showed absorption maxima at 213, 242, 259, and 380 nm. The ^1H and ^{13}C NMR data (Table 1) of **3** were comparable to those of mansonone D[3] (**10**), which was isolated from the dark heartwood of this plant. The difference between these two compounds was that **3** contained an additional isopropyl group, which appeared as two methyl singlet signals at δ 1.57 and 1.53 in the ^1H NMR spectrum. HMBC correlations to the oxygenated quaternary carbon at δ 74.9 (C-14) supported the connection of this group to oxygen. In addition, the correlation of oxymethylene protons at δ 3.97 and 3.79 (H_2-13) with C-5 (δ 135.8) and C-14 (δ 74.9), of a *gem*-dimethyl with C-6 (δ 150.1), and of aromatic proton H-7 (δ 6.95) with C-14 (δ 74.9) indicated that a pyran moiety was connected to an aromatic ring at C-5 and C-6. The methine proton on C-11 was deduced to be equatorially oriented from the two small vicinal coupling constants ($J_{11,13\beta}$ = 1.2 Hz and $J_{11,13\alpha}$ = 2.4 Hz). Therefore, compound **3** was named populene C.

Compound **4** was a brown gum having the molecular formula $C_{18}H_{24}O_3$ (HREIMS). The IR spectrum exhibited an OH absorption at 3417 cm^{-1}. In the ^1H NMR (Table 1) spectrum, an aromatic proton signal at δ 6.95 and an aromatic methyl at δ 2.62, as found in **3**, were missing in **4** and the signals of $-CH(CH_3)CH_2-$ were

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Chart 1

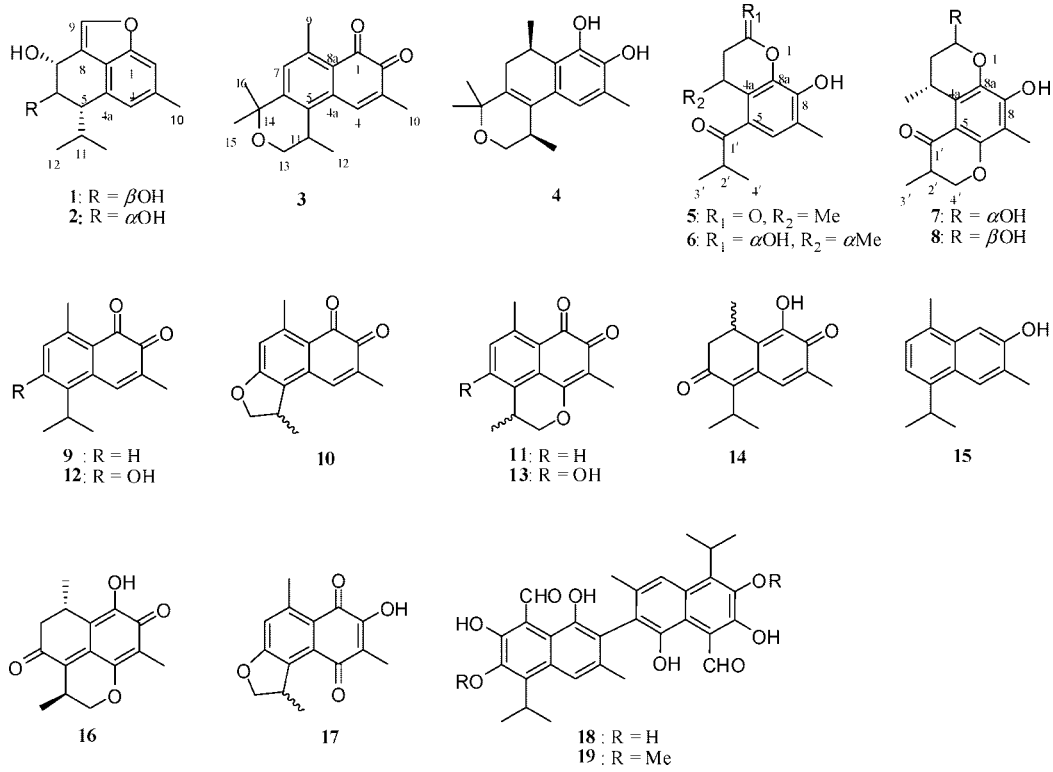

Table 1. ^{1}H and ^{13}C NMR Data for Compounds **1**−**4** (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) in $CDCl_3$

	1		**2**		**3**		**4**	
position	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C
1		153.5		153.6		181.7		140.3
2	7.10 (br s)	109.3	7.14 (br s)	109.8		181.6		140.9
3		135.8		135.7		135.8		121.0
4	7.02 (br s)	121.6	6.91 (br s)	124.5	7.52 (d, 1.2)	137.3	6.65 (s)	117.0
4a		131.4		129.8		128.4		125.0
5	3.02 (dd, 7.8, 3.9, H_β)	49.8	2.90 (dd, 8.7, 3.3, H_β)	53.5		135.8		128.7
6	4.01 (dd, 7.8, 7.8, H_α)	75.7	4.38 (dd, 3.3, 3.3, H_β)	73.4		150.1		132.2
7	4.90 (dd, 7.8, 0.9, H_β)	70.5	5.08 (m, H_β)	65.6	6.95 (s)	131.2	2.00 (d, 15.3, H_β) 2.36 (dd, 15.3, 5.1, H_α)	31.0
8		118.7		118.2		142.6	3.19 (br dq, 6.9, 6.9, H_α)	25.2
8a		123.7		123.4		133.1		125.2
9	7.50 (d, 0.9)	138.8	7.57 (d,1.5)	140.9	2.62 (s)	23.0	1.04 (d, 6.9)	17.9
10	2.48 (s)	22.4	2.48 (s)	22.2	2.09 (d, 1.2)	16.0	2.25 (s)	15.8
11	2.58 (m)	27.8	1.63 (m)	31.0	3.01 (brq, 6.9, H_α)	29.9	2.68 (m, H_α)	28.4
12	1.16 (d, 7.2)[a]	20.0[b]	1.12 (d, 6.6)[a]	21.3[b]	1.40 (d, 6.9)	21.2	1.14 (d, 6.9)	17.6
13	1.18 (d, 7.2)[a]	20.8[b]	0.94 (d, 6.6)[a]	21.6[b]	3.97 (dd, 11.7, 2.4, H_α) 3.79 (dd, 11.7, 1.2, H_β)	64.9	3.90 (dd, 11.1, 3.0, H_α) 3.66 (dd, 11.1, 2.4, H_β)	65.7
14						74.9		75.0
15					1.53 (s)	31.3	1.26 (s)	23.6
16					1.57 (s)	27.8	1.41 (s)	27.6

[a] May be interchangeable. [b] May be interchangeable.

instead observed at δ 1.04 (3H, d, J = 6.9 Hz, H-9), 3.19 (1H, br dq, J = 6.9, 6.9 Hz, H-8), 2.00 (1H, d, J = 15.3 Hz, H-7), and 2.36 (1H, dd, J = 15.3, 5.1 Hz, H-7). The assignments were confirmed by COSY cross-peaks and HMBC correlations of H_2-7 to C-5 (δ 128.7), C-6 (δ 132.2), and C-9 (δ 17.9) and of H_3-9 to C-7 (δ 31.0) and C-8a (δ 125.2). In addition, the replacement of two carbonyl carbons of the quinone ring at δ 181.7 (C-1) and 181.6 (C-2) in **3** with oxygenated aromatic carbons (δ 140.3 and δ 140.9) in **4** indicated that **4** was a reduced form of **3**. The relative configurations of H-8 and H-11 were elucidated by NOESY experiments as shown in Figure 1, which indicated that Me-9 and Me-12 were on the same side of the molecule. Thus, compound **4** was identified and named populene D.

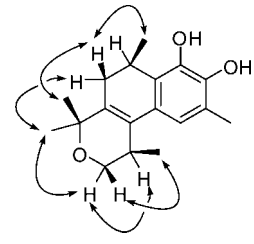

Figure 1. Populene D (**4**) with selected NOESY correlations.

Compound **5** had the molecular formula $C_{15}H_{18}O_4$ (HREIMS). The IR spectrum exhibited absorptions characteristic of carbonyl groups at 1776 (lactone carbonyl) and 1675 cm^{-1} (conjugated

Table 2. ^{1}H and ^{13}C NMR Data for Compounds **5**−**8** in $CDCl_3$

	5[c]		**6**[c]		**7**[c]		**8**[d]	
position	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C	δ_H (mult., *J* in Hz)	δ_C
2		167.4	5.65 (dd, 9.0, 3.0, H_β)	92.6	5.56 (dd, 9.9, 2.7, H_β)	92.2	5.81 (dd, 7.5, 4,5, H_α)	95.9
3	2.72 (d, 3.6)	36.3	1.87 (ddd, 13.5, 9.0, 5.1, H_α) 2.07 (td, 13.5, 3.0, H_β)	36.6	1.84 (ddd, 13.5, 9.9, 5.4, H_α) 2.04 (ddd, 13.5, 13.5, 2.7, H_β)	36.8	2.00 (m)	36.1
4	3.88 (tq, 7.2, 3.6)	27.5	3.84 (m, H_β)	26.2	4.09 (m, H_β)	27.2	4.10 (m)	27.1
4a		127.9		126.3		125.1		127.2
5		126.2		127.1		109.4		111.4
6	7.40 (s)	127.8	7.18 (s)	125.0		157.7		158.7
7		123.5		121.0		110.4		110.6
8		145.4		146.2		149.3		149.9
8a		139.2		140.0		134.6		134.9
1′		205.8		207.1		195.3		196.1
2′	3.47 (sept, 6.9)	37.2	3.45 (sept, 6.9)	37.4	2.75 (dq, 6.9, 5.1)	41.2	2.75 (m)	42.1
3′	1.21 (d, 6.9)[a]	19.0[b]	1.17 (d, 6.9)[a]	19.1[b]	1.16 (d, 6.9)	11.0	1.17 (d, 6.5)	11.8
4′	1.14 (d, 6.9)[a]	19.4[b]	1.15 (d, 6.9)[a]	19.6[b]	4.03 (dd, 11.1, 11.1) 4.43 (dd, 11.1, 5.1)	71.6	4.05 (dd, 11.5, 11.5) 4.45 (dd, 11.5, 5.5)	72.6
4-Me	1.31 (d, 7.2)	20.2	1.25 (d, 6.9)	22.3	1.28 (d, 6.9)	22.4	1.32 (d, 7.0)	23.0
7-Me	2.30 (s)	15.5	2.23 (s)	15.3	2.09 (s)	8.1	2.11 (s)	9.0

[a] May be interchangeable. [b] May be interchangeable. [c] 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. [d] 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR.

carbonyl). The ^{13}C NMR spectrum (Table 2) showed 15 resonances, which corresponded by DEPT analysis to three methines (one sp^2), one methylene, four methyls, and seven sp^2 quaternary carbons including two carbonyl carbons (δ_C 167.4 and 205.8). The ^{1}H NMR (Table 2) and COSY spectra allowed assignment of signals to a dihydrocoumarin moiety[19,20] at δ 1.31 (3H, d, J = 7.2 Hz, 4-Me), 2.72 (2H, d, J = 3.6 Hz, H_2-3), 3.88 (1H, tq, J = 7.2, 3.6 Hz, H-4), and 7.40 (1H, s, H-6). This moiety was also supported by the ^3J HMBC correlations between the methine proton H-4 and aromatic carbons C-5 (δ 126.2) and C-8a (δ 139.2), and a lactone carbonyl (δ 167.4). Signals of a 2-methyl-1-oxopropyl unit [δ 3.47 (1H, sept, J = 6.9, H-2′), 1.21 (3H, d, J = 6.9 Hz, H-3′), and 1.14, (3H, d, J = 6.9, H-4′)] were also observed in the ^{1}H NMR spectrum, whose HMBC correlation between an aromatic proton H-6 (δ 7.40) and C-1′ (δ 205.8) supported its connection at C-5 of the dihydrocoumarin moiety. An aromatic methyl signal at δ 2.30 was attributed to 7-Me due to its HMBC correlation with C-6 (δ 127.8), C-7 (δ 123.5), and C-8 (δ 145.4). Additionally, a downfield chemical shift of C-8 to δ 145.4 indicated its connection to an OH group. Compound **5** was named populene E.

Compound **6** was obtained as a yellow gum ($C_{15}H_{20}O_4$ on the basis of HREIMS). The UV and IR spectra were similar to those of **5**, but with one carbonyl absorption at 1668 cm^{-1}. The NMR (Table 2) data were comparable to those of **5**, except for the replacement of a lactone carbonyl (δ 167.4) in **5** with a hemiacetal proton signal of H-2 at δ_H 5.65 (dd, J = 9.0, 3.0 Hz; δ_C 92.6) in **6**. The large coupling constant (13.5 Hz) was characteristic of geminal methylene protons, H-3β (2.07, td, J = 13.5, 3.0 Hz) and H-3α (1.87,ddd, J = 13.5, 9.0, 5.1 Hz), while the vicinal coupling constants of 9.0 and 5.1 Hz indicated pseudo-*trans*-diaxial coupling of H-3α with H-2 and H-4, respectively. This was also in agreement with the multiplicity of H-3β observed as a triplet of doublets with a large (J_{gem} = 13.5 Hz) and a small ($J_{ax\text{-}eq}$ = 3.0 Hz) coupling constant, justifying its *syn* relationship to H-2 and H-4. Compound **6** was thus identified and named populene F.

Compound **7** was obtained as a yellow gum ($C_{15}H_{18}O_5$). The ^{1}H and ^{13}C NMR spectra (Table 2) were similar to those of **6** except that an aromatic proton (H-6) present in **6** was absent and a methyl signal (Me-4′) was replaced by oxymethylene protons resonating at δ 4.43 (1H, dd, J = 11.1, 5.1 Hz, H-4′) and 4.03 (1H, dd, J = 11.1, 11.1 Hz, H-4′) in **7**. A ^3J HMBC correlation between oxymethylene protons (H_2-4′) with C-6 (δ 157.7) of an aromatic moiety established their fusion by an ether linkage at C-6. The small coupling constant ($J_{2',4'ax}$ = 5.1 Hz) indicated that H-2′ was equatorially oriented. Thus, compound **7** was named populene G.

Compound **8** had the molecular formula $C_{15}H_{18}O_5$. The mass and NMR spectra of **7** and **8** indicated that they were diastereomers. The main spectroscopic differences were the downfield shift of H-2 in **8** at δ 5.81 and the smaller coupling constants (dd, J = 7.5, 4.5 Hz) as compared to those of **7** at δ 5.56 (dd, J = 9.9, 2.7 Hz). The coupling constant J_{2-3} of 7.5 and 4.5 Hz indicated $J_{eq\text{-}ax}$ and $J_{eq\text{-}eq}$, therefore suggesting an α-orientation of H-2. Thus, compound **8** was named populene H.

All of the isolated compounds except for **1**, **2**, **5**, **8**, **9**, and **12**, for which insufficient materials were available, were evaluated for cytotoxicity against four human cancer cell lines: breast cancer (MCF-7), cervical cancer (HeLa), colon cancer (HT-29), and oral cavity cancer (KB). They were also tested for antibacterial activity against both Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Enterococcus faecalis*, *Salmonella typhi*, *Shigella sonei*, and *Pseudomonas aeruginosa*) bacteria. The results are summarized in Table 3. (+)-Gossypol (**18**) exhibited potent cytotoxic activity against HeLa and KB cell lines, with IC_{50} values of 0.08 and 0.04 μg/mL, respectively. Mansonone E (**11**) showed good activity against all four cancer cell lines, especially MCF-7 (IC_{50} 0.05 μg/mL). Populene D (**4**) and mansonone D (**10**) possessed strong inhibitory activity against HeLa and MCF-7, respectively, whereas populene C (**3**) exhibited moderate inhibitory activity against all four cell lines. Antibacterial activity against *B. subtilis* was found for 7-hydroxycadalene (**15**). (+)-6,6′-Methoxygossypol (**19**) was weakly active against *E. faecalis*, *B.subtilis*, and *S. aureus*, whereas (+)-gossypol (**18**) exhibited moderate activity against *B. subtilis* and *S. aureus*. None of the compounds were active against *S. typhi*, *S. sonei*, or *P. aeruginosa*. Compounds **6**, **7**, **13**, and **17** showed no cytotoxic or antibacterial activity.

Experimental Section

General Experimental Procedures. Melting points were determined on an Electrothermal 9100 melting point apparatus and were uncorrected. Optical rotation was measured in $CHCl_3$ on a JASCO P-1020 polarimeter. UV spectra were measured with a SPECORD S100 spectrophotometer (Analytikjena). The IR spectra were measured with a FTS 165 FT-IR Perkin-Elmer spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using Bruker Avance 300 and 500 MHz spectrometers. The EIMS and HREIMS mass spectra were obtained from a Micromass LCT mass spectrometer. Quick column chromatography (QCC) was carried out on silica gel 60 F_{254} (Merck). Precoated plates of silica gel 60 GF_{254} were used for analytical purposes.

Material. Fresh stems of *T. populnea* were collected from Suratthani Province in the Southern part of Thailand in 2005. The plant was

Table 3. Cytotoxic and Antibacterial Activities of Compounds Isolated from *T. populnea*

	cytotoxicity against human cancer cell lines, IC_{50} (μg/mL)				antibacterial activity, MIC (μg/mL)		
compound	MCF-7	HeLa	HT-29	KB	*B. subtilis*	*S. aureus*	*E. faecalis*
3	2.35	3.40	2.90	3.00	4.69	–[b]	–
4	1.85	0.95	2.37	3.10	4.69	–	–
10	0.80	2.80	>5	4.90	2.34	–	–
11	0.05	0.55	0.18	0.40	4.69	–	–
14	>5	>5	>5	>5	–	–	–
15	>5	>5	>5	>5	0.59	–	–
16	>5	>5	>5	>5	–	–	–
18	NT[a]	0.08	>5	0.04	1.17	1.17	–
19	4.00	>5	3.00	>5	2.34	4.69	1.17

[a] NT = not tested. [b] Inactive (>10 μg/mL).

identified by Prof. Puangpen Sirirugsa, and a voucher specimen (No. SB 01-001) has been deposited at the Herbarium of the Department of Biology, Prince of Songkla University (PSU).

Extraction and Isolation of Compounds from the Dark Heartwood of *T. populnea*. The air-dried heartwood of *T. populnea* (2.10 kg) was extracted with CH_2Cl_2 over a period of 5 days at room temperature. Evaporation of the solvent under reduced pressure furnished a dark residue (37.5 g). This was subjected to QCC on silica gel, eluting with CH_2Cl_2, and separated into eight fractions (A−H). Fraction A was purified by QCC using a gradient of hexane−acetone to afford nine fractions (A_1−A_9). Fractions A_2 and A_3 were combined and purified by QCC using a gradient of acetone−hexane as a mobile phase to give **15** (10.2 mg), **17** (8.3 mg), and **9** (2.5 mg), respectively. Fractions A_5 and A_6 were combined and then separated by QCC with a gradient system of acetone−hexane to afford **5** (2.0 mg) and **12** (2.0 mg). Fractions A_7 and A_8 were separately purified by QCC using a gradient of CH_2Cl_2−hexane to yield **19** (4.0 mg) from A_7 and **14** (4.5 mg), **11** (18.1 mg), and **18** (3.3 mg) from A_8. Fraction F was separated by QCC with a gradient system of increasing CH_2Cl_2 in hexane to afford nine fractions (F_1−F_9). Fraction F_4 was further purified by QCC using a gradient of CH_2Cl_2−hexane to give **3** (10.0 mg) and **4** (14.9 mg). Fraction F_6 was subjected to QCC using 20% acetone in hexane to afford four fractions (F_{6A}−F_{6D}). Fraction F_{6B} was further separated by QCC with a solvent system of 2% acetone−$CHCl_3$ to afford **6** (12.6 mg). Fraction F_{6C}, upon standing overnight at room temperature, gave a yellow solid of **8** (4.2 mg), and the mother liquor gave **7** (4.1 mg). Fraction G was purified by QCC with a gradient of acetone−CH_2Cl_2 to give five fractions (G_A−G_E). Fraction G_A was subjected to precoated TLC using 50% CH_2Cl_2−hexane (4 runs) to give **16** (5.1 mg). Fraction G_C gave **10** (93.0 mg). Fraction H, upon standing overnight at room temperature, gave red-brown crystals of **13** (30.5 mg).

Extraction and Isolation of Compounds from the Wood of *T. populnea*. The air-dried wood of *T. populnea* (1.40 kg) was extracted with CH_2Cl_2 over a period of 5 days at room temperature. Evaporation of the solvent under reduced pressure furnished a dark green residue (10.2 g). This was subjected to QCC on silica gel, eluted with a gradient of hexane−acetone to give six fractions (A−F). Fraction C was then purified by QCC using a gradient of hexane−acetone to afford **18** (22.6 mg). Fraction D, upon standing overnight at room temperature, gave **19** (20.3 mg). Fraction E was separated by QCC with a gradient system of increasing polarity (acetone−hexane) to afford five fractions (E_1−E_5). Fraction E_2 was subjected to precoated plates using 50% CH_2Cl_2−hexane as a mobile phase (4 runs) to give **11** (1.6 mg). Fraction E_3 was subjected to precoated plates using 3% MeOH−CH_2Cl_2 as a mobile phase (4 runs) to give **1** (2.3 mg) and **2** (2.1 mg).

Populene A (1): yellow gum; $[\alpha]^{25}_D$ +57.9 (*c* 0.54, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 216 (4.22), 251 (3.98), 259 (3.91), 279 (3.44), 289 (3.40) nm; IR (neat) ν_{max} 3365, 2959, 2870, 1617, 1591, 758 cm^{-1}; NMR data see Table 1; EIMS *m/z* 246 $[M]^+$ (8), 211 (18), 185 (33), 169 (25), 72 (100), 69 (47); HREIMS *m/z* 246.1262 (calcd for $C_{15}H_{18}O_3$, 246.1256).

Populene B (2): yellow gum; $[\alpha]^{25}_D$ −63.6 (*c* 0.37, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 213 (4.15), 251 (3.85), 259 (3.80), 278 (3.32), 290 (3.29) nm; IR (neat) ν_{max} 3387, 2959, 2871, 1716, 1524, 754 cm^{-1}; NMR data see Table 1; EIMS *m/z* 246 $[M]^+$ (50), 199 (31), 185 (100), 157 (23), 129 (46); HREIMS *m/z* 246.1255 (calcd for $C_{15}H_{18}O_3$, 246.1256).

Populene C (3): orange solid; mp 168−170 °C; $[\alpha]^{25}_D$ −46.0 (*c* 0.27, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 213 (4.18), 242 (3.79), 259 (3.98), 380 (3.03) nm; IR (neat) ν_{max} 2974, 2930, 2871, 1757, 1698, 1657 cm^{-1}; NMR data see Table 1; EIMS *m/z*, 286.1556 $[M + 2]^+$ (17), 271 (53), 241 (72), 85 (66), 83 (100); HREIMS *m/z* 286.1556 $[M+2]^+$ (calcd for $C_{18}H_{24}O_3$, 284.1412).

Populene D (4): brown gum; $[\alpha]^{25}_D$ −21.9 (*c* 0.75, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 219 (4.10), 264 (3.92), 277sh (3.81), 366 (2.86) nm; IR (neat) ν_{max} 3417, 2967, 2930, 2863, 1653, 754 cm^{-1}; NMR data see Table 1; EIMS *m/z* 288 $[M]^+$ (15), 274 (21), 241 (20), 273 (100); HREIMS *m/z* 288.1736 (calcd for $C_{18}H_{24}O_3$, 288.1725).

Populene E (5): yellow-brown gum: $[\alpha]^{25}_D$ +30.1 (*c* 0.58, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 228 (4.11), 273 (3.86) nm; IR (neat) ν_{max} 3410, 2970, 2925, 2873, 1776, 1675, 1616 cm^{-1}; NMR data see Table 2; EIMS *m/z* 262 $[M]^+$ (31), 220 (34), 191 (43), 219 (100); HREIMS *m/z* 262.1210 (calcd for $C_{15}H_{18}O_4$, 262.1205).

Populene F (6): yellow gum; $[\alpha]^{25}_D$ +7.5 (*c* 0.23, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 219 (4.23), 232 (4.14), 281 (3.00) nm; IR (neat) ν_{max} 3417, 2967, 2930, 2871, 1668, 1576 cm^{-1}; NMR data see Table 2; EIMS *m/z* 264 $[M]^+$ (27), 221 (100), 203 (22), 193 (26), 179 (44), 177 (25), 151 (20); HREIMS *m/z* 264.1353 (calcd for $C_{15}H_{20}O_4$, 264.1362).

Populene G (7): yellow gum; $[\alpha]^{25}_D$ +62.7 (*c* 0.07, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 214 (4.09), 235 (3.98), 286 (3.95), 339 (3.66) nm; IR (neat) ν_{max} 3424, 2959, 2930, 2871, 1661, 1591, 1429 cm^{-1}; NMR data see Table 2; EIMS *m/z* 278 $[M]^+$ (98), 249 (27), 239 (100), 208 (36), 192 (35); HREIMS *m/z* 278.1196 (calcd for $C_{15}H_{18}O_5$, 278.1154).

Populene H (8): yellow gum; $[\alpha]^{25}_D$ +43.7 (*c* 0.04, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 214 (4.06), 237 (3.95), 286 (3.96), 339 (3.60) nm; IR (neat) ν_{max} 3417, 2967, 2930, 2871, 1661, 1587 cm^{-1}; NMR data see Table 2; EIMS *m/z* 278 $[M]^+$ (54), 234 (56), 208 (25), 192 (24), 72 (100); HREIMS *m/z* 278.1159 (calcd for $C_{15}H_{18}O_5$, 278.1154).

Antimicrobial Assay. The compounds isolated from *T. populnea* were tested against the microorganisms *Bacillus subtilis* (obtained from Department of Industrial Biotechnology, PSU), *Staphylococcus aureus* (TISTR517) (obtained from Microbial Resources Center (MIRCEN), Bangkok, Thailand), *Pseudomonas aeruginosa*, *Enterococcus faecalis*, *Shigella sonei*, and *Salmonella typhi*. The last four microorganisms were obtained from the Department of Pharmacognosy and Botany, PSU. The antibacterial assay employed was the same as described in Boonsri et al.[10] Vancomycin, which was used as a standard, showed an antibacterial activity of 0.078 μg/mL.

Cytotoxic Assay. The procedure for the cytotoxic assay was performed by the sulforhodamine B (SRB) assay as described by Skehan et al.[21] In this study, four cancer cell lines obtained from the National Cancer Institute, Bangkok, Thailand, were used: MCF-7 (breast adenocarcinoma), KB (human oral cancer), HeLa (human cervical cancer), and HT-29 (colon cancer). Camptothecin, which was used as a standard, showed cytotoxic activity in the range 0.2−2.0 μg/mL.

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References and Notes

(1) Milbrodt, M.; Konig, W. A.; Hausen, B. M. *Phytochemistry* **1997**, *45*, 1523–1525.
(2) Vasudevan, M.; Parle, M. *Phytomedicine* **2006**, *13*, 677–687.
(3) Puckhaber, L. S.; Stipanovic, R. D. *J. Nat. Prod.* **2004**, *67*, 1571–1573.
(4) Neelakantan, S.; Rajagopalan, V.; Raman, P. V. *Indian J. Chem.* **1983**, *22B*, 95–96.
(5) Tiew, P.; Puntumchai, A.; Kokpol, U.; Chavasiri, W. *Phytochemistry* **2002**, *60*, 773–776.
(6) Wang, D.; Xia, M. Y.; Cui, Z.; Tashiro, S.-I.; Onodera, S.; Ikejima, T. *Biol. Pharm. Bull.* **2004**, *27*, 1025–1030.
(7) Duh, C.-Y.; Chien, S.-C.; Song, P.-Y.; Wang, S.-K.; El-Gamal, A. A. H.; Dai, C.-F. *J. Nat. Prod.* **2002**, *65*, 1853–1856.
(8) Silva, G. H.; Teles, H. L.; Zanardi, L. M.; Yong, M. C. M.; Eberlin, M. N.; Hadad, R.; Pfenning, L. H.; Costa-Neto, C. M.; Castro-Gamboa, I.; Bolzani, V. S.; Araujo, A. R. *Phytochemistry* **2006**, *67*, 1964–1969.
(9) Kim, J.-P.; Kim, W.-G.; Koshino, H.; Jung, J.; Yoo, I.-D. *Phytochemistry* **1996**, *43*, 425–430.
(10) Boonsri, S.; Karalai, C.; Ponglimanont, C.; Kanjana-opas, A.; Chantrapromma, K. *Phytochemistry* **2006**, *67*, 723–727.
(11) Boonnak, N.; Karalai, C.; Chantrapromma, S.; Ponglimanont, C.; Fun, H.-K.; Kanjana-opas, A.; Laphookhieo, S. *Tetrahedron* **2006**, *62*, 8850–8859.
(12) Cheenpracha, S.; Yodsaoue, O.; Karalai, C.; Ponglimanont, C.; Subhadhirasakul, S.; Tewtrakul, S.; Kanjana-opas, A. *Phytochemistry* **2006**, *67*, 2630–2634.
(13) Badria, F. A.; Houssein, W. E.; Zaghloul, M. G.; Halim, A. F. *Pharm. Biol.* **2001**, *39*, 120–126.
(14) Alois, A.; Mace, M. E.; Howell, C. R. *Phytochemistry* **1975**, *14*, 1077–1081.
(15) Tiew, P.; Takayama, H.; Kitajima, M.; Aimi, N.; Kokpol, U.; Chavasiri, W. *Tetrahedron lett.* **2003**, *44*, 6759–6761.
(16) Chantrapromma, S.; Boonsri, S.; Fun, H.-K.; Karalai, C. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2007**, *E63*, o2749−o2750.
(17) Cheenpracha, S.; Srisuwan, R.; Karalai, C.; Ponglimanont, C.; Chantrapromma, K.; Fun, H.-K.; Anjum, S.; Rahman, A.-U. *Tetrahedron* **2005**, *61*, 8656–8662.
(18) Letcher, R. M.; Shirley, I. M. *Phytochemistry* **1992**, *31*, 4171–4172.
(19) Shen, Y.-C.; Wang, L.-T.; Khalil, A. T.; Kuo, Y.-H. *Chem. Pharm. Bull.* **2004**, *52*, 402–405.
(20) Zhang, X.-F.; Wang, H.-M.; Song, Y.-L.; Nie, L.-H.; Wang, L.-F.; Liu, B.; Shen, P.-P.; Liu, Y. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 949–953.
(21) Skehan, P.; Storeng, R.; Scudiero, D.; Monks, A.; McMahon, J.; Vistica, D.; Warren, J. T.; Bokesch, H.; Kenney, S.; Boyd, M. R. *J. Natl. Cancer Inst.* **1990**, *82*, 1107–1112.

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X-Ray Structural Determination: A Powerful Technique for Natural Products Research and Drug Discovery

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ABSTRACT The correct characterization and identification of natural products and natural product artifacts are of paramount importance in natural products research and drug discovery in particular and to the scientific community in general. The simple ability of single crystal X-ray structure determination to characterize and make the differentiation between natural products and natural product artifacts is given for a compound containning a chromene ring, macluraxanthone (which was isolated from *Cratoxylum formosum* subsp. *Pruniflorum*) is a natural product or a natural product artifact. Morover the three examples of co-crystal compounds which were isolated from (i) *Garcinia schomburgkiana* Pierre, (ii) *Artocarpus altilis* and (iii) *Cratoxylum cochinchinense,* medicinal plants in Thailand are presented. A simple technique for finding the absolute configuration of natural product molecules by inserting of heavy-atom containing solvent molecules into the crystal structure will also presented.

(**Keywords:** Natural products, Drug discovery, Crystal structure, Macluraxanthone, Chromene ring, *Garcinia schomburgkiana* Pierre, *Artocarpus altilis*, *Cratoxylum* cochinchinense, Cerbera *odollam*, *Cratoxylum formosum* subsp. *pruniflorum*)

INTRODUCTION

Drug discovery from natural products resources have been extensively studied worldwide because natural product compounds with their great structural diversity have traditionally provided most of the drugs in use. They offer major opportunities for finding novel low molecular weight leading structures that are active against a wide range of assay targets. The most important step in the discovery process is the identification of compounds with interesting biological activity. X-ray structure determination is a powerful technique for natural products research and drug discovery because this technique is able to provide a lot of information on stereochemistry and the detailed three-dimension structures that emerge can be co-related to the activities of these structures. Moreover the absolute configuration of natural products molecules can also be determined by this technique.

This work shall be based on the results from our natural products research. First of all, the structures with disorder and co-crystals structures (see Figure. 1-3) which are not infrequent in natural products compounds are shown. The three examples presented are compounds which were isolated from (i) *Garcinia schomburgkiana* Pierre (Figure. 1), (ii) *Artocarpus altilis* (Figure. 2) and (iii) *Cratoxylum cochinchinense* (Figure. 3) which are medicinal plants in Thailand. Only X-ray single-crystal structure determination technique is able to resolve co-crystal structures.

Secondly, a simple technique for finding absolute configuration of natural products molecules by inserting of heavy-atom containing solvent molecules into the crystal structures have also devised. This technique is applied to a compound isolated from *Cerbera odollam* (Figure. 4) is presented.

Last but not least, natural products are frequently tested for their potential to be used as drugs and the ability to differentiate between natural product and natural product artifact is an extremely important factor in order as not to make the wrong conclusions during testing of these compounds for potential drug application. The correct identification between natural products and natural products artifacts is therefore of paramount importance. The simple ability of X-ray single-crystal structure determination to differentiate between natural producst and natural products artifacts for a compound containing a chromene ring which was isolated from *Cratoxylum formosum* subsp. *pruniflorum*. (Figure. 5) is also presented to demonstrate this principle .

X-RAY DATA STRUCTURE DETERMINATION

A single crystal suitable for X-ray data collection (size smaller than 0.5×0.5×0.5 mm^3 accordingly) was mounted on a glass fiber with epoxy cement. Crystallographic data were collected at 100.0(1) K (for compounds 1-3 and 5) or 297(2) K (for compound 4). The data were collected using a Bruker Apex CCD diffractometer with a graphite monochromated MoKα radiation (λ = 0.71073 Å) at a detector distance of 5 cm and swing angle of –35°. A hemisphere of the reciprocal space was covered by a combination of three sets of exposures using SMART program (Seimens, 1996). Each set had a different φ angle (0, 88, 180°), and each exposure covered 0.3° in ω. Coverage of the unique set is over 99% complete for each case. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analyzing the duplicate reflections, and was found to be negligible. The collected data were reduced using *SAINT* program (Seimens, 1996) and the empirical absorption corrections were performed using *SADABS* program (Sheldrick, 1997). The structure was solved by direct methods and refined by least-squares using the *SHELXTL* software package (Sheldrick, 1998).

RESULTS AND DISCUSSIONS

X-ray crystallographic analysis of compounds 1-5

Compound 1 The co-crystals of Clusciacitran A, Clusciacitran B, Fluorinated clusciacitran A and Fluorinated clusciacitran B from *Garcinia schomburgkiana* Pierre.

Compound **1** (**Figure. 1**) consists of a disordered mixture of clusiacitran A and fluorinated clusiacitran A, clusiacitran B and fluorinated clusiacitran B, giving effectively one molecule overall. In all the components, the cyclohexane rings *D* adopt half-chair conformations (Fun, Koysomboon *et al.*, 2006).

$0.45C_{23}H_{24}O_4.0.45C_{23}H_{24}O_4.$
$0.05C_{23}H_{23}FO_4.0.05C_{23}H_{23}FO_4$, M = 366.24, monoclinic, $P2_1/c$, a = 9.6691(2) Å, b = 10.5583(2) Å, c = 18.9279(3) Å, β = 103.160(1)°, V = 1881.59(6) $Å^3$, Z = 4, D_{cal} = 1.293 $Mg.m^{-3}$, T = 100.0(1) K. Yellow needle single crystal size 0.42 x 0.13 x 0.11 mm. Four thousand three hundred and thirty independent reflections (4330 independent, R_{int} = 0.047) were collected. Largest electron density residue: 0.25 $eÅ^{-3}$, R_1(for $I > 2\sigma(I)$) = 0.057 and wR_2 = 0.135 with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F^2_o - F^2_c)^2 / \Sigma w(F^2_o)^2)^{0.5}$.

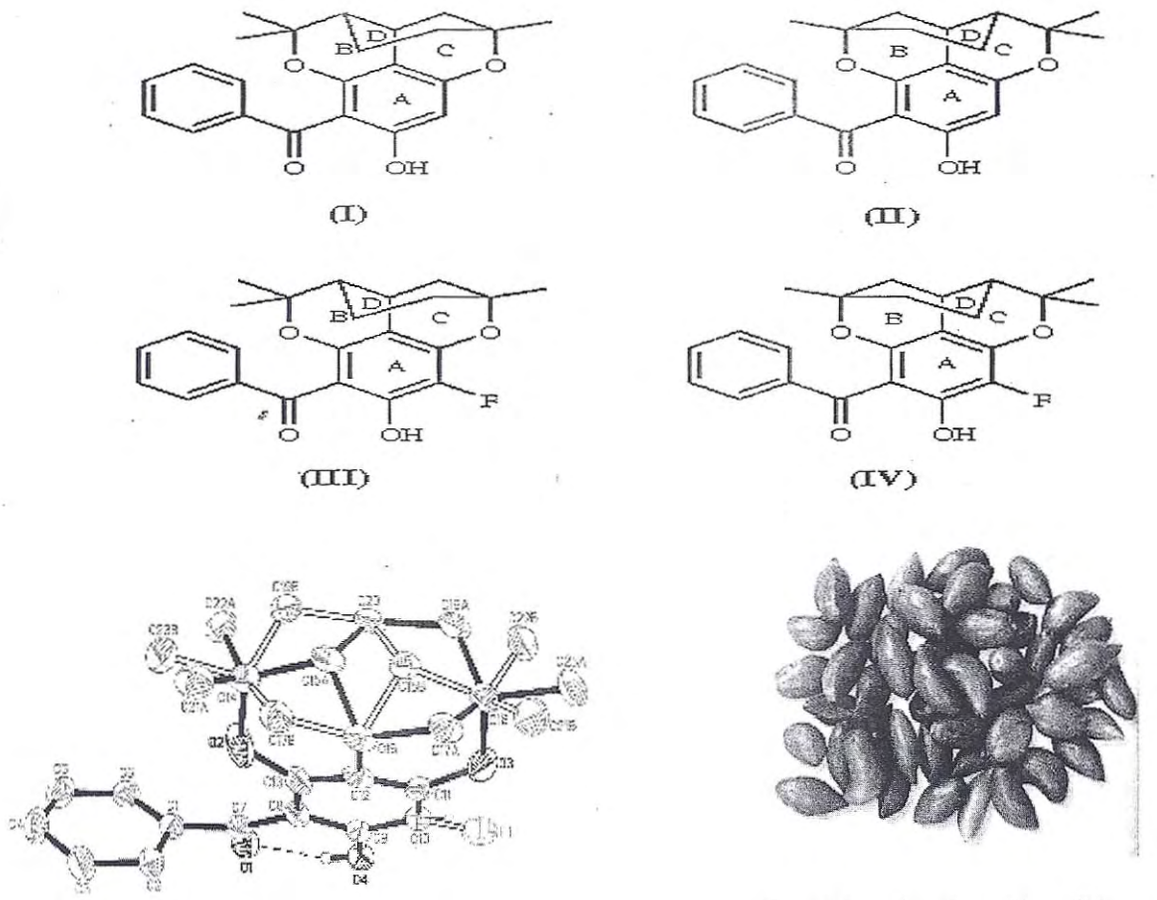


Figure. 1. The chemical diagram and X-ray structure of co-crystals of Clusciacitran A (I), Clusciacitran B (II), Fluorinated clusciacitran A (II) and Fluorinated clusciacitran (IV) (compound **1**) from *Garcinia schomburgkiana* Pierre.

Compound 2 **The co-crytals of Friedelan-3β-ol and Friedelin from *Artocarpus altilis*.**

Compound **2** is a disordered mixture of two compounds, *viz* friedelan-3β-ol and friedelin, which were isolated from *Artocarpus altilis*. The molecular structure of **2** contains a fused ring system *A*/*B*/*C*/*D*/*E* known as the friedelan skeleton. In this skeleton, the *D*/*E* ring junction is cis- fused and the other junctions are trans-fused. The cyclohexane rings *A*, *B* and *C* adopt chair conformations, while ring *D* has a twist-boat conformation and *E* is in a boat conformation. (Fun e*t al.*, 2007).

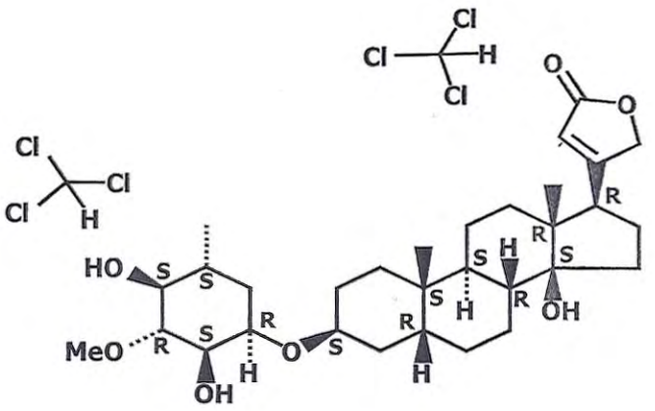
$0.75C_{30}H_{51}O.0.25C_{30}H_{50}O$, M = 428.16, Triclinic, $P1$, a = 6.3422(3) Å, b = 7.3709(4) Å, c = 29.5443(16) Å, α = 90.843(2)°, β = 91.334(2)°, γ = 115.372(2)°, V = 1247.11(11) Å^3, Z = 2, D_{cal} = 1.140 Mg.m^{-3}, T = 100.0(1) K. Colorless plate single crystal size 0.60 x 0.57 x 0.23 mm. Eight thousand four hundred and eighty nine independent reflections (8489 independent, R_{int} = 0.038) were collected. Largest electron density residue: 0.52 eÅ^{-3}, R_1(for $I > 2\sigma(I)$) = 0.053 and wR_2 = 0.145 with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F^2_o - F^2_c)^2 / \Sigma w(F^2_o)^2)^{0.5}$.

Compound 4 The **14β-hydroxy-3β-O-(L-thevetosyl)-5β-card-20(22)-enolide methanol solvate from *Cerbera odollam*.**

Compound 4 contains one cardinolide molecule and two chloroform molecules (Figure. 4). The steroid nucleus has a cis/trans/cis configuration for the *A-B*/*B-C*/*C-D* rings and the cyclohexane *A*, *B* and *C* rings have standard chair conformations; the cyclopentane ring *D* has an envelope conformation. The attached lactone ring (O1/C20-C23) is essentially planar (Chantrapromma *et al.*, 2003).

$C_{30}H_{46}O_8.2CHCl_3$, M = 773.40, Orthorhombic, $P2_12_12_1$, a = 7.6426(4) Å, b = 9.1932(5) Å, c = 54.362(3) Å, $\alpha = \beta = \gamma = 90.00°$, V = 3819.5(4) Å^3, Z = 4, D_{cal} = 1.345 Mg.m^{-3}, T = 297(2) K. Colorless block single crystal size 0.36 x 0.34 x 0.24 mm. Six thousand six hundred and twenty-six independent reflections (6626 independent, R_i= 0.044) were collected. Absolute structure Friedel pairs = 2780 and Flack parameter = 0.14(14). Largest electron density residue: 0.33 eÅ^{-3}, R_1(for $I > 2\sigma(I)$) = 0.077 and wR_2 = 0.227 with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F^2_o - F^2_c)^2 / \Sigma w(F^2_o)^2)^{0.5}$.

Cerbera odollam



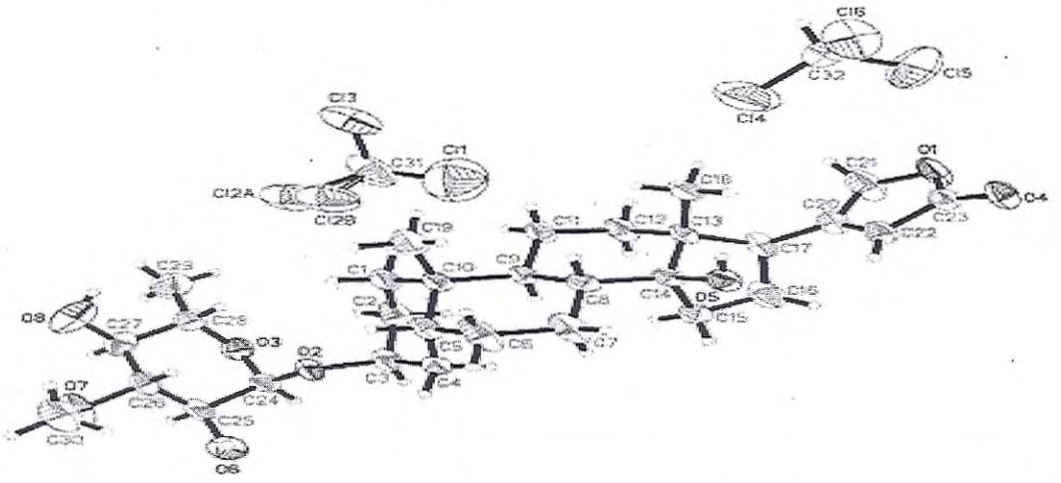


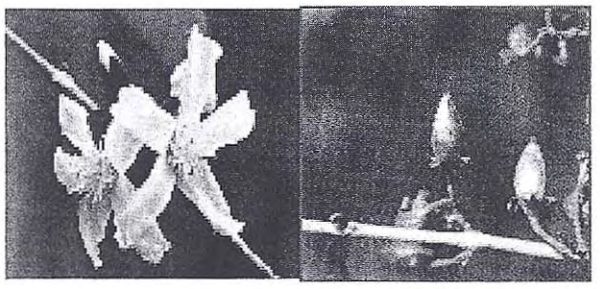
Figure. 4. The absolute configuration and X-ray structure of 14β-hydroxy-3β-O-(L-thevetosyl)-5β-card-20(22)-enolide methanol solvate (compound **4**) from *Cerbera odollam*.

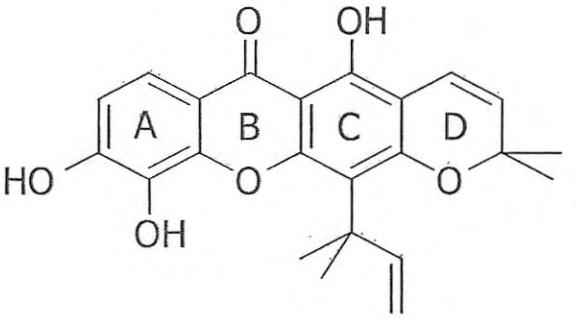
Compound 5 ***M*acluraxanthone from *Cratoxylum formosum* subsp. *pruniflorum*.**

In the molecular structure of Macluraxanthone (compound **5**) (Figure. 5), the xanthene ring system is almost planar, with all atoms lying within 0.066(2) Å of the mean plane. The three individual rings of xanthene (*A*, *B* and *C*) are each essentially planar. The chromene ring, *D*, adopts a

screw-boat conformation. The three hydroxyl groups are each coplanar with the attached rings (Fun, Ng *al.*, 2006).

$C_{23}H_{22}O_6$, M = 394.41, monoclinic, $P2_1/c$, a = 14.0220(8) Å, b = 16.1568(8) Å, c = 8.4157(4) Å, β = 104.423(4)°, V = 1846.49(17) Å^3, Z = 4, D_{cal} = 1.419 Mg.m^{-3}, T = 100.0(1) K. Yellow needle single crystal size 0.46 x 0.08 x 0.04 mm. Four thousand four hundred and fifty-two independent reflections (4452 independent, R_{int} = 0.076) were collected. Largest electron density residue: 0.34 eÅ^{-3}, R_1(for $I > 2\sigma(I)$) = 0.055 and wR_2 = 0.145 with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F^2_o - F^2_c)^2 / \Sigma w(F^2_o)^2)^{0.5}$.





***Cratoxylum formosum* subsp. *pruniflorum*.**

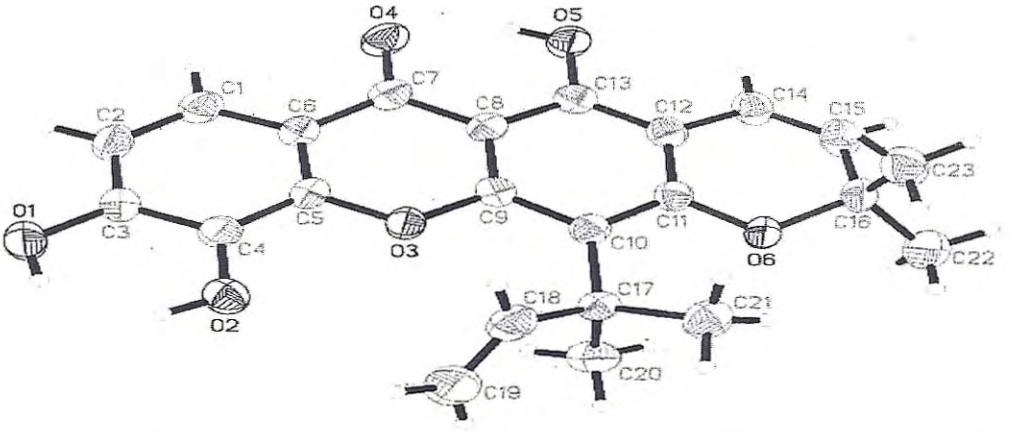


Figure 5. The chemical diagram and X-ray structure of macluraxanthone (compound **5**) from *Cratoxylum formosum* subsp. *pruniflorum*.

Macluraxanthone, a compound containing a chromene ring (ring D in Figure. 5) and with no chiral center, was isolated from *Cratoxylum formosum* subsp. *Pruniflorum*. Compound **5** is a chiral molecule because its mirror image cannot be superposed onto itself. Compound **5** crystallized out in the centrosymmetric space group $P2_1/c$.

Since natural products are produced by enzymatic reactions and therefore each compound only exists as an enantiomerically pure compound, natural products can only crystallized out in the chiral

space groups (space groups with no inversion center, mirror plane nor glide planes) similar to proteins and nucleic acids. The X-ray result indicates that the crude extract from which **5** was obtained is a racemic mixture and that **5** was a natural product artifact.

CONCLUSION

The importance of correct characterization and identifying whether compounds extracted/isolated from plants are really natural products or just artifacts arises from the fact that these compounds are regularly tested for potential uses as drugs. A natural product artifact contains two enantiomers. For these artifacts, the separation of the enantiomers must be done first before conducting the bioactive testing in order to eliminate incorrect conclusions resulting from such testing. This article has given the results and conclusively shown that X-ray single-crystal structure determination is an important, essential and indispensible component for natural products research and drug discovery.

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REFERENCES

1. Boonnak, N., Chantrapromma, S., Fun, H. K. and Karalai, C., 2008, CCDC deposition number CCDC689924.
2. Chantrapromma, S., Usman, A., Fun, H. K., Laphookhieo, S. Karalai, C., Rat-a-pa, Y. And Chantrapromma, K., 2003, *Acta Cryst.*; **C59**, o68-o70.
3. Fun, H. K., Boonnak, N. and Chantrapromma, S., 2007. *Acta Cryst.*, **E63**, o2014-o2016.
4. Fun, H. K., Koysomboon, S., Chantrapromma, K. and Chantrapromma, S., 2006. *Acta Cryst.*, **E62**, o3228-o3230.
5. Fun, H. K., Ng, S. L., Razak, I. A., Boonnak, N. and Chantrapromma, S., 2006. *Acta Cryst.*, **E62**, o130-o132.
6. Seimens, *SMART* and *SAINT*, 1996, *Seimens Analytical X-ray Instruments Inc*, Madison, Wisconsin, USA.
7. Sheldrick, G. M., 1997, *SADABS Program for Empirical Absorption Correction of Area Detector Data*, University of Gottingen.,Germany.
8. Sheldrick, G. M., 1998. *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.