CHEMICAL CONSTITUENTS OF THE RESIN OF *GARCINIA HANBURYI*

By

Chalotorn Boonlua

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

Department of Chemistry

Graduate School

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การศึกษาองค์ประกอบทางเคมีของยางรงทอง

โดย
นางสาวชโลธร บุญเหลือ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมีอินทรีย์
ภาควิชาเคมี
บัณฑิตวิทยาลัย มหาวิทยาลัยศิลปากร
ปีการศึกษา 2550

The graduate school, Silpakorn University accepted thesis entitled "CHEMICAL CONSTITUENTS OF THE RESIN OF *GARCINIA HANBURYI*" by Chalotorn Boonlua in partial fulfillment of the requirements for the degree of master of science, program of organic chemistry.

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Dean of Graduate School

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Thesis advisor

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Thesis committees

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(Opa Bangcharoenpornpong, Ph. D.)

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(Prof. Pittaya Tuntiwachwuttikul, Ph.D.)

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(Somkiat Thadaniti, Ph.D.)

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(Assoc.Prof. Surachai Nimgirawath, Ph.D.)

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(Assoc.Prof. Chutima Limmatvapirat, Ph.D.)

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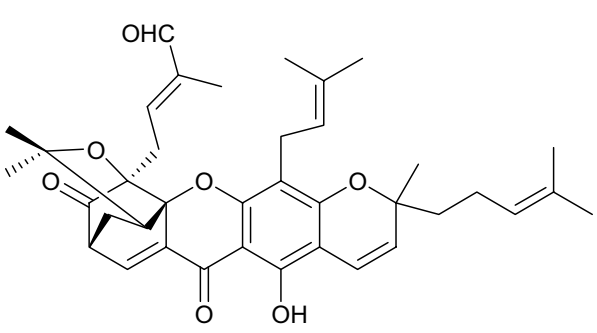
48302201 : สาขาวิชาเคมีอินทรีย์

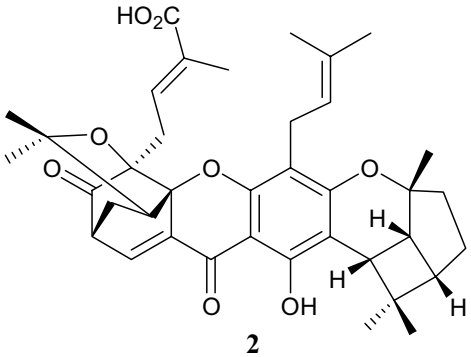
คำสำคัญ : *GARCINIA HANBURYI*; รงทอง; GUTTIFERAE; GAMBOGE; XANTHONES

ชโลธร บุญเหลือ : การศึกษาองค์ประกอบทางเคมีของยางรงทอง อาจารย์ที่ปรึกษาวิทยานิพนธ์ : ศ. ดร. พิทยา ตันติเวชวุฒิกุล. 133 หน้า.

การศึกษาองค์ประกอบทางเคมีของยางรงทอง(*G. hanburyi*) พบสารประกอบประเภทแซนโทน 17 ตัว ในจำนวนนี้ 4 ตัวเป็นสารใหม่ที่พบในธรรมชาติ คือ isogambogenal (**1**), gamboginaic acid A (**2**), isogamboginaic acid B (**3**) และ isogamboginolic acid (**4**) อีก 13 ตัว เป็นสาร known คือ deoxymorellin (**5**), morellin (**6**) isomorellin (**7**), morellic acid (**8**), isomorellic acid (**9**), isomorellinol (**10**), gambogin (**11**), gambogic acid (**12**), isogambogic acid (**13**), gambogenin (**14**), isogambogenin (**15**), gambogenic acid (**16**) และ isogambogenic acid (**17**) พิสูจน์โครงสร้างของสารประกอบด้วยเทคนิคสเปกโตรสโกปี



1



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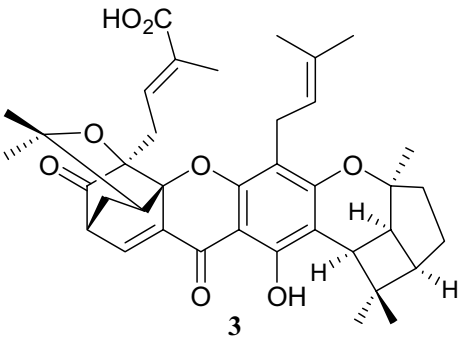

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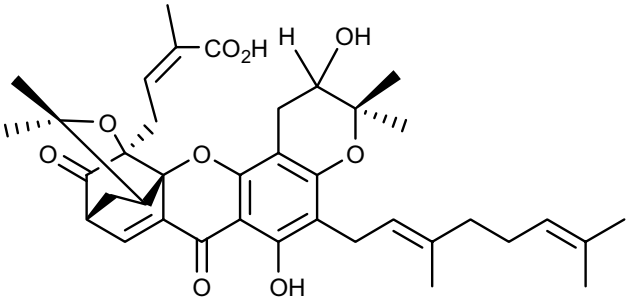

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ภาควิชาเคมี บัณฑิตวิทยาลัย มหาวิทยาลัยศิลปากร ปีการศึกษา 2550

ลายมือชื่อนักศึกษา.....

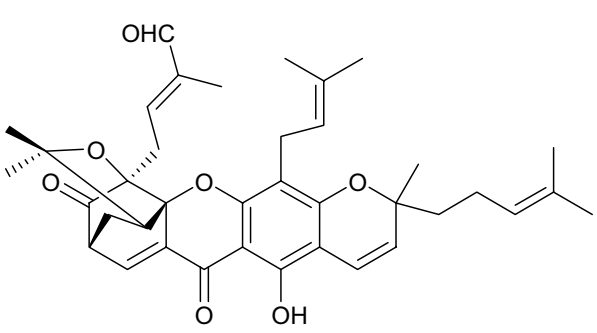
ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์.....

48302201 : MAJOR : ORGANIC CHEMISTRY

KEY WORDS : *GARCINIA HANBURYI*; GUTTIFERAE; GAMBOGE; XANTHONE;

CHALOTORN BOONLUA : CHEMICAL CONSTITUENTS OF THE RESIN OF *GARCINIA HANBURYI*. THESIS ADVISOR : PROF. PITTAYA TUNTIWACHWUTTIKUL, Ph.D. 133 pp.

Seventeen xanthones (**1**-**17**) were isolated from the resin of *Garcinia hanburyi*. Four of them, isogambogenal (**1**), isogamboginaic acid A (**2**), isogamboginaic acid B (**3**) and gamboginolic acid (**4**) were new compounds and thirteen compounds, deoxymorellin (**5**), morellin (**6**) isomorellin (**7**), morellic acid (**8**), isomorellic acid (**9**), isomorellinol (**10**), gambogin (**11**), gambogic acid (**12**), isogambogic acid (**13**), gambogenin (**14**), isogambogenin (**15**), gambogenic acid (**16**) and isogambogenic acid (**17**) were known structures. The structures were determined on the basis of spectroscopic analysis.



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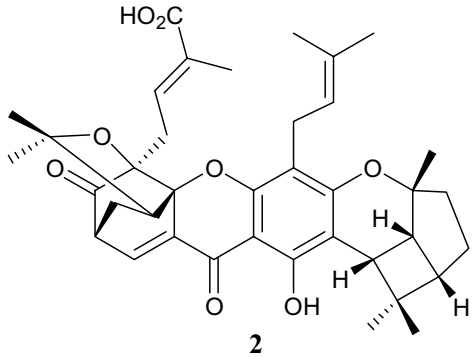

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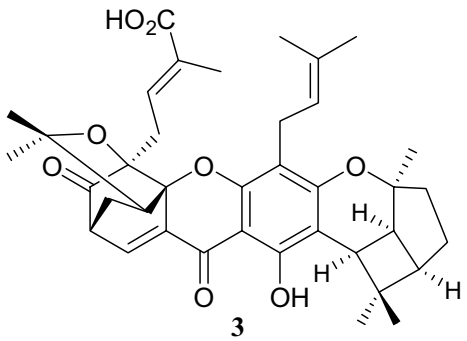

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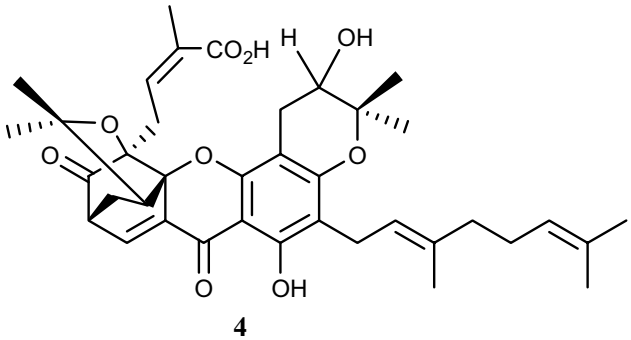

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Department of Chemistry Graduate School, Silpakorn University Academic Year 2007

Student's signature .....

Thesis advisor's signature .....

ACKNOWLEDGMENTS

I wish to express my deepest and sincere gratitude to my advisor, Professor Pittaya Tantiwachwuttikul, for her valuable instructions, expert guidance, excellent suggestions and kindness which are more than I can describe here. Everything will always be in my mind.

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I would like to express my appreciation to the staffs of the Department of Chemistry, Faculty of Science, Silpakorn University for their help and making this thesis possible.

I would like to express my sincere appreciation to the Development and Promotion of Science and Technology Talents project (DPST).

Finally, none of this thesis would have been possible without love and encouragement of my family and friends. I thank them all for their kindness and valuable advice. Everything will always kept in my mind.

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CHAPTER 1

INTRODUCTION

Garcinia is a plant genus of the family Gutiferae, sub-family Clusiaceae native to Asia, Australia, tropical and southern Africa, and Polynesia. The genus, with between 150-300 species of evergreen trees and shrubs, is dioecious and several of its elements are apomictic. The genus *Garcinia* is mainly grown in lowland rain forests of the tropical world and found from sea level to the tops of the highest mountains.

Garcinia hanburyi Hook. f. (Guttiferae) or Gamboge tree grows widely in the tropical rain forest area. Gamboge tree is a native of Cambodia, Southern Vietnam and Thailand. Its common name is *Rongthong* and *Gamboge.*

G. hanburyi is a small to medium-sized tree, up to 15 m tall, with short and straight trunk, up to 20 cm. in diameter, grey bark, smooth and 4-6 mm. thick, exuding a yellow gum-resin. Leaves are opposite, leathery, elliptic or ovate-lanceolate, 10-25 cm. x 3-10 cm., cuneate at base, acuminate at apex and short stalk. Flowers are in clusters or solitary in the axils of fallen leaves, 4-merous, pale yellow and fragrant, unisexual or bisexual. Fruits are a globose berry, 2-3 cm. in diameter, smooth, with recurved sepals at the base and crowned by the persistent stigma, 1-4 seeded. Seeds are 15-20 mm long, surrounded by a pulpy aril. Normally it flowers in November and December and fruits from February to April.

The species are closely related to *G. morella* and G. hanburyi has been considered in the past as a variety of *G. morella*.

Figure 1 *Garcinia hanburyi* Hook. f.

pipe gamboge

resin gamboge

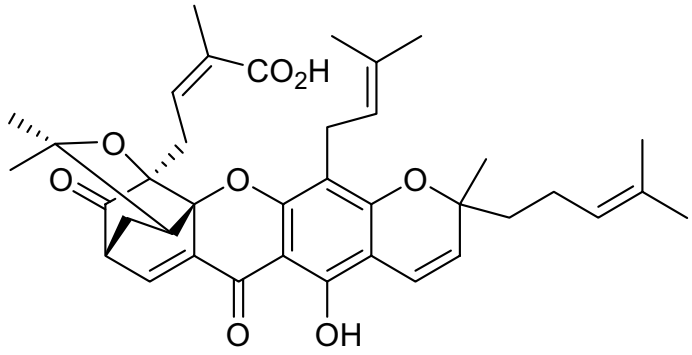
powder gamboge

Figure 2 Gamboge of *G. hanburyi*.

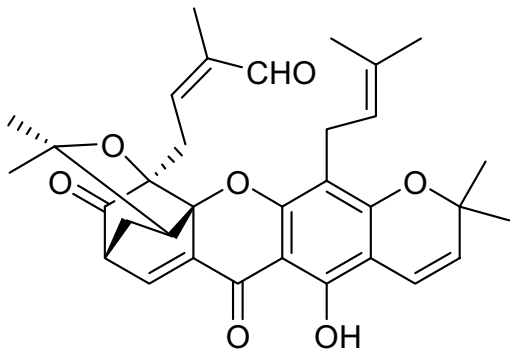
The gum-resin (gamboge), obtained from incisions of the bark of G. *hanburyi*, is used as a golden-yellow colouring matter for varnishes, lacquer, paints and ink. Gamboge is used in traditional medicine as a drastic purgative, an emetic and a vermifuge for treating tape worm. Gamboge is a powerful hydragogue cathartic, causing in large doses much irritation and griping. It is employed in dropsical conditions and in cerebral congestion when it is desirable to lower blood-

pressure rapidly, but is rarely used alone on account of its drastic action. Sometimes it is given to cows as purgative. For external use, the resin, mixed with coconut milk, is applied for treatment of chronic dermatitis. It is well known that gamboge is rich in a variety of compounds such as xanthones, benzophenones, flavonoids, biflavonoids, chalcones and triterpenes.

Gambogic acid (**12**) is the major principal of *G. hanburyi*. Due to the complexity of this type of xanthone derivatives, chemical studies have been carried out on gambogic acid and a related compound, morellin (**6**) [1-5]. The structure of *p*-bromo-benzenesulphonyl ester of morellin has been established by X-ray crystallographic study [3] and structure of gambogic acid was deduced inferentially [2].

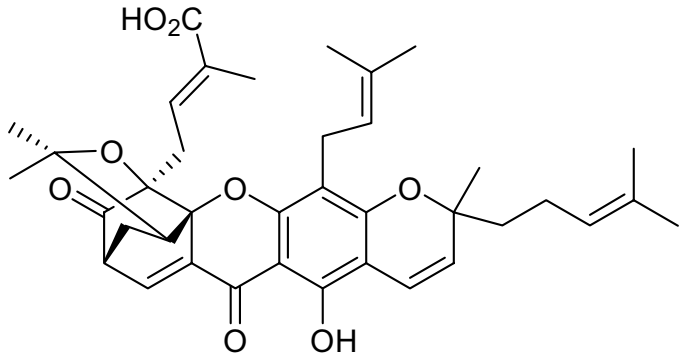


12 (gambogic acid)

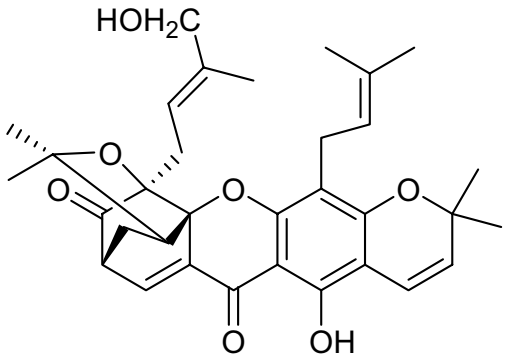


6 (morellin)

In 1993, Cordell *et al*. isolated three xanthone derivatives, gambogic acid (**12**), isogambogic acid (**13**) and isomorellinol (**10**) from the dry latex of *G. hanburyi* [6]. Determination of the structures and stereochemistry were achieved by high-field NMR experiments including COSY, ROESY, HMQC, HMBC and selective INEPT. Cytotoxic evaluation revealed that all three derivatives were active against KB and drug-resistant KB-V1 cell lines.

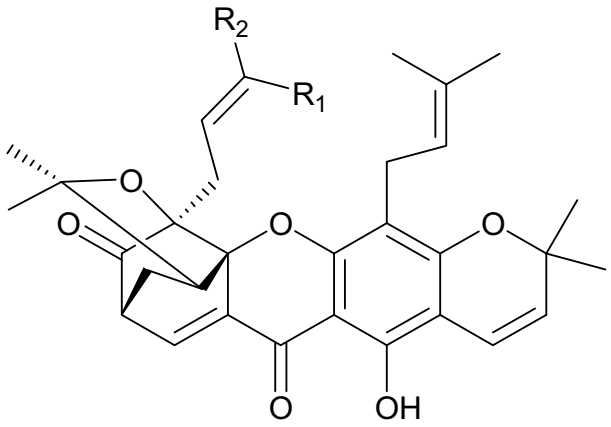


13 (isogambogic acid)



10 (isomorellinol)

In 1996, Tada *et al*. isolated eleven novel cytotoxic caged-polyprenylated xanthones, gambogin (**11**), morellin dimethyl acetal (**18**), isomoreollin B (**19**), moreollic acid (**20**), gambogenin (**14**), isogambogenin (**15**), desoxygambogenin (**21**), gambogenin dimethyl acetal (**22**), gambogenic acid (**16**), gambogellic acid (**23**) and hanburin (**24**) together with four known xanthones, desoxymorellin (**5**) [7], isomorellin (**7**) [8], morellic acid (**8**) [9] and gambogic acid (**12**) [6], from the dry latex of *G. hanburyi* [10]. The structures were elucidated by spectroscopic analysis and comparison of the NMR spectral data with those reported previously. Cytotoxicity against HeLa and HEL cells of the compounds was reported.



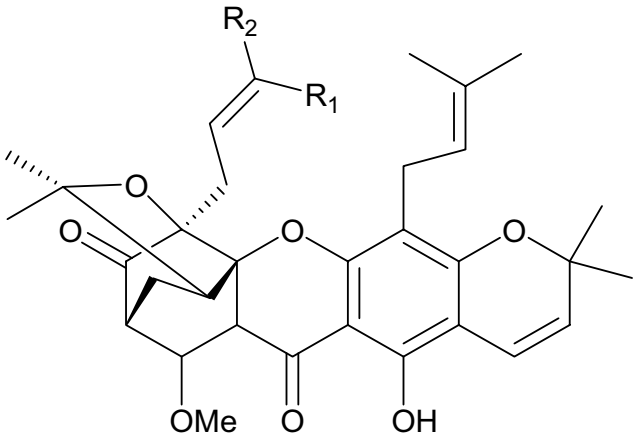
5 : R_1 = Me, R_2 = Me (desoxymorellin)

7 : R_1 = Me, R_2 = CHO (isomorellin)

8 : R_1 = CO_2H, R_2 = Me (morellic acid)

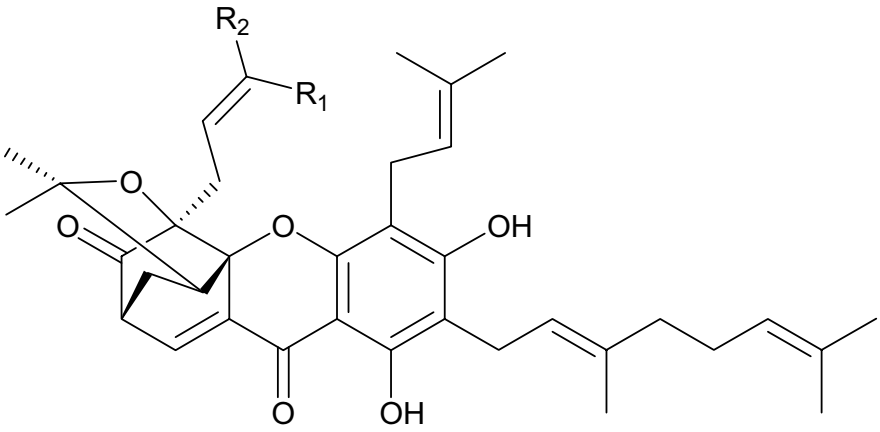
9 : R_1 = Me, R_2 = CO_2H (isomorellic acid)

18 : R_1 = $CH(OMe)_2$, R_2 = Me (morellin dimethyl acetal)



19 : R_1 = Me, R_2 = CHO (isomoreollin B)

20 : R_1 = CO_2H, R_2 = Me (moreollic acid)



14 : R_1 = CHO, R_2 = Me (gambogenin)

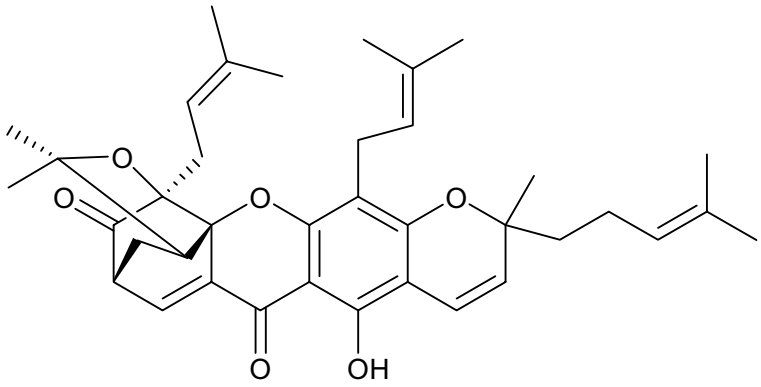
15 : R_1 = Me, R_2 = CHO (isogambogenin)

16 : R_1 = CO_2H, R_2 = Me (gambogenic acid)

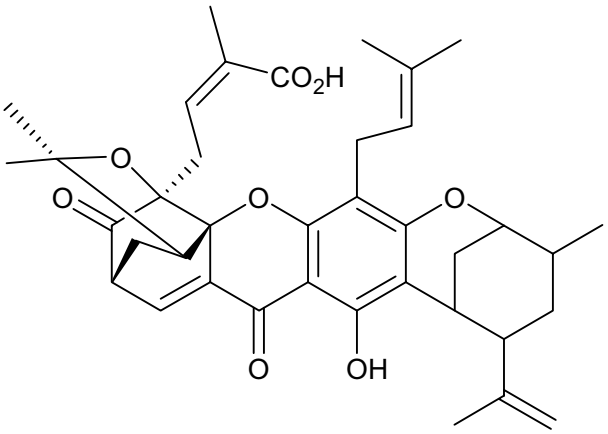
17 : R_1 = Me, R_2 = CO_2H (isogambogenic acid)

21 : R_1 = Me, R_2 =Me (desoxygambogenin)

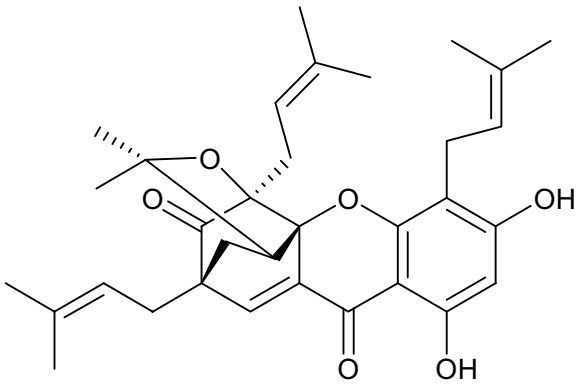
22 : R_1 = $CH(OMe)_2$, R_2 = Me (gambogenin dimethyl acetal)



11 (gambogin)

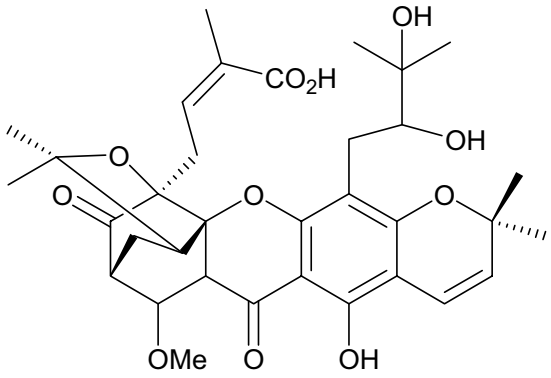


23 (gambogellic acid)



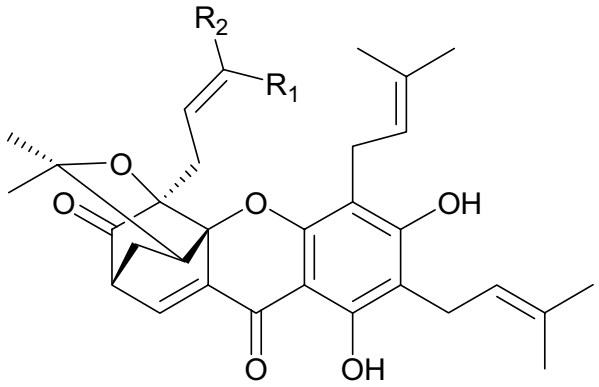
24 (hanburin)

In 2005, Rukachaisirikul *et al*. reported the isolation of a new caged-tetraprenylated xanthone, hanburinone (**25**), from the fresh fruits of *G. hanburyi* together with four known xanthones, isomoreollin B (**19**), morellin (**6**), moreollic acid (**20**) and morellic acid (**8**) [11]. The structures were elucidated by spectroscopic analysis and comparison of their spectral data with those reported previously. Compounds **20** and **8** showed moderately antibacterial activity against methicillin-resistant *Staphylococcus aureus* with a MIC value of 25 μg/mL.



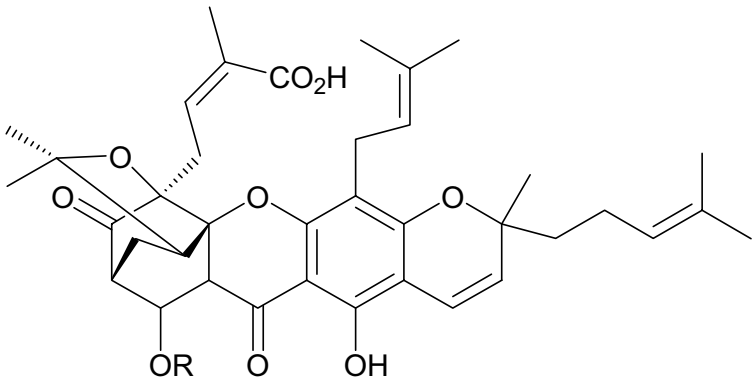
25 (hanburinone)

In 2006, Hong-Xi *et al*. found two new compounds, gaudichaudic acid (**26**) and isogambogenic acid (**17**), and one new natural product, deoxygaudichaudione A (**27**) [13] from the resin of *G. hanburyi* together with ten known xanthones, gambogoic acid A (**28**) [12], gambogoic acid B (**29**) [12], gambogic acid (**12**), isogambogic acid (**13**), gambogenic acid (**16**), desoxygambogenin (**21**), desoxymorellin (**5**), morellic acid (**8**), isomorellic acid (**9**) and isomorellinol (**10**) [14]. The structures were elucidated by spectroscopic analysis. Ten of these xanthones were test for cytotoxicity against human leukemia K562 (K562/S) and doxorubicin-resistant K562 (K562/ADR) cell lines.



26 : $R_1 = CO_2H$, $R_2 = Me$ (gaudichaudic acid)

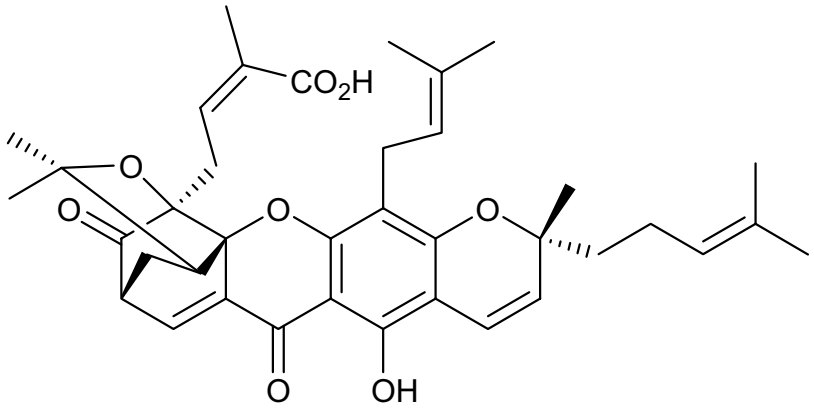
27 : $R_1 = Me$, $R_2 = Me$ (deoxygaudichaudione A)



28 : $R = CH_3$ (gambogoic acid A)

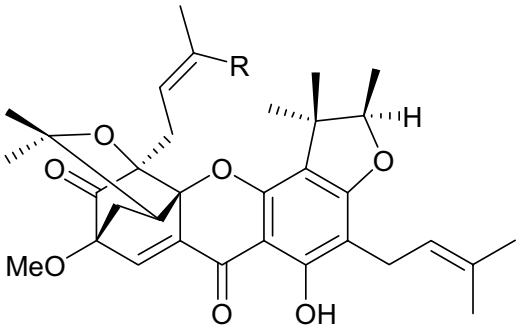
29 : $R = CH_2CH_3$ (gambogoic acid B)

In 2006, Xu *et al*. have set up a recycling counter-current chromatgraphic system with a high-speed counter-current chromatography instrument, coupled with a column switching valve. This method has been successfully applied in the preparative separation of epimers, gambogic acid (**12**) and epigambogic acid (**12'**) from *G. hanburyi* using *n*-hexane/methanol/water as the two-phase solvent system. From 50 mg of the mixture, 28.2 mg gambogic acid and 18.4 mg epigambogic acid were separated and their purities were both above 97 % as determined by HPLC. The chemical structures were identified by ^{1}H-NMR and ^{13}C-NMR spectra [15].



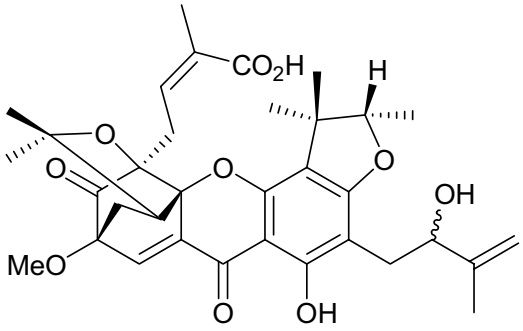
12' (epigambogic acid)

In 2000, Rukachaisirikul *et al*. isolated three new caged-tetraprenylated xanthones, scortechinone A (**30**), scortechinone B (**31**) and scortechinone C (**32**) from the twigs of *G. scortechinii* together with friedelin (**33**) and stigmasterol (**34**) [16]. The structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously.

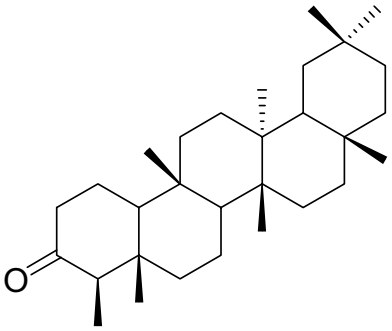


30 R = Me (scortechinone A)

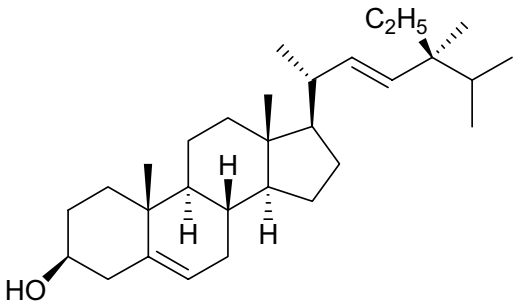
31 R = CO_2H (scortechinone B)



32 (scortechinone C)

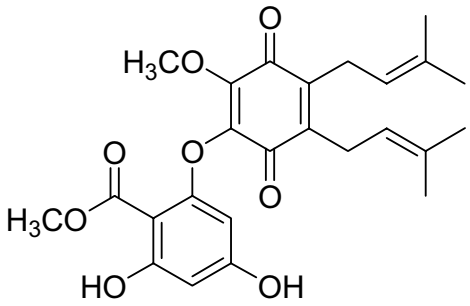


33 (friedelin)

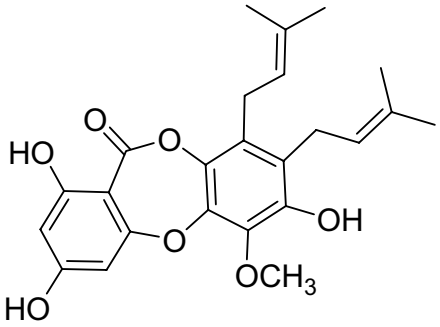


34 (stigmasterol)

In 2001, Permana *et al*. reported the isolation of two new prenylated compounds, the benzoquinone atrovirinone (**35**) and the depsidone atrovirisidone (**36**) from th MeOH extract of the roots of *G. atroviridis* [17]. Their structures were determined on the basis of spectroscopic analysis. Compound **36** showed some cytotoxicity against HeLa cells, and both compounds **35** and **36** were only mildly inhibitory against *Bacillus circus* and *Staphylococcus aureus*.

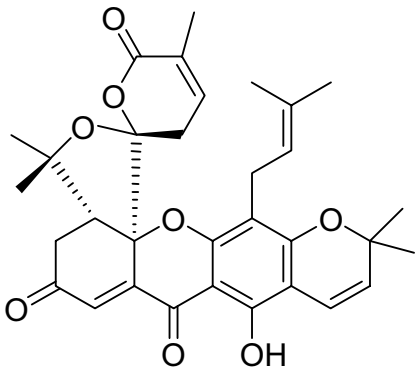


35 (atrovirinone)

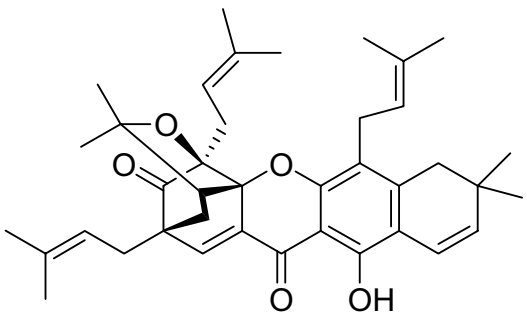


36 (atrovirisidone)

In 2001, Goh *et al.* isolated a novel degraded and rearranged tetraprenylated xanthone, gaudispirolactone (**37**) from the bark of *G. gaudichaudii* together with 7-isoprenylmorellic acid (**38**) [18]. The structures were elucidated by analysis of spectroscopic data. A plausible biosynthetic route for **37** involving morellic acid, which is the major natural product from the bark, was given.

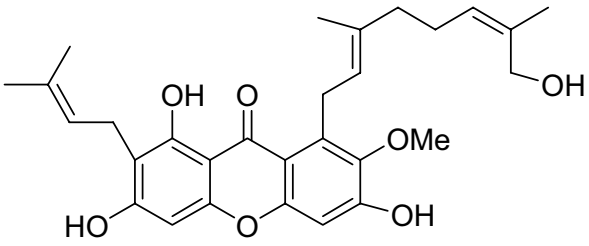


37 (gaudispirolactone)

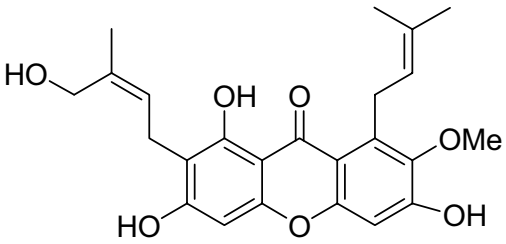


38 (7-isoprenylmorellic acid)

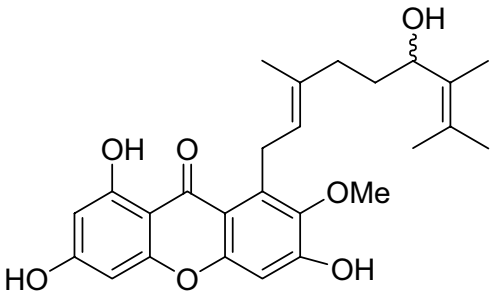
In 2001, Goh *et al.* isolated nine new xanthones, parvixanthone A (**39**), parvixanthone B (**40**), parvixanthone C (**41**), parvixanthone D (**42**), parvixanthone E (**43**), parvixanthone F (**44**), parvixanthone G (**45**), parvixanthone H (**46**) and parvixanthone I (**47**) from the dried bark of *G. parvifolia* [19]. The structures were determined on the basis of spectroscopic analysis.



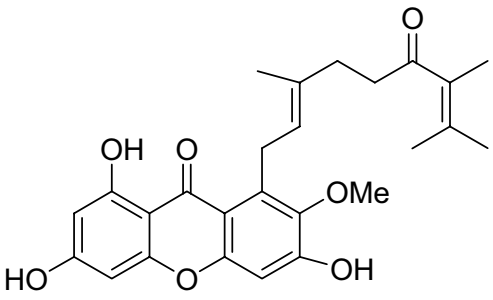
39 (parvixanthone A)



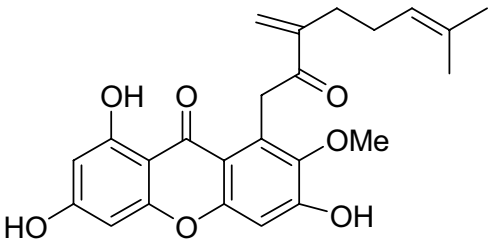
40 (parvixanthone B)



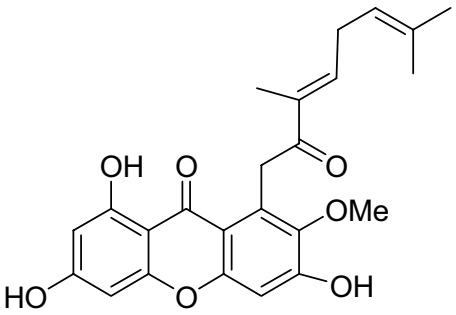
41 (parvixanthone C)



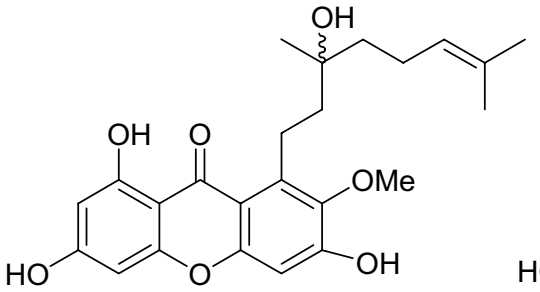
42 (parvixanthone D)



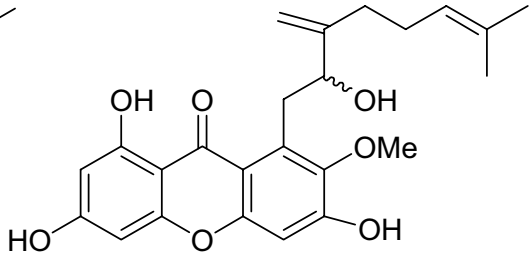
43 (parvixanthone E)



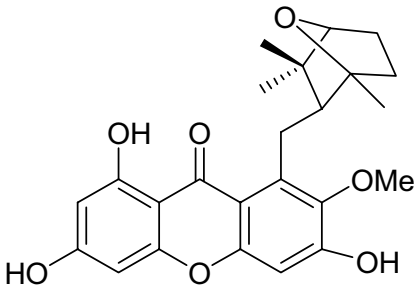
44 (parvixanthone F)



45 (parvixanthone G)

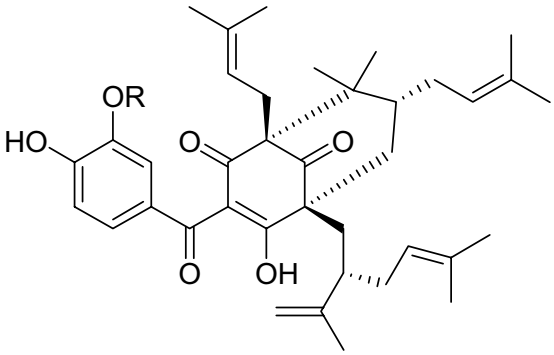


46 (parvixanthone H)



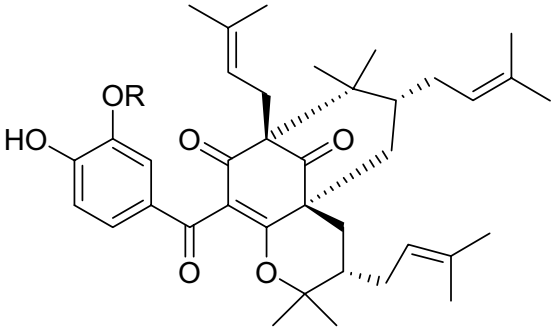
47 (parvixanthone I)

In 2003, Itoigawa *et al*. studied the chemical constituents of *G. assigu* and isolated two new benzophenones, garcinol 13-*O*-methyl ether (**48**) and isogarcinol 13-*O*-methyl ether (**49**) from the EtOH extract of dried stem bark together with four known benzophenones, clusianone (**50**), garcinol (**51**), isogarcinol (**52**) and maclurin (**53**) [20]. The structures were elucidated by spectroscopic analysis and comparison of their spectral data with those reported previously. The cyclized polyprenylbenzophenones (**48-52**) showed stronger potential cancer chemopreventive activity when compared to glycyrrhetinic acid, a known anti-tumor promoter.



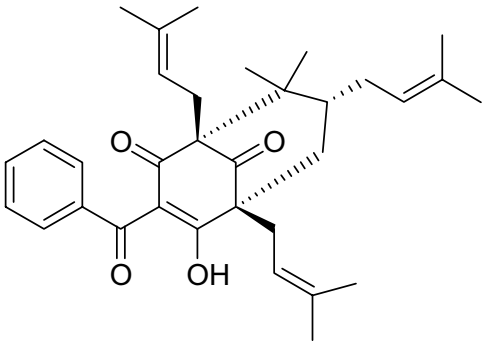
51 : R = H (garcinol)

48 : R = Me (garcinol 13-*O*-methyl ether)

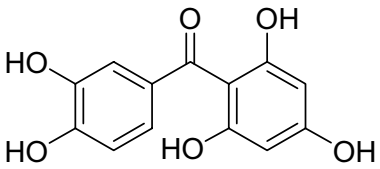


52 : R = H (isogarcinol)

49 : R = Me (isogarcinol 13-*O*-methyl ether)

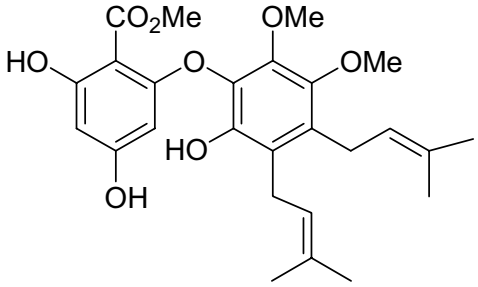


50 (clusianone)

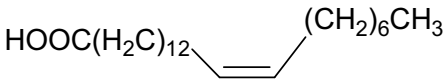


53 (maclurin)

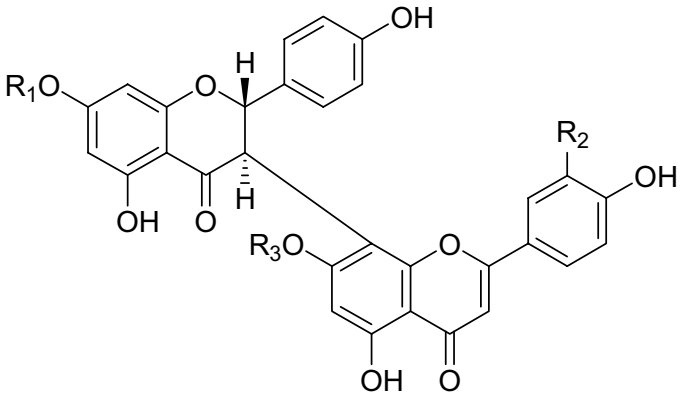
In 2003, Lajis *et al*. isolated a new prenylated hydroquinone, 4-methylhydroatrovirinone (**54**) together with six known compounds, atrovirinone (**35**), atrovirisidone (**36**), 14-*cis*-docosenoic acid (**55**), morelloflavone (**56**), morelloflavone 7-*O*-β-D-glucopyranoside (**57**) and fukugiside (**58**) from the MeOH extract of the roots of *G. atroviridis* [21]. The structures were determined on the basis of the analysis of spectroscopic data and mass spectroscopy.



54 (4-methylhydroatrovirinone)



55 (14-*cis*-docosenoic acid)

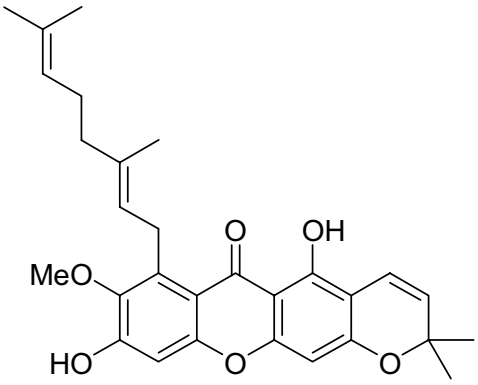


56 : $R_1 = R_3 = H$, $R_2 = OH$ (morelloflavone)

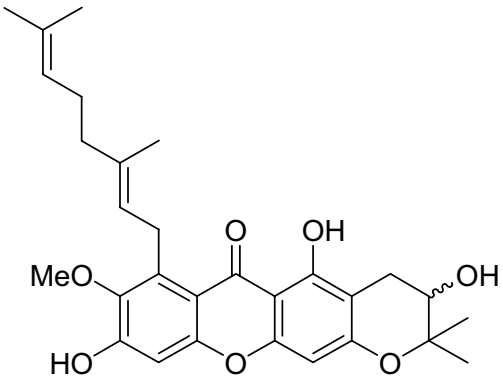
57 : $R_1 = \beta$-D-Glc, $R_2 = OH$, $R_3 = H$ (morelloflavone-7-*O*-D-glucopyranoside)

58 : $R_1 = H$, $R_2 = OH$, $R_3 = \beta$-D-Glc (fukugiside)

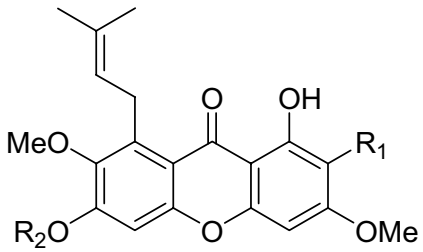
In 2003, Itoigawa *et al*. investigated the chemical constituents of the stem bark of *G. fusca*, eight new xanthones, fuscaxanthone A (**59**), fuscaxanthone B (**60**), fuscaxanthone C (**61**), fuscaxanthone D (**62**), fuscaxanthone E (**63**), fuscaxanthone F (**64**), fuscaxanthone G (**65**) and fuscaxanthone H (**66**) were isolated together with eight known xanthones, cowanin (**67**), cowanol (**68**), cowaxanthone (**69**), rubraxanthone (**70**), α-mangostin (**71**), β-mangostin (**72**), 7-*O*-methylgarcinone (**73**) and norcowanin (**74**) [22]. Their structures were determined on the basis of spectroscopic analysis. A primary screening of eleven xanthones, **64-74**, were examined for their possible inhibitory effect on EBV-EA activation.

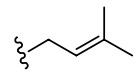


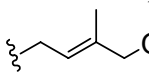
59 (fuscaxanthone A)

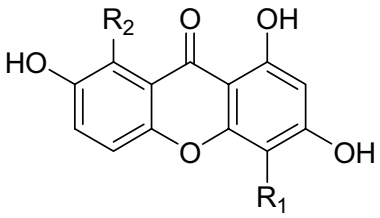


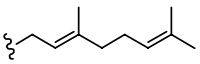
60 (fuscaxanthone B)

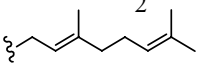


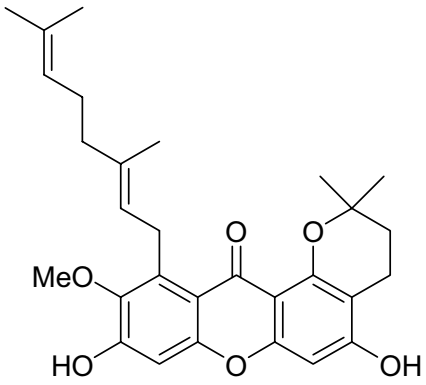
61 : R_1 =  , R_2 = Me (fuscaxanthone C)

62 : R_1 =  , R_2 = H (fuscaxanthone D)

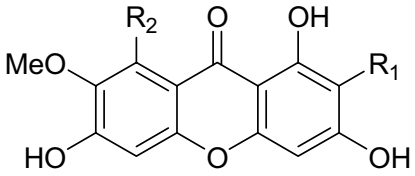


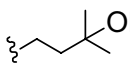
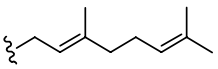
63 : R_1 =  , R_2 = H (fuscaxanthone E)

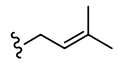
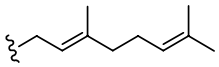
64 : R_1 = H, R_2 =  (fuscaxanthone F)

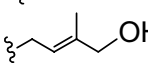
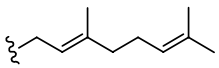


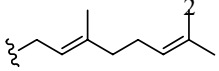
65 (fuscaxanthone G)

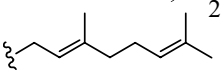


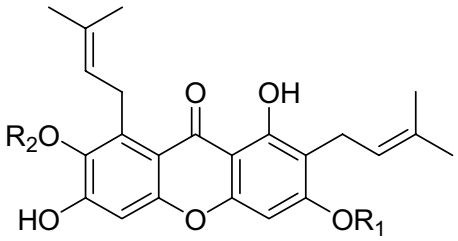
66 : R_1 =  , R_2 =  (fuscaxanthone H)

67 : R_1 =  , R_2 =  (cowanin)

68 : R_1 =  , R_2 =  (cowanol)

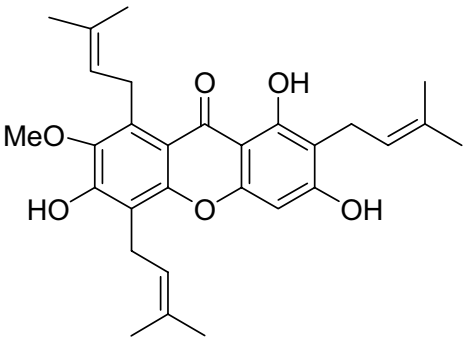
69 : R_1 =  , R_2 = H (cowaxanthone)

70 : R_1 = H, R_2 =  (rubraxanthone)

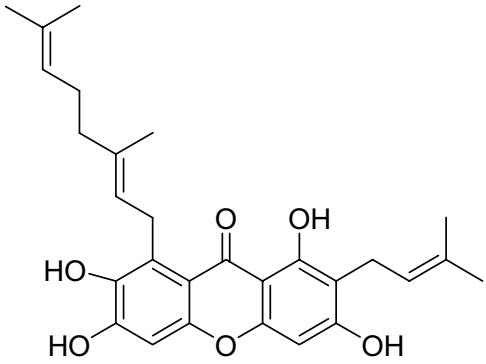


71 : R_1 = H, R_2 = Me (α-mangostin)

72 : R_1 = R_2 = Me (β-mangostin)

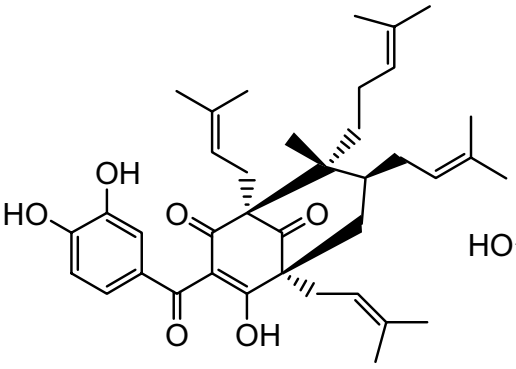


73 (7-*O*-methylgarcinone)

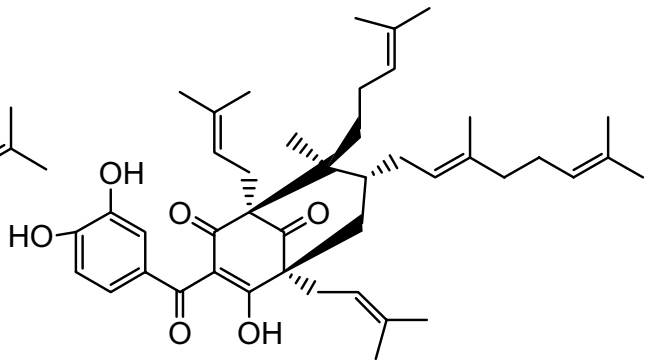


74 (norcowanin)

In 2003, Williams *et al*. reported the isolation of guttiferone G (**75**) , a new guttiferone analogue from the EtOAc extract of the twigs of *G. macrophylla* together with guttiferone A (**76**) and friedelin (**33**) [23]. Their structures were determined on the basis of spectroscopic analysis.

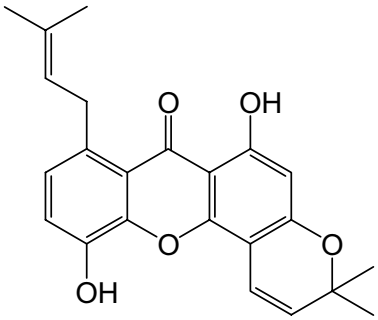


75 (guttiferone G)

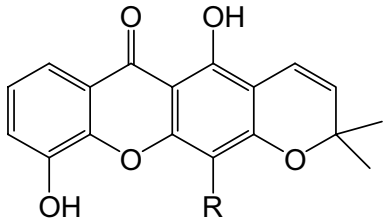


76 (guttiferone A)

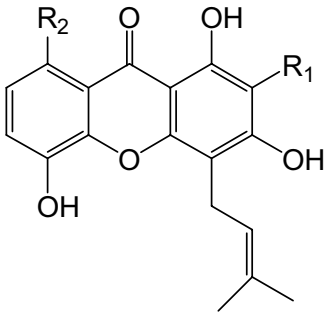
In 2003, Nguyen *et al.* isolated a new xanthone, merguenone (**77**) and nine known xanthones, 6-deoxyjacareubin (**78**), 8-deoxygartanin (**79**), 1,3,5-trihydroxy-4,8-di(3-methylbut-2-enyl)-xanthone (**80**), morusignin G (**81**), rheediachromenoxanthone (**82**), 1,5-dihydroxy-6'-methyl-6'-(4-methyl-3-pentenyl)-pyrano (2',3':3,2)-xanthone (**83**), 6-deoxyisojacareubin (**84**), rheediaxanthone A (**85**) and subelliptenone H (**86**) from a petroleum ether extract of the bark of *G. merguensis* [24]. Their structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously.

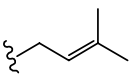


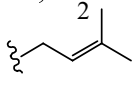
77 (merguenone)

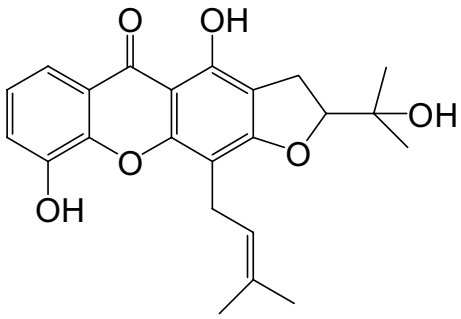


78 (6-deoxyjacareubin)

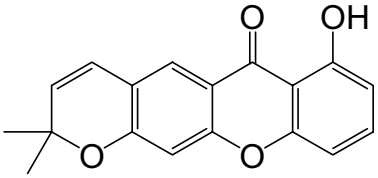


79 : R_1 =  , R_2 = H (8-deoxygartanin)

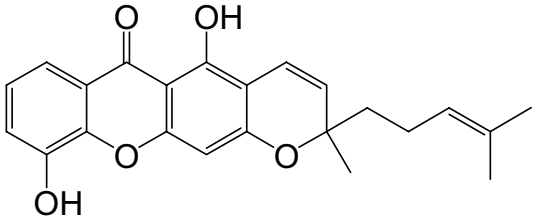
80 : R_1 = H, R_2 =  (1,3,5-trihydroxy-4,8-di(3-methylbut-2-enyl)-xanthone)



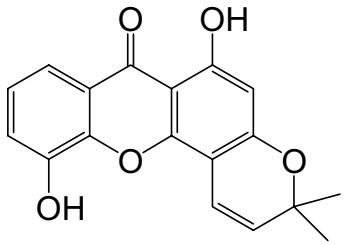
81(morusignin G)



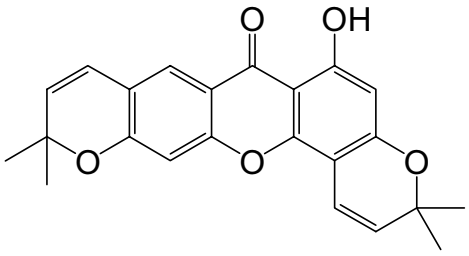
82 (rheediachromenoxanthone)



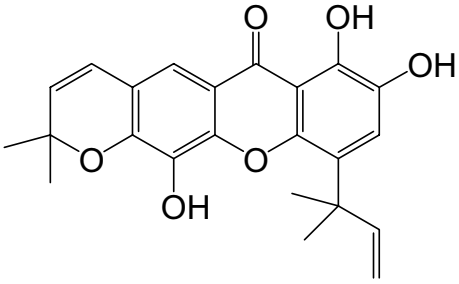
83 (1,5-dihydroxy-6'-methyl -6'-(4-methyl-3-pentenyl)- pyrano(2',3':3,2)-xanthone)



84 (6-deoxyisojacareubin)

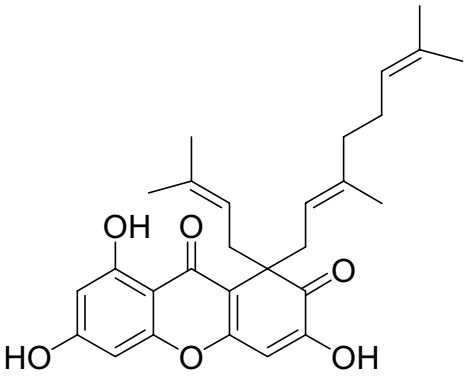


85 (rheediaxanthone A)

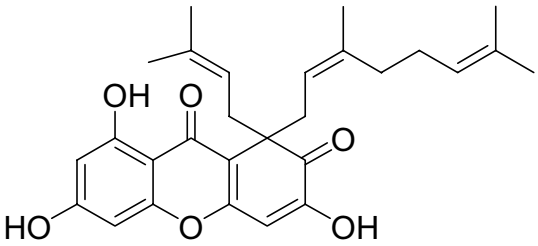


86 (subelliptenone H)

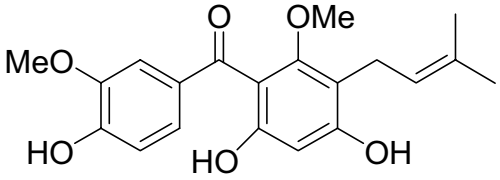
In 2003, Kuo *et al*. reported the isolation of two new xanthone derivatives, garcinianones A (**87**) and garcinianones B (**88**), two new benzophenone derivatives, 4,6,4'-trihydroxy-2,3'-dimethoxy-3-prenylbenzophenone (**89**) and 4,6,3',4'-tetrahydroxy-2-methoxybenzophenone (**90**) and a new inseparable mixture of (1*E*,22*Z*)-1,22-diferuloyloxydocosane (**91**) and (1*E*,24*Z*)-1,24-diferuloyloxyteracosane (**92**), together with the previously known 3,8-dihydroxy-2,4,6-trimethoxyxanthone (**93**), 6,3'-dihydroxy-2,4-dimethoxybenzophenone (**94**), maclurin (**95**), 2,4,6,3'-tetrahydroxylbenzophenone (**96**) and naringenin (**97**) were isolated from the stems of *G. multiflora* [25]. The structures were elucidated by a detailed spectroscopic analysis and comparison of their spectral data with those reported previously. The compounds were evaluated in the brine shrimp lethality test and in the DPPH antioxidant assay.



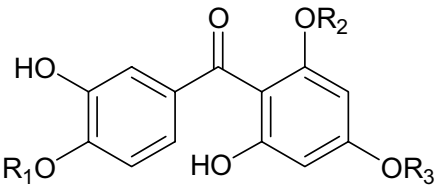
87 (garcinianones A)



88 (garcinianones B)



89 (4,6,4'-trihydroxy-2,3'-dimethoxy-3-prenylbenzophenone)

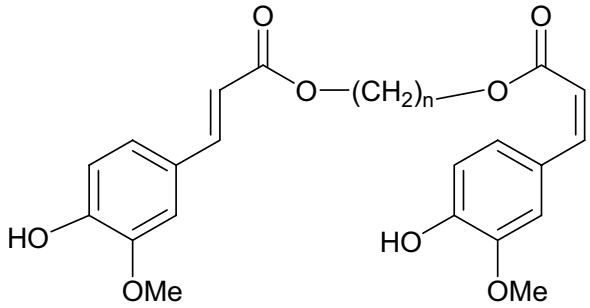


90 : R_1 = OH, R_2 = Me, R_3 = H (4,6,3',4'-tetrahydroxy-2-methoxybenzophenone)

94 : R_1 = H, R_2 = R_3 = Me (6,3'-dihydroxy-2,4-dimethoxybenzophenone)

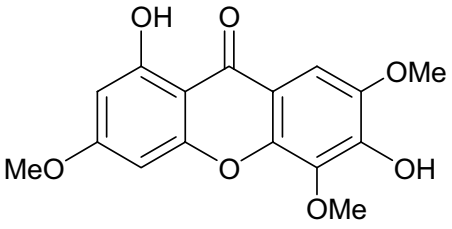
95 : R_1 = OH, R_2 = R_3 = H (maclurin)

96 : R_1 = R_2 = R_3 = Me (2,4,6,3'-tetrahydroxybenzophenone)

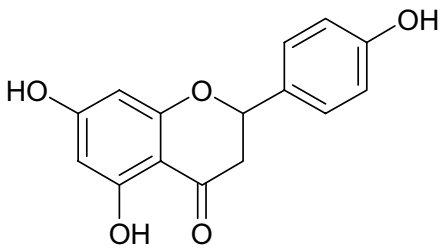


91 : n = 22 ((1*E*,22*Z*)-1,22-diferuloyloxydocosane)

92 : n = 24 ((1*E*,24*Z*)-1,24-diferuloyloxyteracosane)

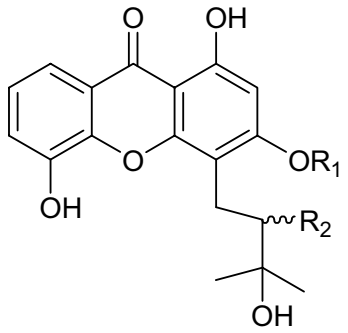


93 (3,8-dihydroxy-2,4,6-trimethoxyxanthone)



97 (naringenin)

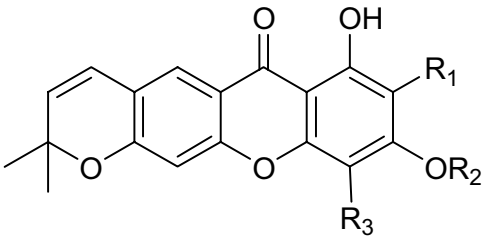
In 2003, Rukachaisirikul *et al*. isolated nine new xanthones, nigrolineaxanthone A (**98**), nigrolineaxanthone B (**99**), nigrolineaxanthone C (**100**), nigrolineaxanthone D (**101**), nigrolineaxanthone E (**102**), nigrolineaxanthone F (**103**), nigrolineaxanthone G (**104**), nigrolineaxanthone H (**105**) and nigrolineaxanthone I (**106**) together with nine known xanthones, 1,3,5-trihydroxy-4-(3-hydroxy-3-methylbutyl)xanthone (**107**), 1,3,7-trihydroxy-2-(3-hydroxy-3-methylbutyl)xanthone (**108**), 6-deoxyjacreubin (**78**), morusignin C (**109**), rheediachromenoxanthone (**82**), tovoxanthone (**110**), latisxanthone D (**111**), rheediaxanthone A (**85**) and brasillixanthone (**112**) from the methanol extract of the stem bark of *G. nigrolineata* [26]. The structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously. The xanthones isolated from the stem bark were evaluated for antibacterial activity against methicilin-resistant *Staphylococcu aureus*. Compounds **103**, **111** and **112** showed significant activity with the MIC value of 2 μg/mL.

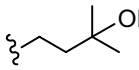


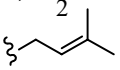
98 : R_1 = Me, R_2 = H (nigrolineaxanthone A)

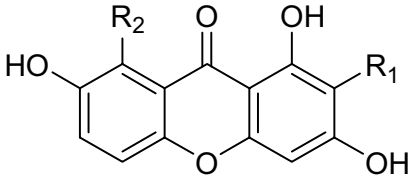
100 : R_1 = Me, R_2 = OH (nigrolineaxanthone C)

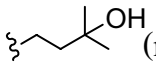
107 : R_1 = R_2 = H (1,3,5-trihydroxy-4-(3-hydroxy-3-methylbutyl)xanthone)

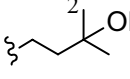


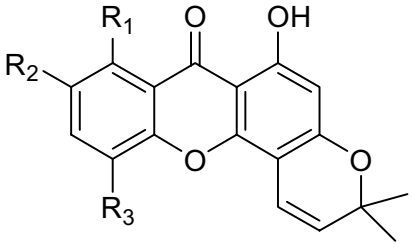
99 : R_1 = H, R_2 = Me, R_3 =  (nigrolineaxanthone B)

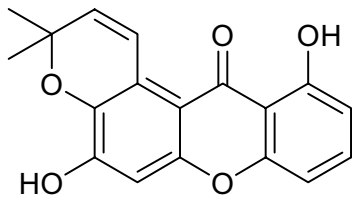
111 : R_1 =  , R_2 = R_3 = H (latisxanthone D)



101 : R_1 = H, R_2 =  (nigrolineaxanthone D)

108 : R_1 =  , R_2 = H (1,3,7-trihydroxy-2-(3-hydroxy-3-methylbutyl)xanthone)

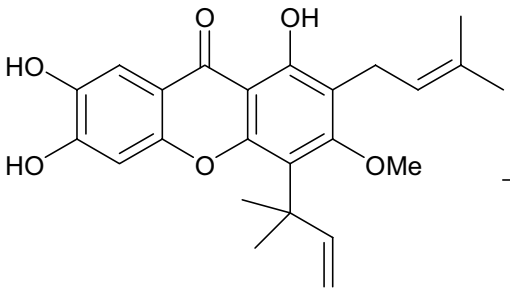




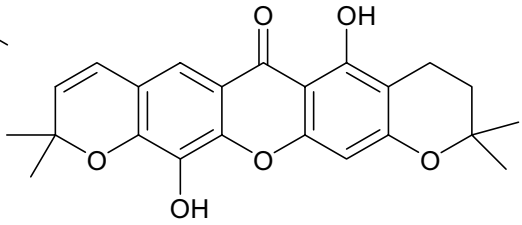
103 : R_1 = R_3 = H, R_2 = OH (nigrolineaxanthone F)

109 : R_1 = R_3 = OH, R_2 = H (morusignin C)

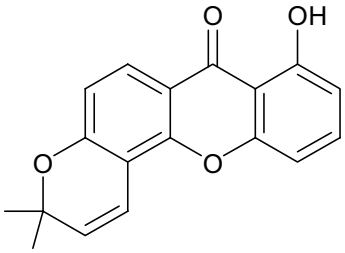
110 (tovoxanthone)



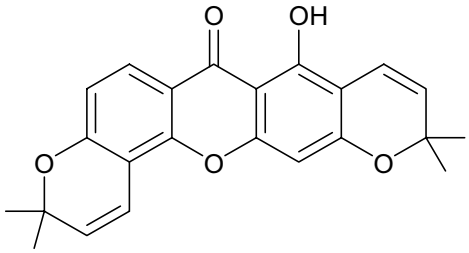
102 nigrolineaxanthone E



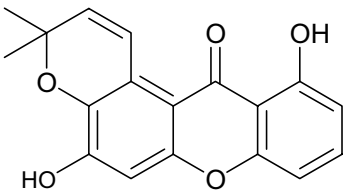
104 nigrolineaxanthone G



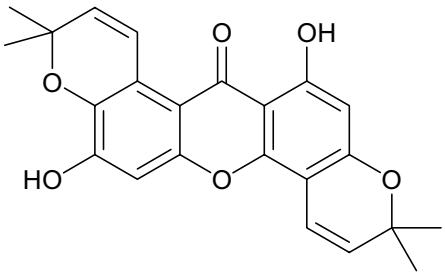
105 nigrolineaxanthone H



106 nigrolineaxanthone I

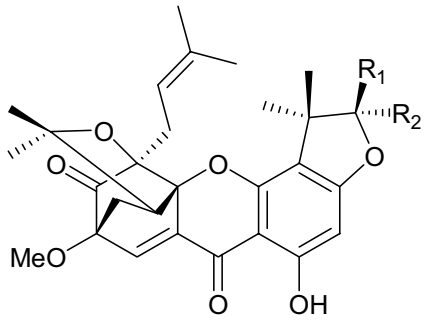


110 (tovoxanthone)



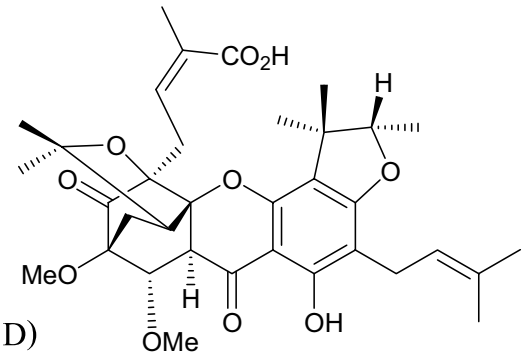
112 brasillixanthone

In 2003 Rukachaisirikul *et al*. isolated eight new caged-polyprenylated xanthones, scortechinone D (**113**), scortechinone E (**114**), scortechinone F (**115**), scortechinone G (**116**), scortechinone H (**117**), scortechinone I (**118**), scortechinone J (**119**) and scortechinone K (**120**) from the latex of *G. scortechinii* [27]. The structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously.

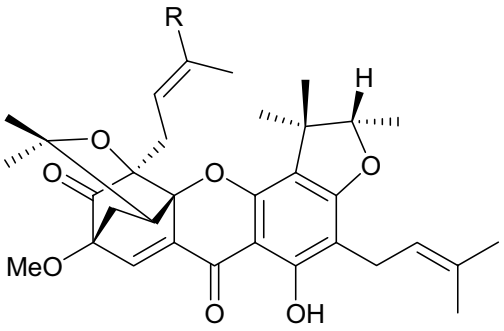


113 : R_1 = Me, R_2 = H (scortechinone D)

114 : R_1 = H, R_2 = Me (scortechinone E)



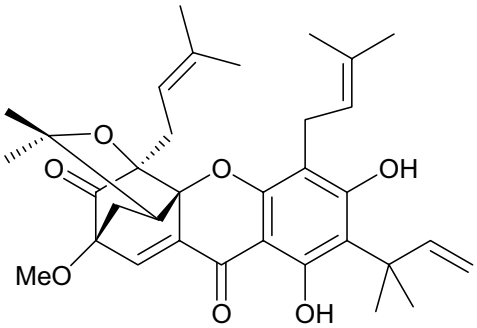
118 (scortechinone I)



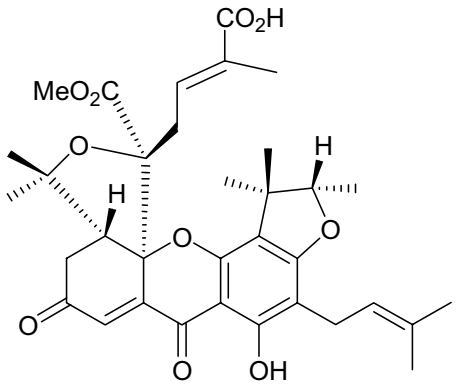
115 : R = CO_2H (scortechinone F)

116 : R = CO_2Me (scortechinone G)

117 : R = CHO (scortechinone H)

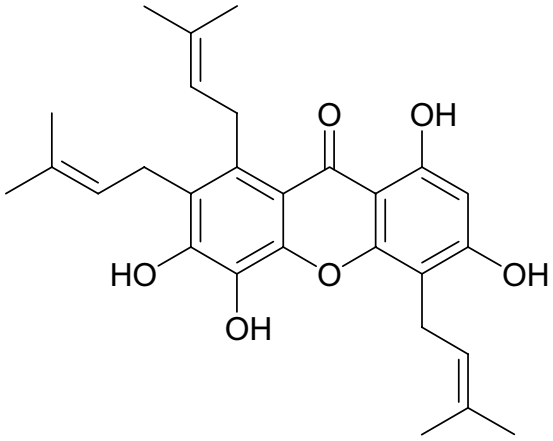


119 (scortechinone J)

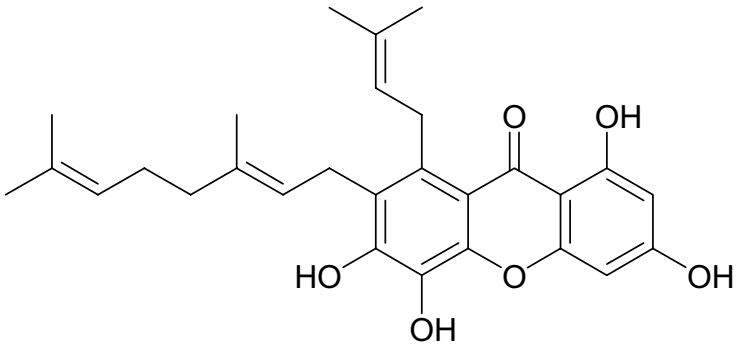


120 (scortechinone K)

In 2003, Ishibashi, *et al*. reported the isolation of a new prenylated xanthone, 1,3,5,6-tetrahydroxy-4,7,8-tri(3-methyl-2-butenyl)xanthone (**121**) from the wood of *G. xanthochymus* together with a known xanthone, garciniaxanthone E (**122**) [28]. The structures were determined by spectroscopic analysis. Compounds **121** (3 mM) and **122** (10 mM) elicited marked enhancement of nerve growth factor-mediated neurite outgrowth in PC12D cells.

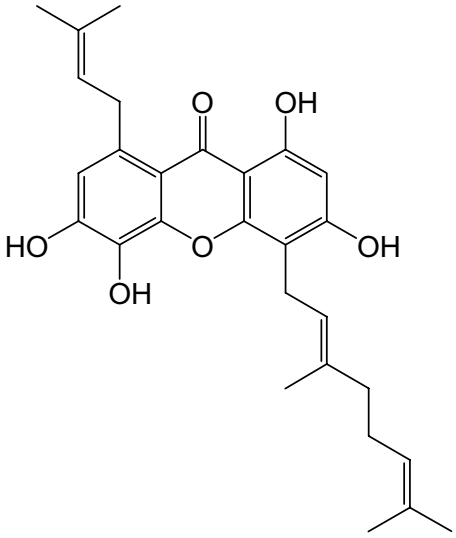


121 (1,3,5,6-tetrahydroxy-4,7,8-tri(3-methyl-2-butenyl)xanthone)

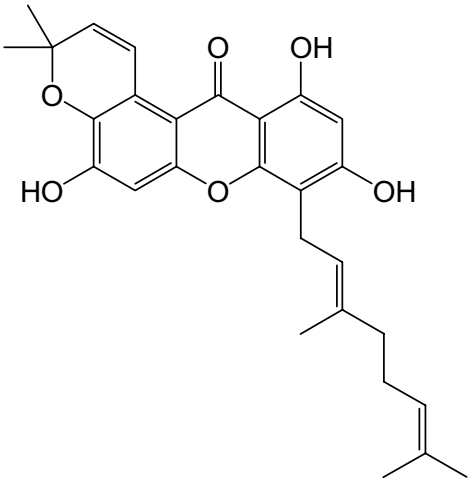


122 (garciniaxanthone E)

In 2004, Richomme *et al*. isolated two xanthones, virgataxanthone A (**123**) and virgataxanthone B (**124**), along with two formylated tocotrienols and the known δ-tocotrienol, griffipavixanthone and cotoin from the stem bark of G. *virgata* [29]. The structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously.



123 (virgataxanthone A)

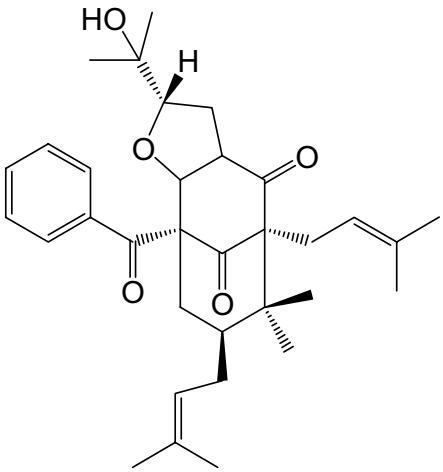


124 (virgataxanthone B)

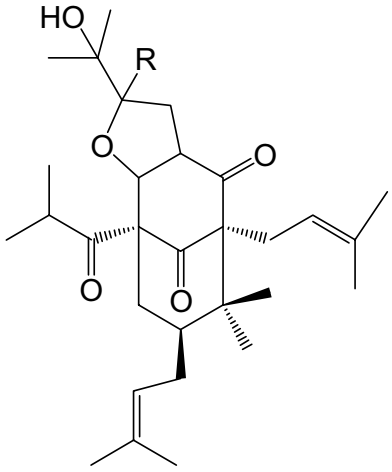
In 2004, Lin *et al*. reported the isolation of three new phloroglucinols, garcinielliptone K (**125**), garcinielliptone L (**126**) and garcinielliptone M (**127**), and two new terpenoids, garcinielliptone N (**128**) and garcinielliptone O (**129**) from the seeds of *G. subelliptica* [30]. Compounds **126** and **127** showed potent inhibitory effects on the release of β-glucuronidase and histamine, respectively, from peritoneal mast cells stimulated with *p*-methoxy-*N*-methylphenethylamine in a concentration-dependent manner and showed potent effects on NO production in culture media of RAW 264.7 cells in response to lipopolysaccharide (LPS).

Compound **126** also showed a potent effect on NO production in culture media of N9 cells in response to LPS/interferon-ε (IFN-ε).

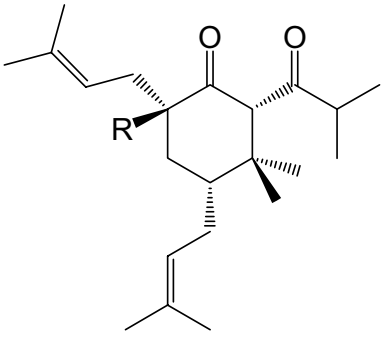
In 2005 a new benzophenone, garcinielliptone FA (**130**) and a new benzoylphloroglucinol, garcinielliptone FB (**131**) were isolated from the pericarp of the same plant [31]. Compound **131** exhibited cytotoxic activity against several human cancer cell lines. The structures including their relative configurations were elucidated by spectroscopic methods and supported by computer-generated molecular modeling.



125 (garcinielliptone K)

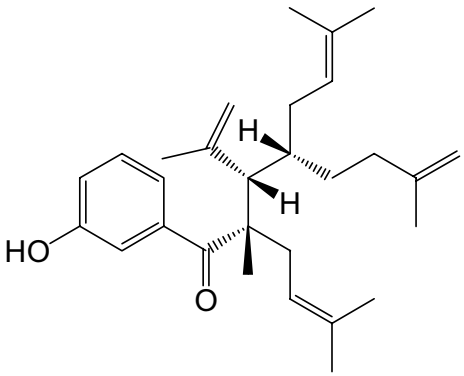


126 : R = H (α) (garcinielliptone L)
127 : R = H (β) (garcinielliptone M)

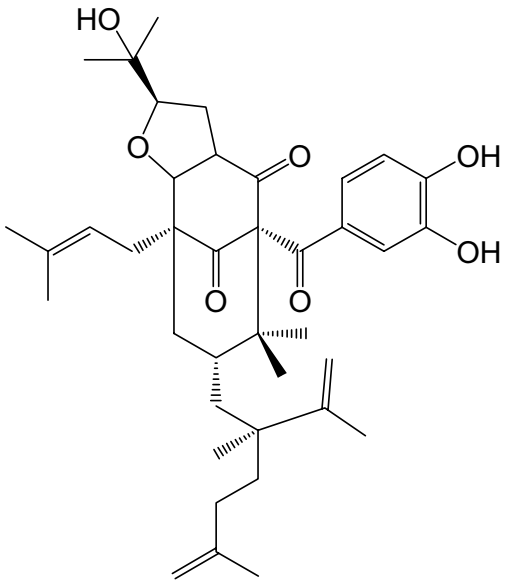


128 : R = H (garcinielliptone N)

129 : R= CO_2CH_3 (garcinielliptone O)

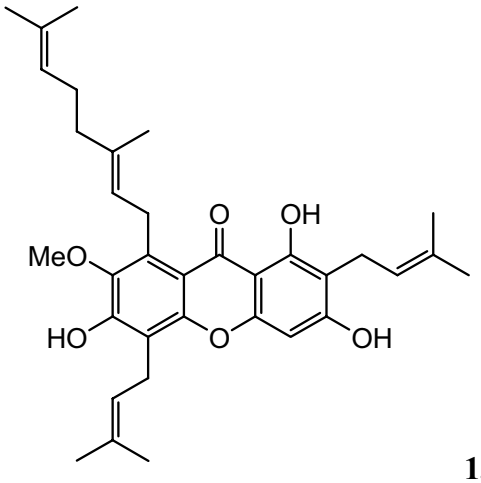


130 (garcinielliptone FA)

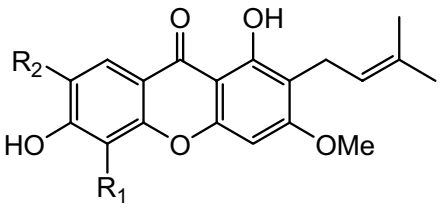


131 (garcinielliptone FB)

In 2005, Mahabusarakam *et al*. isolated five new xanthones, cowagarcinone A (**132**), cowagarcinone B (**133**), cowagarcinone C (**134**), cowagarcinone D (**135**) and cowagarcinone E (**136**) from the acetone extract of the latex of *G. cowa* Roxb together with six known xanthones, cowanin (**67**), cowanol (**68**), cowaxanthone (**69**) and 1,3,6-trihydroxy-7-methoxy-2,5-*bis*(3-methyl-2-butenyl)xanthone (**137**), mangostinone (**138**) and fuscaxanthone A (**59**) [32]. The structures were elucidated by a detailed spectroscopic analysis and comparison of their spectral data with those reported previously. The crude latex and the isolated compounds were investigated for their radical scavenging activities.

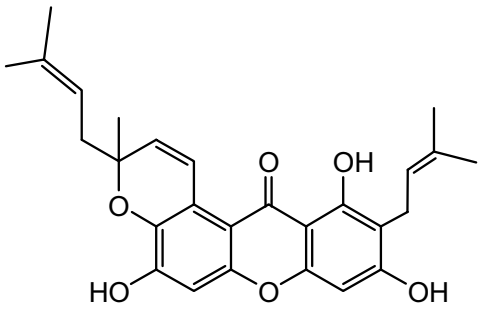


132 (cowagarcinone A)

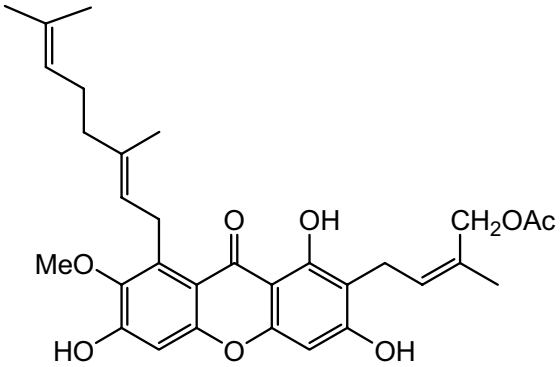


133 : R_1 = H, R_2 = OCH_3 (cowagarcinone B)

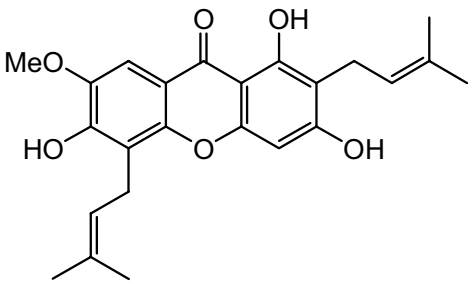
134 : R_1 = OCH_3, R_2 = H (cowagarcinone C)



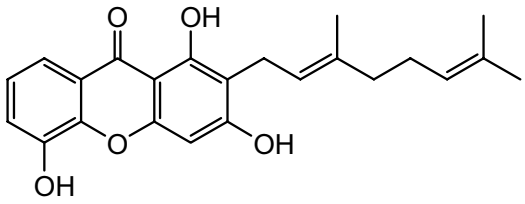
135 (cowagarcinone D)



136 (cowagarcinone E)

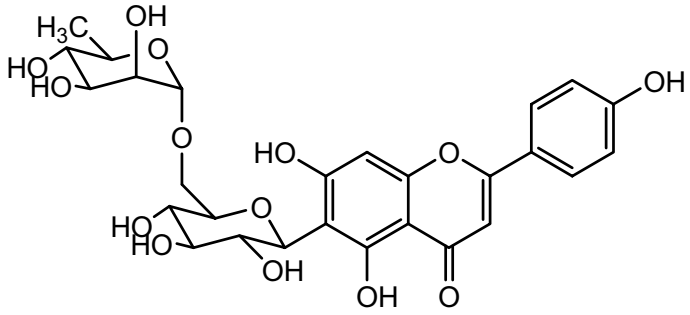


137 (1,3,6-trihydroxy-7-methoxy-2,5-*bis*(3-methyl-2-butenyl)xanthone)

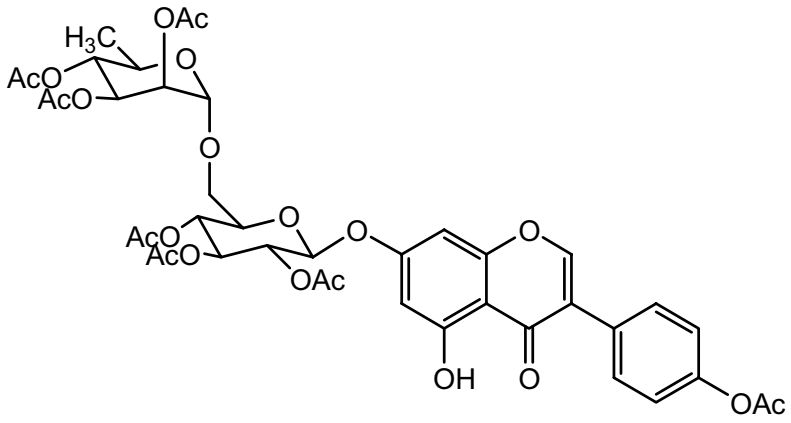


138 (mangostinone)

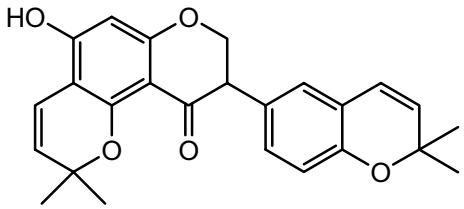
In 2005, Mahabusarakam *et al*. reported the isolation and structural elucidation of dulcinoside (**139**), dulcisisoflavone (**140**), dulcisxanthone A (**141**) and sphaerobioside acetate (**142**) together with 22 known compounds from the green fruit of *G. dulcis*. Dulcisflavan (**143**), dulcisxanthone B (**144**) and isonormangostin (**145**) together with 22 known compounds were isolated from the ripe fruit of the same plant [33]. The structures were elucidated by a detailed spectroscopic analysis and comparison of their spectral data with those reported previously. The radical scavenging and antibacterial activities of some of the compounds were investigated.



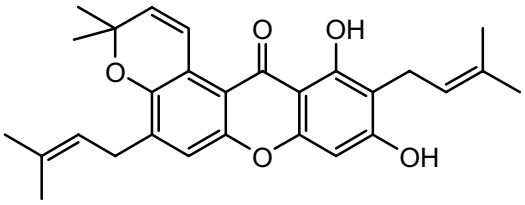
139 (dulcinoside)



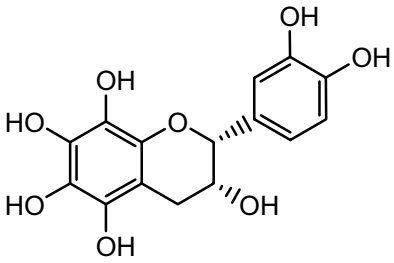
142 (sphaerobioside acetate)



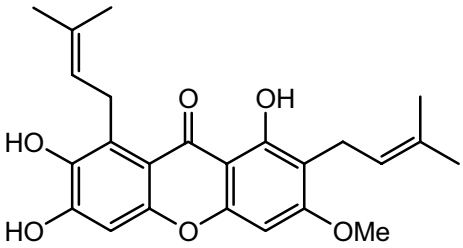
140 (dulcisisoflavone)



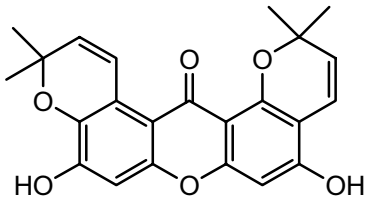
141 (dulcisxanthone A)



143 (dulcisflavan)

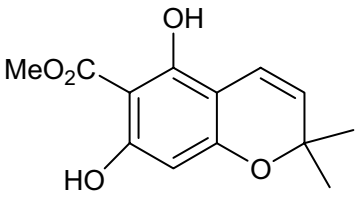


144 (dulcisxanthone B)

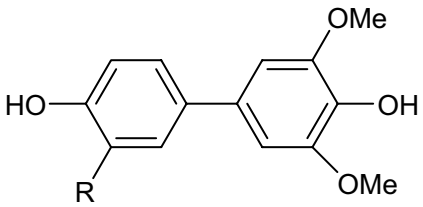


145 (isonormangostin)

In 2005, Rukachaisirikul *et al*. reported the isolation of one new benzopyran, nigrolineabenzopyran A (**146**), two new biphenyls, nigrolineabiphenyl A (**147**) and nigrolineabiphenyl B (**148**), and four new tetraoxygenated xanthones, nigrolineaxanthone T (**149**), nigrolineaxanthone U (**150**), nigrolineaxanthone V (**151**) and nigrolineaxanthone W (**152**) from the methanol extract of the twigs of *G. nigrolineata* along with eleven known xanthones [34]. Their structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously. The xanthones isolated from the twig as well as those from the stem bark were evaluated for antibacterial activity against methicilin-resistant *Staphylococcus aureus*.

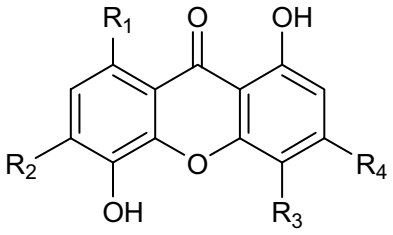


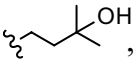
146 (nigrolineabenzopyran A)

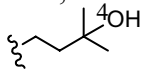


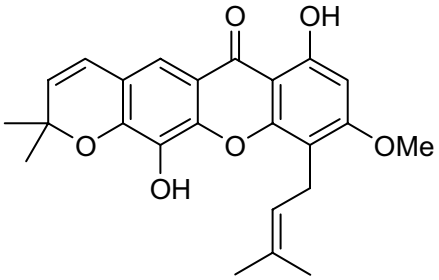
147 : R = OH (nigrolineabiphenyl A)

148 : R = OMe (nigrolineabiphenyl B)

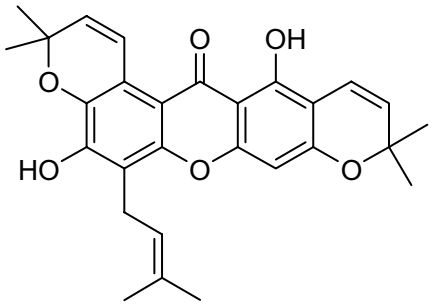


149 : R_1 = H, R_2 = OH, R_3 =  , R_4 = OMe (nigrolineaxanthone T)

150 : R_1 = R_4 = OH, R_2 = H, R_3 =  (nigrolineaxanthone U)

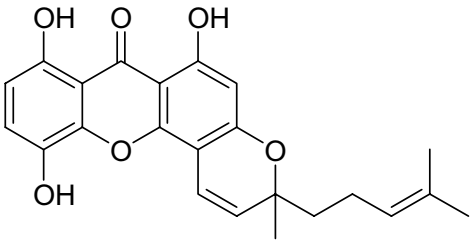


151 (nigrolineaxanthone V)

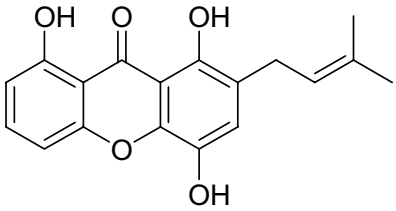


152 (nigrolineaxanthone W)

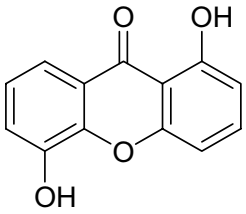
In 2005, Lannang *et al*. isolated two xanthones, bangangxanthone A (**153**) and bangangxanthone B (**154**), along with two known xanthones, 1,5-dihydroxyxanthone (**155**), 2-hydroxy-1,7-dimethoxyxanthone (**156**) and the pentacyclic triterpenoids, friedelin (**33**), oleanolic acid and lupeol from the chloroform extract of the stem bark of *G. polyantha* [35]. Their structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously. Compound **153-156** showed antioxidant DPPH radical scavenging activity.



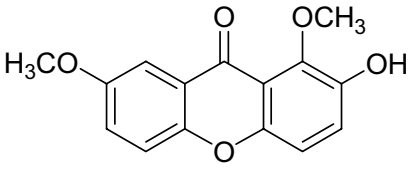
153 (bangangxanthone A)



154 (bangangxanthone B)

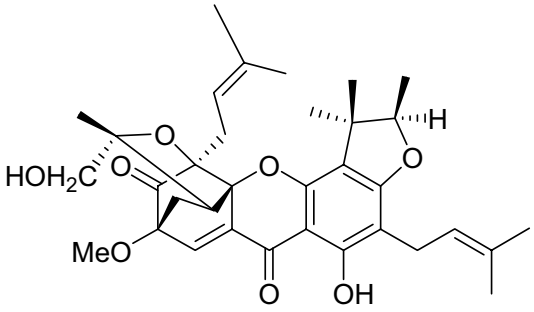


155 (1,5-dihydroxyxanthone)

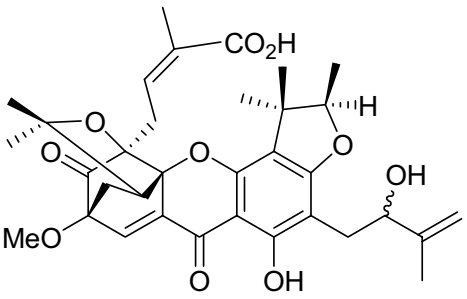


156 (2-hydroxy-1,7-dimethoxyxanthone)

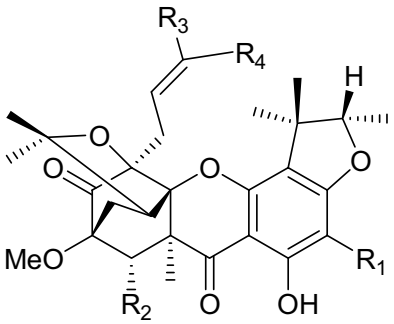
In 2005, Rukachaisirikul *et al*. reported the isolation of ten new compounds, eight caged-tetraprenylated xanthones, scortechinone Q (**157**), scortechinone R (**158**), scortechinone S (**159**), scortechinone T (**160**), scortechinone U (**161**), scortechinone V (**162**), scortechinone W (**163**) and scortechinone X (**164**), and two sesquiterpene derivatives, scortechterpene A (**165**) and scortechterpene B (**166**), together with fourteen known compounds from the fruits of *G. scortechinii* [36]. Their structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously. All xanthone derivatives were evaluated for antibacterial activity against methicilin-resistant *Staphylococcus aureus*.

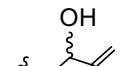


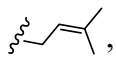
157 (scortechinone Q)

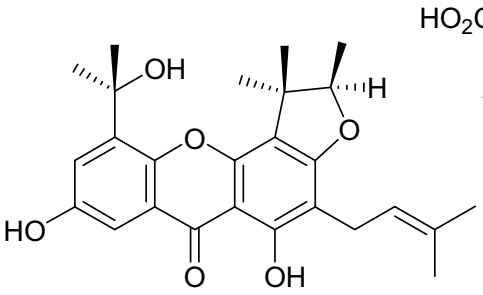


158 (scortechinone R)

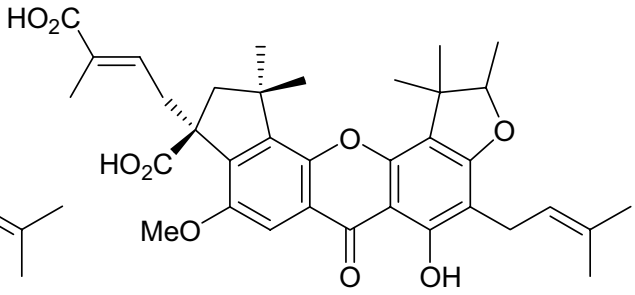


159 : R_1 =  , R_2 = OMe, R_3 = CO_2H (scortechinone S)

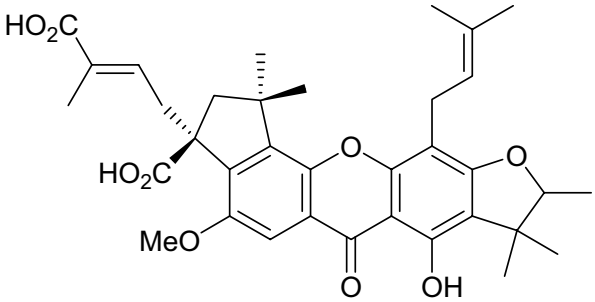
160 : R_1 =  , R_2 = OMe, R_3 = CHO (scortechinone T)



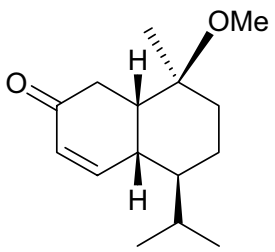
161 (scortechinone U)



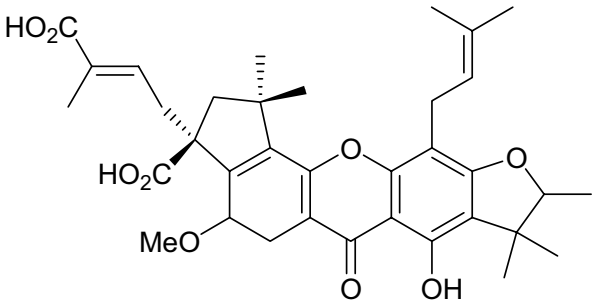
162 (scortechinone V)



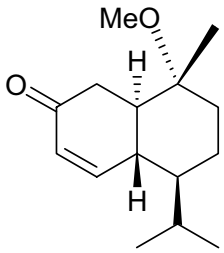
163 (scortechinone W)



165 (scortechterpene A)

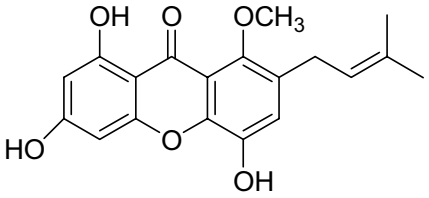


164 (scortechinone X)

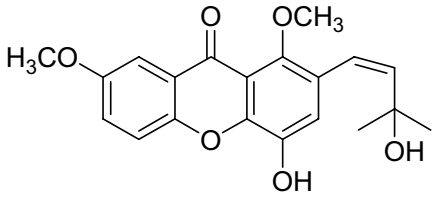


166 (scortechterpene B)

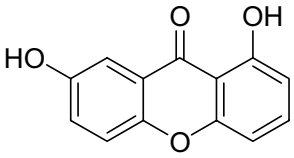
In 2006, Waffo *et al*. isolated two new prenylated xanthones, afzeliixanthones A (**167**) and afzeliixanthones B (**168**), together with three known xanthones, 1,5-dihydroxyxanthone (**155**), 1,7-dihydroxyxanthone (**169**) and 1,3,7-trihydroxy-2-(3-methylbut-2-enyl)xanthone (**170**) and two phytosterols, β-sitosterol (**171**) and stigmasterol (**34**) from the CH_2Cl_2/MeOH extract of the stem bark of *G. afzelii* [37]. The structures were established using one and two-dimensional NMR and mass spectroscopy. The antioxidant activities of the crude extracts as well as of the new compounds **167** and **168** were evaluated.



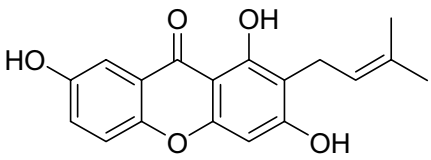
167 (afzeliixanthones A)



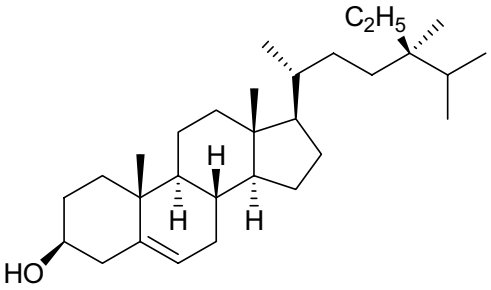
168 (afzeliixanthones B)



169 (1,7-dihydroxyxanthone)

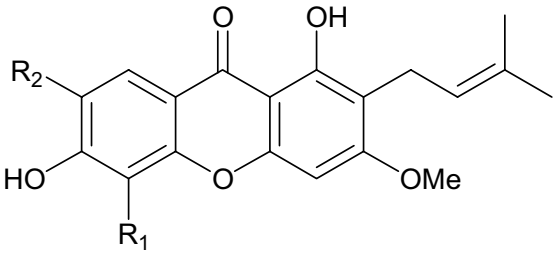


170 (1,3,7-trihydroxy-2-(3-methylbut-2-enyl)xanthone)



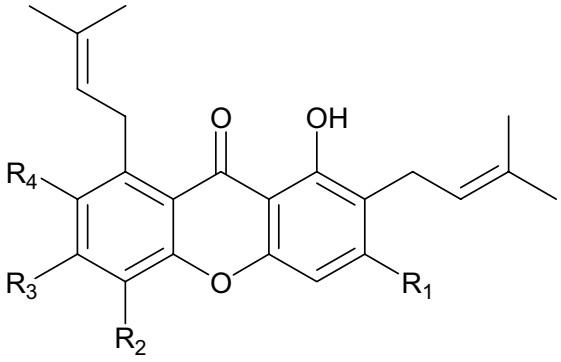
171 (β-sitosterol)

In 2006, Panthong *et al.* isolated five new tetraoxygenated xanthones, cowaxanthones A (**172**), cowaxanthones B (**173**), cowaxanthones C (**174**), cowaxanthones D (**175**) and cowaxanthones E (**176**), together with 10 previously reported tetraoxygenated xanthones, l,6-dihydroxy-3,7-dimethoxy-2-(3-methyl-2-butenyl)xanthone (**177**), 7-*O*-methylgarcinone E (**178**), mangostanin (**179**), 6-*O*-methylmangostanin (**180**), fuscaxanthone C (**61**), cowaxanthone (**69**), cowanin (**67**), cowanol (**68**), α-mangostin (**71**) and β-mangostin (**72**) from the hexane extract of the fruits of *G. cowa* [38]. Two new xanthones, 1,5,6-trihydroxy-3-methoxy-4-(3-hydroxyl-3-methylbutyl)xanthone (**181**) and 1,5-dihydroxy-3-methoxy-6',6'-dimethyl-2*H*-pyrano(2',3':6,7)-4-(3-methylbut-2-enyl)xanthone (**182**), were isolated together with six known xanthones, 1,3,5-trihydroxy-6',6'-dimethyl-2*H*-pyrano(2',3':6,7) xanthone (**183**), dulxanthone A (**184**), 1,5,6-trihydroxy-3,7-dimethoxyxanthone (**185**), 1,7-dihydroxyxanthone (**186**), 1,3,5-trihydroxy-6-methoxyxanthone (**187**) and 1,3,6,7-tetra-hydroxyxanthone (**188**) from the 95% EtOH extract of the stems of *G. cowa* by Yang *et al*. [39]. Their structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously.

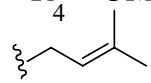


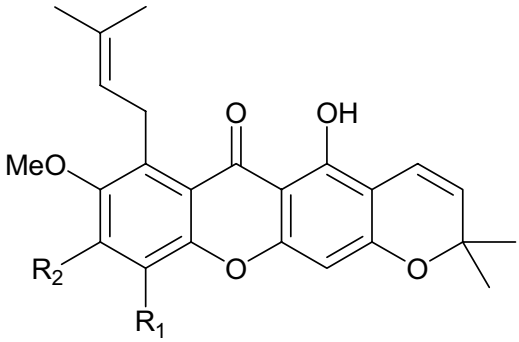
172 : R_1 = OMe, R_2 = H (cowaxanthone A)

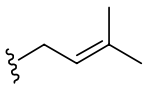
177 : R_1 = H, R_2 = OMe (l,6-dihydroxy-3,7-dimethoxy -2-(3-methyl-2-butenyl)xanthone)



173 : R_1 = OH, R_2 =H, R_3 = R_4 = OMe (cowaxanthone B)

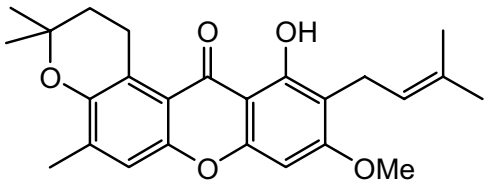
178 : R_1 = R_3 = OH, R_2 =  , R_4 = OMe (7-*O*-methylgarcinone E)



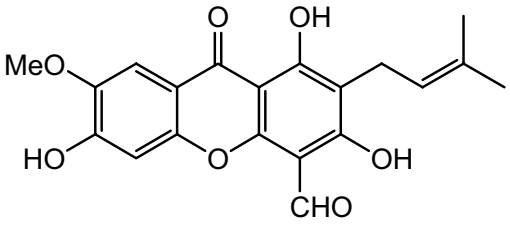
174 : R_1 =  , R_2 = OH (cowaxanthone C)

179 : R_1 = H, R_2 = OH (mangostanin)

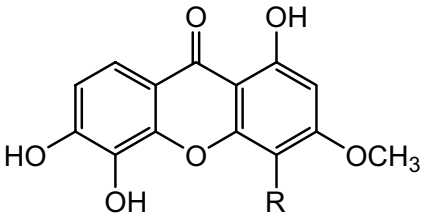
180 : R_1 = H, R_2 = OMe (6-*O*-methylmangostanin)

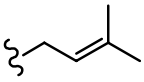


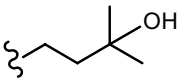
175 (cowaxanthone D)

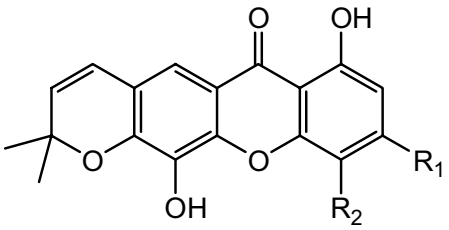


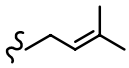
176 (cowaxanthone E)



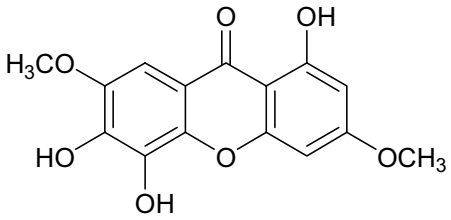
184 : R =  (dulxanthone A)

181 : R =  (1,5,6-trihydroxy-3-methoxy-4-(3-hydroxyl-3-methylbutyl) xanthone)

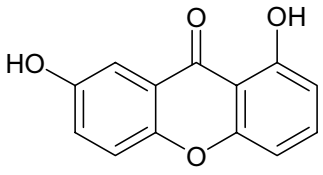


182 : R_1 = OMe, R_2 =  (1,5-dihydroxy-3-methoxy-6',6'-dimethyl-2H-pyrano (2',3':6,7)-4-(3-methylbut-2-enyl)xanthone)

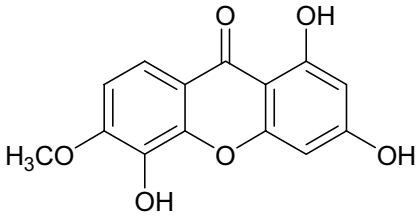
183 : R_1 = OH, R_2 = H (1,3,5-trihydroxy-6',6'-dimethyl-2H-pyrano(2',3':6,7) xanthone)



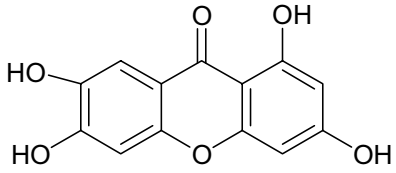
185 (1,5,6-trihydroxy-3,7-dimethoxyxanthone)



186 (1,7-dihydroxyxanthone)

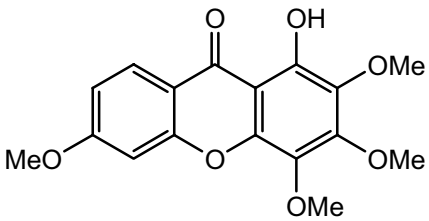


187 (1,3,5-trihydroxy-6-methoxyxanthone)

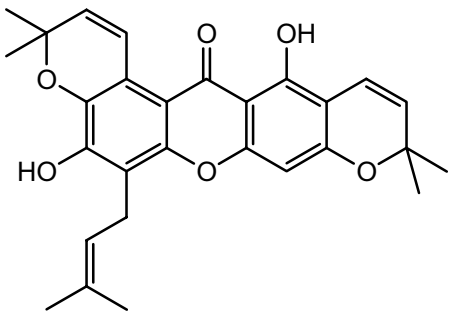


188 (1,3,6,7-tetra-hydroxyxanthone)

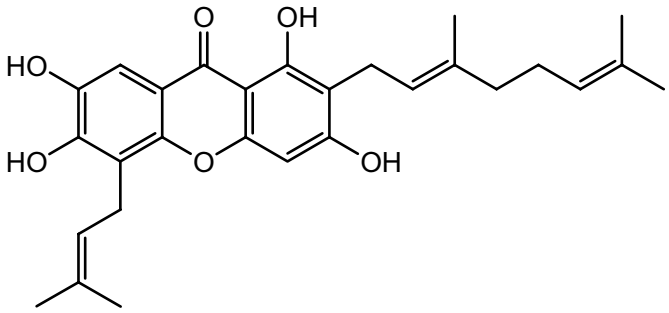
In 2006, Mahabusarakam *et al*. reported the isolation and structural of five new xanthones, dulcisxanthone C (**189**), dulcisxanthone D (**190**), dulcisxanthone E (**191**), dulcisxanthone F (**192**) and dulcinone (**193**) together with 22 known compounds from the acetone extract of the flowers of *G. dulcis* [40]. Their structures were elucidated by analysis of spectroscopic data. The radical scavenging and antibacterial activities of some of the compounds were investigated.



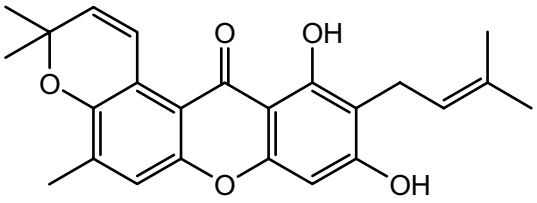
189 (dulcisxanthone C)



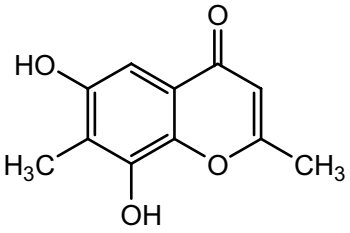
190 (dulcisxanthone D)



191 (dulcisxanthone E)



192 (dulcisxanthone F)



193 (dulcinone)

CHAPTER 2

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured in methanol solution with sodium D line (590 nm) on JASCO P-1010 Polarimeter. Ultraviolet spectra (UV) were measured with HP-8453 UV-vis spectrophotometer. Infrared spectra (IR) were recorded by Perkin Elmer spectrum GX FT-IR system. Major bands (ν_{max}) were recorded in wavenumber (cm^{-1}). ^{1}H and ^{13}C-NMR were measured in $CDCl_3$ on a Bruker AVANCE 300 (300 MHz for ^{1}H-NMR and 75 MHz for ^{13}C-NMR) spectrometer. Chemical shifts are in δ (ppm) with tetramethylsilane as an internal standard. MS were recorded on a VG 7070 mass spectrometer operating at 70 eV or with a VG Quattro triple quadrupole mass spectrometer for the electrospray mass spectra. Column chromatography was carried out using silica gel 60 (Merck, 70-230 or 230-400 mesh) and Lichroprep RP-18 (Merck, 40-63 μm). Pre-coated silica gel 60 F_{254} (Merck, layer thickness 0.25 mm) and precoated RP-18 F_{254s} (Merck) were used for thin-layer chromatography (TLC) and the compounds were visualized under ultraviolet light or sprayed with 1% $CeSO_4$ in 10% aq. H_2SO_4 following by heating. Preparative layer chromatography (PLC) was performed on glass plate using pre-coated silica gel 60 F_{254} (Merck, 20x20 cm, layer thickness 0.25, 0.5 or 1.0 mm).

Extraction and isolation of the resin of *G. hanburyi*

The dried and powdered gamboge resin of *G. hanburyi* (30 g) was heated at 100 ^{O}C for 1 hr., the color of gamboge was changed from yellow to orange then brown and melted. The melted gamboge was cooled down at room temperature to give a brown solid (28.35 g). The brown solid (25.45 g) was extracted first with CH_2Cl_2 2 times (750 and 250 mL) and with MeOH 2 times (500 and 100 mL) in a separatiory funnel. The extracts were filtered and evaporated under reduced pressure to give an orange solid of the CH_2Cl_2-soluble extract (19.55 g, GH-D) and a brown solid of the MeOH-soluble extract (1.73 g).

GH-D (an orange solid, 19.55 g) was separated by flash column chromatography using silica gel 60 [Merck, 230-400 mesh, diameter x height (13.0 cm x 5.0 cm)]. The column was eluted with 500 mL each fraction of hexane, gradient of hexane/EtOAc, and EtOAc and were evaporated under reduced pressure to give 19 fractions (**Table 1**).

Fraction GH-D3 (a yellow oil, 85.7 mg) was separated on preparative TLC (silica gel 60 F_{254}, layer thickness 1.0 mm) using benzene:EtOAc (5:1, 1 run) as the developing solvent to give GH-D3-1 as an orange wax (42.7 mg). The orange wax (42.7 mg) was further purified on a column of Lichroprep RP-18 (Merck, 40-63 μm) and eluted with CH_3CN/H_2O (10:1) to give 2 compounds, **GH-1** as an orange oil (22.0 mg) and **GH-2** as an orange oil (6.0 mg).

Table 1 Fractions obtained from GH-D.

Fraction No.	Eluent	Weight (mg)	Physical characteristic
GH-D1	5 % EtOAc in hexane	67.0	a yellow oil
GH- D2	10 % EtOAc in hexane	48.5	a yellow oil
*GH- D3	10 % EtOAc in hexane	85.7	a yellow oil
GH-D4	10 % EtOAc in hexane	52.5	a yellow oil
GH-D5	15 % EtOAc in hexane	66.4	a yellow oil
*GH-D6	15 % EtOAc in hexane	192.2	an orange solid
*GH-D7	20 % EtOAc in hexane	613.1	an orange solid
*GH-D8	20 % EtOAc in hexane	3475.0	an orange solid
GH-D9	25 % EtOAc in hexane	2864.0	a brown resin
GH-D10	25 % EtOAc in hexane	2171.0	a brown resin
GH-D11	30 % EtOAc in hexane	1005.0	a brown resin
*GH-D12	40 % EtOAc in hexane	1589.0	a brown resin
GH-D13	50 % EtOAc in hexane	1010.0	a brown resin
GH-D14	60 % EtOAc in hexane	957.9	an orange solid
GH-D15	70 % EtOAc in hexane	672.1	an orange solid
GH-D16	80 % EtOAc in hexane	416.4	an orange solid
GH-D17	90 % EtOAc in hexane	160.9	an orange solid
GH-D18	EtOAc	115.9	an orange solid
GH-D19	EtOAc	85.9	an orange solid

* Fractions were further investigated.

Fraction GH-D6 (an orange solid, 192.0 mg) was separated on a column of silica gel 60 (Merck, 70-200 mesh) using benzene and bezene:EtOAc (20:1) as the eluent to give 10 fractions (**Table 2**). Fraction GH-D6-3 (a yellow resin, 6.7 mg) and GH-D6-4 (a yellow resin, 12.3 mg) were combined and purified by column chromatography using Lichroprep RP-18 (Merck, 40-63 μm) as the stationary phase and CH_3CN/H_2O (5:1) as the mobile phase to give 2 compounds, **GH-3** as a yellow resin (8.5 mg) and **GH-4** as a yellow solid (3.1 mg). Fraction GH-D6-6 (a yellow resin, 14.4 mg) was further purified on a column of Lichroprep RP-18 (Merck, 40-63 μm) using CH_3CN/H_2O (5:1) as the mobile phase to give **GH-5** as a yellow resin (7.8 mg).

Table 2 Fractions obtained from GH-D6.

Fraction No.	Weight (mg)	Physical characteristic
GH-D6-1	9.8	a yellow resin
GH-D6-2	8.6	a yellow resin
*GH-D6-3	6.7	a yellow resin
*GH-D6-4	12.3	a yellow resin
GH-D6-5	19.7	a yellow resin
*GH- D6-6	14.4	a yellow resin
GH- D6-7	13.6	a yellow resin
GH-D6-8	16.4	a yellow solid
GH-D6-9	12.4	a yellow solid
GH-D6-10	15.9	a yellow solid

* Fractions were further investigated.

Fraction GH-D7 (an orange solid, 613.1 mg) was separated by column chromatography using silica gel 60 (Merck, 70-200 mesh) and the column was eluted with bezene:EtOAc (3:1) to give 7 fractions (**Table 3**). Fraction GH-D7-2 (an orange resin, 63.1 mg) was further purified on a column of Lichroprep RP-18 (Merck, 40-63 μm) using CH_3CN/H_2O (5:1) as the mobile phase to give 3 compounds, **GH-3** as a yellow resin (8.5 mg), **GH-4** as a yellow solid (3.1 mg) and **GH-5** as a yellow resin (21.9 mg).

Table 3 Fractions obtained from GH-D7.

Fraction No.	Weight (mg)	Physical characteristic
GH-D7-1	37.3	an orange resin
*GH-D7-2	63.1	an orange resin
GH-D7-3	24.1	an orange resin
GH-D7-4	27.1	an orange resin
GH-D7-5	39.1	a yellow resin
GH-D7-6	105.7	an orange foam
GH-D7-7	205.1	an orange resin

* Fractions were further investigated.

Fraction GH-D8 (403 mg) was purified by column chromatography using Lichroprep RP-18 (Merck, 40-63 μm) as the stationary phase and CH_3CN/H_2O (5:1.5) as the mobile phase to give 5 fractions (**Table 4**). Fractions GH-D8-1 (a yellow resin, 56.1mg) and GH-D8-5 (a red resin, 190.3 mg) were identified as compounds **GH-6** and **GH-7**, respectively. Fraction GH-D8-3 (an orange resin, 77.5 mg) was further purified by preparative TLC (silica gel 60 F_{254}, layer thickness 1.0 mm) using benzene:EtOAc (3:1, 1 run) as the developing solvent to give **GH-8** as a yellow resin (16.5 mg).

Table 4 Fractions obtained from GH-D8.

Fraction No.	Weight (mg)	Physical characteristic
*GH-D8-1	56.1	a yellow resin
GH-D8-2	53.9	a yellow resin
*GH-D8-3	99.4	an orange resin
GH-D8-4	101.8	an orange resin
*GH-D8-5	190.3	a red resin

* Fractions were further investigated.

Fraction GH-D12 (a brown resin, 1.59 g) was separated by column chromatography using silica gel 60 (Merck, 70-200 mesh) and the column was eluted with the gradient of increasing polarity CH_2Cl_2/MeOH/H_2O to give 10 fractions (**Table 5**). Fraction GH-D12-4 (a yellow resin, 414.5 mg) was further purified on a column of Lichroprep RP-18 (Merck, 40-63 μm) using CH_3CN/H_2O (5:1.3) as the eluent to give 3 fractions (**Table 6**). Fractions GH-D12-4-1 (a yellow resin, 84.5 mg) was identified to be compounds **GH-9**. Fraction GH-D12-4-2 (a yellow resin, 64.2 mg) was further purified on preparative TLC (silica gel 60 F_{254}, layer thickness 1.0 mm) using CH_2Cl_2/MeOH/H_2O (100:3:1, 2 runs) and CH_2Cl_2/MeOH/H_2O (50:3:1, 2 runs) as the developing solvent to give 2 compounds, **GH-10** as an orange solid (14.3 mg), and **GH-11** as a yellow solid (28.4 mg). Fraction GH-D12-4-3 (a yellow resin, 110.2 mg) was separated on preparative TLC (silica gel 60 F_{254}, layer thickness 1.0 mm) using CH_2Cl_2/MeOH/H_2O (100:3:1, 2 runs) and CH_2Cl_2/MeOH/H_2O (50:3:1, 2 runs) as the developing solvent to give GH-D12-4-3-2 as a yellow resin (90.3 mg). The yellow resin (41.2 mg) was purified on preparative TLC (silica gel 60 F_{254}, layer thickness 0.5 mm) using benzene:EtOAc (5:1, 6 runs) as the developing solvent to give 3 compounds, **GH-12** as a yellow solid (4.6 mg), **GH-13** as a yellow solid (3.1 mg) and **GH-14** as a yellow resin (8.9 mg).

Table 5 Fractions obtained from GH-D12.

Fraction No.	Weight (mg)	Physical characteristic
GH-D12-1	17.5	a yellow resin
GH-D12-2	24.0	a yellow resin
GH-D12-3	323.0	a yellow resin
*GH-D12-4	414.5	a yellow resin
GH-D12-5	229.9	a yellow resin
GH-D12-6	91.9	a yellow foam
GH-D12-7	73.9	a yellow foam
GH-D12-8	65.0	a yellow foam
GH-D12-9	73.0	a yellow foam
GH-D12-10	103.4	a yellow foam

* Fraction was further investigated.

Table 6 Fractions obtained from GH-D12-4.

Fraction No.	Weight (mg)	Physical characteristic
GH-D12-4-1	84.5	a yellow resin
*GH-D12-4-2	64.2	a yellow resin
*GH-D12-4-3	110.2	a yellow resin

* Fractions were further investigated.

Extraction and isolation of the resin of *G. hanburyi* was repeated, following the above procedure. The dried and powdered gamboge resin of *G. hanburyi* (30 g) was heated at 100 ^{o}C for 1 hr., the color of gamboge was changed from yellow to orange then brown and melted. The melted gamboge was cooled down at room temperature to give a brown solid (28.25 g). The brown solid (27.56 g) was extracted first with CH_2Cl_2 2 times (750 and 250 mL) and with MeOH 2 times (500 and 100 mL) in a separatiory funnel. The extracts were filtered and evaporated under reduced pressure to give an orange solid of the CH_2Cl_2-soluble extract (21.45 g, GH2-D) and a brown solid of the MeOH-soluble extract (1.85 g).

GH2-D (an orange solid, 21.45 g) was separated by flash column chromatography using silica gel 60 [Merck, 230-400 mesh, diameter x height (13.0 cm x 5.0 cm)]. The column was eluted with 500 mL each fraction of hexane, gradient of hexane/EtOAc, and EtOAc and were evaporated under reduced pressure to give 19 fractions (**Table 7**).

Table 7 Fractions obtained from GH2-D.

Fraction No.	Eluent	Weight (mg)	Physical characteristic
GH2-D1	5 % EtOAc in hexane	8.0	a yellow oil
GH2-D2	10 % EtOAc in hexane	79.0	a yellow oil
GH2-D3	10 % EtOAc in hexane	55.3	a yellow oil
GH2-D4	10 % EtOAc in hexane	58.6	a yellow oil
GH2-D5	15 % EtOAc in hexane	247.7	a yellow oil
* GH2-D6	15 % EtOAc in hexane	1363.8	an orange solid
GH2-D7	20 % EtOAc in hexane	3714.2	an orange solid
GH2-D8	20 % EtOAc in hexane	4892.5	an orange solid
GH2-D9	25 % EtOAc in hexane	2864.8	a brown resin
GH2-D10	25 % EtOAc in hexane	1373.7	a brown resin
GH2-D11	30 % EtOAc in hexane	1037.1	a brown resin
* GH2-D12	40 % EtOAc in hexane	1159.8	a brown resin
GH2-D13	50 % EtOAc in hexane	863.7	a brown resin
GH2-D14	60 % EtOAc in hexane	735.2	an orange solid
GH2-D15	70 % EtOAc in hexane	657.8	an orange solid
GH2-D16	80 % EtOAc in hexane	364.1	an orange solid
GH2-D17	90 % EtOAc in hexane	134.8	an orange solid
GH2-D18	EtOAc	109.5	an orange solid
GH2-D19	EtOAc	58.6	an orange solid

* Fractions were further investigated.

Fraction GH2-D6 (1.36 g) was separated by column chromatography using silica gel 60 [Merck, 70-200 mesh) benzene and bezene:EtOAc (3:1) as the eluent to give 8 fractions (**Table 8**). Fraction GH2-D6-2 (a yellow resin, 49.7 mg) was further purified on preparative TLC (silica gel 60 F_{254}, layer thickness 0.5 mm) using benzene:EtOAc (5:1, 4 runs) as the developing solvent to give 2 compounds, **GH-3** as a yellow resin (7.2 mg) and **GH-15** as a yellow solid (13.7 mg). Fraction GH2-D6-3 (a yellow resin, 84.8 mg) was further separated on a column of Lichroprep RP-18 (Merck, 40-63 μm) using CH_3CN/H_2O (5:1) as the eluent to give GH2-D6-3-3 as a yellow resin. The yellow resin (43.8 mg) was further purified on preparative TLC (silica gel 60 F_{254}, layer thickness 0.50 mm) using benzene:EtOAc (15:1, 6 runs) as the developing solvent to give 2 compounds, **GH-16** as a yellow solid (7.1 mg) and **GH-5** as a yellow resin (12.7 mg).

Table 8 Fractions obtained from GH2-D6.

Fraction No.	Weight (mg)	Physical characteristic
GH-D6-1	11.3	a yellow resin
*GH-D6-2	49.7	a yellow resin
*GH-D6-3	84.8	a yellow resin
GH-D6-4	117.4	a yellow resin
GH-D6-5	89.4	a yellow foam
GH-D6-6	544.3	a yellow foam
GH-D6-7	210.6	a yellow resin
GH-D6-8	289.9	a yellow resin

* Fractions were further investigated.

Fraction GH2-D12 (a brown resin, 1.16 g) was separated by column chromatography using silica gel 60 (Merck, 70-200 mesh) and the column was eluted with the gradient of increasing polarity of CH_2Cl_2/MeOH/H_2O to give 9 fractions (**Table 9**). Fraction GH2-D12-2 (a yellow resin, 467.2 mg) was further isolated on a column of Lichroprep RP-18 (Merck, 40-63 μm) using CH_3CN/H_2O (5:1) as the eluent to give GH2-D12-2-4 as a yellow resin. The yellow resin (55.4 mg) was further purified on preparative TLC (silica gel 60 F_{254}, layer thickness 1.0 mm) using benzene:EtOAc (5:1, 1 run) and CH_2Cl_2/MeOH/H_2O (50:3:1, 2 runs) as the developing solvent to give 2 compounds, **GH-17** as a yellow solid (6.3 mg) and **GH-10** as an orange solid (15.6 mg).

Table 9 Fractions obtained from GH2-D12.

Fraction No.	Weight (mg)	Physical characteristic
GH2-D12-1	173.4	a yellow resin
*GH2-D12-2	465.2	a yellow resin
GH2-D12-3	232.8	a yellow resin
GH2-D12-4	14.6	a yellow resin
GH2-D12-5	18.6	a yellow resin
GH2-D12-6	28.0	a yellow foam
GH-D12-7	14.4	a yellow foam
GH2-D12-8	5.0	a yellow foam
GH2-D12-9	15.0	a yellow foam

* Fraction was further investigated.

GH-1

GH-1 is an orange oil; $[\alpha]_D^{30.9}$-346° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 204 (4.43), 290 (4.20), 360 (4.14); IR $\nu_{max}^{thin\ film}$ cm^{-1}: 3425, 2974, 2925, 2851, 1735, 1685, 1636, 1595, 1435, 1382, 1329, 1171; ^{1}H–NMR ($CDCl_3$) : see **Table 10**; ^{13}C–NMR ($CDCl_3$) : see **Table 11**.

GH-2

GH-2 is an orange oil; $[\alpha]_D^{26.5}$ -351° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 282 (4.11), 292 (4.17), 362 (4.05); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3435, 2974, 2927, 2850, 1733, 1682, 1635, 1592, 1436, 1329, 1170; ^{1}H–NMR ($CDCl_3$) : see **Table 15**; ^{13}C–NMR ($CDCl_3$) : see **Table 16**.

GH-3

GH-3 is a yellow resin; $[\alpha]_D^{25.4}$-436° (*c* = 0.09, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 215 (4.88), 277 (4.29), 356 (4.32); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3383, 2975, 2925, 2855, 1737, 1686, 1633, 1597, 1437, 1383, 1334; EI MS m/z (relative intensity, %) : 614 [M^+] (32), 529 (36), 491 (34), 368 (100), 353 (35), 243 (41), 236 (34); ^{1}H–NMR ($CDCl_3$) : see **Table 19**; ^{13}C–NMR ($CDCl_3$) : see **Table 20**.

GH-4

GH-4 is a yellow solid; $[\alpha]_D^{29.3}$-361° (*c* = 0.12, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 225 (4.67), 288 (4.39), 360 (4.33); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3379, 2971, 2925, 2855, 1737, 1689, 1633, 1593, 1436, 1382, 1331, 1174 1138, 1048, 958, 811; EI MS m/z (relative intensity, %) : 612 [M^+] (0.6), 559 (4), 227 (4), 215 (10), 189 (6), 145 (4), 129 (6), 91 (10), 69 (70), 55 (100);^{1}H–NMR ($CDCl_3$) : see **Table 15**; ^{13}C–NMR ($CDCl_3$) : see **Table 16**.

GH-5

GH-5 is a yellow resin; m.p. 84-86 ^oC; $[\alpha]_D^{25.4}$-435° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 278 (4.01), 298 (3.93), 359 (3.94); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3409, 2974, 2923, 1736, 1686, 1632, 1592, 1436, 1331, 1187, 1165, 1140, 1046; ^{1}H–NMR ($CDCl_3$) : see **Table 10**; ^{13}C–NMR ($CDCl_3$) : see **Table11.**

GH-6

GH-6 is a yellow resin; m.p. 90-92 ^oC; UV λ_{max}^{MeOH} (log ε) nm : 278 (4.04), 295 (4.00), 361 (3.95); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3383, 2972, 1735, 1688, 1647, 1631, 1593, 1458, 1434, 1332, 1142, 1046; ^{1}H–NMR ($CDCl_3$) : see **Table 12**; ^{13}C–NMR ($CDCl_3$) : see **Table 13**.

GH-7

GH-7 is a red resin; m.p. 86-88 ^oC; UV λ_{max}^{MeOH} (log ε) nm : 277 (4.41), 317 (3.97), 362 (3.64); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3429, 2970, 2918, 1736, 1692, 1628, 1593, 1454, 1436, 1374, 1175, 1154, 1125, 1045; ^{1}H–NMR ($CDCl_3$) : see **Table 17**; ^{13}C–NMR ($CDCl_3$) : see **Table 18.**

GH-8

GH-8 is a yellow resin; m.p. 77-78 ^{O}C; $[\alpha]_D^{25.4}$-529° (*c* = 0.15, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 270 (4.50), 357 (4.09); IR $\nu_{max}^{thin\ film}$ cm^{-1}: 3383, 2963, 2851, 1739, 1689, 1633, 1604, 1438, 1385, 1335, 1261, 1138, 1098, 1045; EI MS m/z (relative intensity, %) : 628 [M^+] (100), 602 (32), 545 (51), 507 (39), 476 (21), 368 (98), 351 (22), 295 (31), 256 (46), 236 (51); ^{1}H–NMR ($CDCl_3$) : see **Table 21**; ^{13}C–NMR ($CDCl_3$) : see **Table 22**.

GH-9

GH-9 is a yellow resin; $[\alpha]_D^{25.6}$-287° (*c* = 0.08, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 202 (4.36), 277 (4.07), 360 (3.95); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3384, 2975, 1738, 1687, 1645, 1633, 1593, 1459, 1436, 1333, 1145, 1046; EI MS m/z (relative intensity, %) : 560 [M^+] (5), 545 (2), 517 (2), 312 (2), 256 (3), 228 (12), 213 (5), 185 (13), 157 (8), 129 (25), 97 (30), 73 (66), 55 (100); ^{1}H–NMR ($CDCl_3$) : see **Table 12**; ^{13}C–NMR ($CDCl_3$) : see **Table 13**.

GH-10

GH-10 is an orange solid; m.p. 66-68 ^{O}C; $[\alpha]_D^{25.6}$-412° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 277 (4.44), 287 (4.46), 357 (4.34); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3525, 2973, 2851, 1737, 1645, 1630, 1592, 1460, 1436, 1330, 1186, 1164, 1140, 1119, 1047; EI MS m/z (relative intensity, %) : 546 [M^+] (38), 518 (29), 503 (67), 485 (23), 459 (11), 405 (65), 389 (29), 363 (40), 349 (44), 307 (47), 231 (100); ^{1}H–NMR ($CDCl_3$) : see **Table 14**; ^{13}C–NMR ($CDCl_3$) : see **Table 13**.

GH-11

GH-11 is a yellow solid; m.p. 80-82^{O} C; $[\alpha]_D^{25.6}$-398° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 270 (4.50), 357 (4.14); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3379, 2963, 2850, 1738, 1689, 1633, 1600, 1438, 1383, 1334, 1261, 1137, 1098, 1045; EI MS m/z (relative intensity, %) : 628 [M^+] (24), 545 (18), 507 (38), 476 (22), 381 (27), 351 (38), 325 (35), 295 (67), 253 (100), 231 (53); ^{1}H–NMR ($CDCl_3$) : see **Table 21**; ^{13}C–NMR ($CDCl_3$) : see **Table 22**.

GH-12

GH-12 is a yellow solid; m.p. 88-90 ^{O}C; $[\alpha]_D^{25.4}$-410° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 279 (4.21), 290 (4.23), 359 (4.18); IR $\nu_{max}^{thinfilm}$ cm^{-1} : 3184, 2968, 2921, 2851, 1737, 1687, 1642, 1632, 1593, 1456, 1436, 1331, 1175, 1137, 1045, 1018, 959, 812; EI MS m/z (relative intensity, %) : 628 [M^+] (4), 545 (11), 517 (3), 419 (2), 284 (5), 256 (16), 213 (10), 185 (11), 129 (27), 97 (35), 56 (100); ^{1}H–NMR ($CDCl_3$) : see **Table 17**; ^{13}C–NMR ($CDCl_3$) : see **Table 18.**

GH-13

GH-13 is a yellow solid; UV λ_{max}^{MeOH} (log ε) nm : 215 (4.48), 357 (4.07); IR $\nu_{max}^{thin\ film}$ cm^{-1} :2952, 2923, 1737, 1690, 1634, 1594, 1433, 1374, 1365, 1333, 1321, 1269, 1182, 1139, 1111, 1048, 958, 812; EI MS m/z (relative intensity, %) : 628 [M^+] (9), 545 (22), 517 (6), 473 (5), 395 (4), 285 (4), 245 (8), 215 (14), 189 (10), 147 (9), 129 (16), 97 (23), 69 (91), 55 (100); ^{1}H–NMR ($CDCl_3$) : see **Table 23**; ^{13}C–NMR ($CDCl_3$) : see **Table 24**.

GH-14

GH-14 is a yellow resin; UV λ_{max}^{MeOH} (log ε) nm : 215 (4.48), 359 (4.02); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 2952, 2927, 2859, 1739, 1688, 1632, 1593, 1434, 1374, 1366, 1332, 1319, 1270, 1182, 1139, 1112, 1065, 1049, 958, 811; EI MS m/z (relative intensity, %) : 628 [M^+] (4), 545 (14), 517 (1), 313 (2), 256 (4), 236 (4), 245 (8), 215 (11), 185 (9), 157 (7), 129 (19), 97 (28), 69 (78), 55 (100); ^{1}H–NMR ($CDCl_3$) : see **Table 23**; ^{13}C–NMR ($CDCl_3$) : see **Table 24**.

GH-15

GH-15 is a yellow solid; $[\alpha]_D^{25.6}$-440° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 215 (4.81), 277 (4.25), 356 (4.22); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3383, 2975, 2925, 2854, 1737, 1685, 1633, 1596, 1437, 1383, 1333, 1256, 1216, 1172, 1048, 958, 811; ^{1}H–NMR ($CDCl_3$) : see **Table 19**; ^{13}C–NMR ($CDCl_3$) : see **Table 20**.

GH-16

GH-16 is a yellow solid; $[\alpha]_D^{25.6}$-320° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 225 (4.88), 277 (4.59), 360 (4.54); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3389, 2975, 2925, 1735, 1684, 1633, 1592, 1437, 1333, 1185, 1165, 1141, 1045, 956, 813; ^{1}H–NMR ($CDCl_3$) : see **Table 10**; ^{13}C–NMR ($CDCl_3$) : see **Table 11**.

GH-17

GH-17 is a yellow solid; $[\alpha]_D^{28.7}$-266° (*c* = 0.10, MeOH); UV λ_{max}^{MeOH} (log ε) nm : 213 (4.52), 359 (4.10); IR $\nu_{max}^{thin\ film}$ cm^{-1} : 3429, 2975, 2924, 2853, 1736, 1699, 1645, 1632, 1592, 1455, 1399, 1338, 1259, 1216, 1175, 1048, 959, 812, 758; ^{1}H–NMR ($CDCl_3$) : see **Table 25**; ^{13}C–NMR ($CDCl_3$) : see **Table 26**.

Table 10 ^{1}H-NMR spectral data of **GH-1**, **GH-16** and **GH-5**.

position	**GH-1** [deoxymorellin, **5**]	**GH-16** [morellin, **6**]	**GH-5** [isomorellin, **7**]
1	12.97 (1H, s)	12.71 (1H, s)	12.97 (1H, s)
7	3.51 (1H, dd, 4.5, 6.9)	3.55 (1H, dd, 2.4, 6.8)	3.55 (1H, dd, 2.4, 6.8)
8	7.45 (1H, d, 6.9)	7.55 (1H, d, 6.9)	7.59 (1H, d, 6.9)
10	6.66 (1H, d, 9.9)	6.62 (1H, d, 10.0)	6.64 (1H, d, 10.0)
11	5.54 (1H, d, 9.9)	5.54 (1H, d, 10.0)	5.54 (1H, d, 10.0)
13	1.46 (3H, s)	1.47 (3H, s)	1.46 (3H, s)
14	1.46 (3H, s)	1.53 (3H, s)	1.48 (3H, s)
15	3.35 (2H, m)	3.33 (2H, m)	3.25 (2H, m)
16	5.23 (1H, t, 6.6)	5.19 (1H, t, 6.3)	5.11 (1H, t, 6.3)
18	1.69 (3H, s)	1.77 (3H, s)	1.80 (3H, s)
19	1.62 (3H, s)	1.66 (3H, s)	1.67 (3H, s)
Ha-20	2.58 (2H, d, 7.2)	2.88 (1H, dd, 7.6, 15.8)	2.76 (1H, dd, 7.6, 15.8)
Hb-20		2.66 (1H, dd, 6.9, 15.8)	2.66 (1H, dd, 6.9, 15.8)
21	4.44 (1H, t, 7.8)	6.07 (1H, t, 6.3)	6.41 (1H, t, 6.3)
23	1.39 (3H, overlapped)	9.59 (1H, s)	1.34 (3H, s)
24	1.04 (3H, s)	1.33 (3H, s)	9.25 (1H, s)
Ha-25	1.40 (1H, overlapped)	1.46 (1H, overlapped)	1.45 (1H, overlapped)
Hb-25	2.34 (1H, dd, 4.5, 15.0)	2.39 (1H, dd, 4.6, 13.3)	2.39 (1H, dd, 4.6, 13.3)
26	2.51 (1H, d, 9.3)	2.58 (1H, d, 9.3)	2.59 (1H, d, 9.3)
28	1.30 (3H, s)	1.32 (3H, s)	1.34 (3H, s)
29	1.74 (3H, s)	1.75 (3H, s)	1.76 (3H, s)

Table 11 ^{13}C-NMR spectral data of **GH-1, GH-16** and **GH-5**.

position	**GH-1** [deoxymorellin, **5**]	**GH-16** [morellin, **6**]	**GH-5** [isomorellin, **7**]
1	157.8	157.0	157.3
2	102.9	103.2	102.9
3	160.6	161.1	161.3
4	106.4	108.1	108.1
4a	157.5	157.6	157.7
4b	90.5	90.8	91.0
5	84.6	84.1	83.9
6	203.5	203.0	203.0
7	46.9	46.9	46.9
8	133.8	135.1	135.6
8a	133.7	133.4	133.2
9	179.6	178.8	178.8
9a	100.7	100.4	-
10	115.5	115.3	115.3
11	126.2	126.4	126.4
12	78.4	79.0	79.0
13	28.8	28.4	28.3
14	28.8	16.5	28.4
15	21.6	21.7	28.9
16	122.2	121.9	121.8
17	131.6	132.2	131.8
18	25.8	18.2	18.2

Table 11 (continued).

position	**GH-1** [deoxymorellin, **5**]	**GH-16** [morellin, **6**]	**GH-5** [isomorellin, **7**]
19	18.1	25.7	25.6
20	29.0	26.7	30.0
21	117.8	140.1	140.0
22	134.9	146.5	146.5
23	16.7	194.5	8.6
24	25.5	16.7	194.8
25	25.4	25.7	25.6
26	49.2	49.0	49.0
27	83.1	84.1	83.9
28	29.1	28.6	28.9
29	30.1	30.0	29.9

Table 12 ^{1}H-NMR spectral data of **GH-6** and **GH-9**.

position	**GH-6** [morellic acid, **8**]	**GH-9** [isomorellic acid, **9**]
1	12.71 (1H, s)	12.75 (1H, s)
7	3.51 (1H, dd, 4.4, 6.7)	3.53 (1H, dd, 4.4, 6.9)
8	7.57 (1H, d, 6.9)	7.58 1H, (d, 6.9)
10	6.57 (1H, d, 10.0)	6.64 (1H, d, 10.0)
11	5.47 (1H, d, 10.0)	5.53 (1H, d, 10.0)
13	1.40 (3H, s)	1.44 (3H, s)
14	1.43 (3H, s)	1.45 (3H, s)
Ha-15	3.15 (1H, dd,5.4, 14.5)	3.28 (2H, d, 7.1)
Hb-15	3.32 (1H, dd,8.4, 14.4)	
16	5.05 (1H, dd, 5.4, 8.4)	5.14 (1H, t, 7.1)
18	1.76 (3H, s)	1.76 (3H, s)
19	1.66 (3H, s)	1.67 (3H, s)
Ha-20	2.98 (2H, d, 6.8)	2.58 (1H, dd, 7.0)
Hb-20		2.67 (1H, dd, 8.4, 15.5)
21	6.08 (1H, t, 6.8)	6.60 (1H, dd, 8.4, 15.5)
23	-	1.37 (3H, s)
24	1.76 (3H, s)	-
Ha- 25	1.40 (1H, overlapped)	1.40 (1H, overlapped)
Hb- 25	2.33 (1H, dd, 4.7, 13.5)	2.36 (1H, dd, 4.9, 13.6)
26	2.54 (1H, d, 9.3)	2.60 (1H, d, 9.2)
28	1.31 (3H, 3H, s)	1.32 (3H, 3H, s)
29	1.66 (3H, 3H, s)	1.74 (3H, 3H, s)

Table 13 ^{13}C-NMR spectral data of **GH-6, GH-9** and **GH-10**.

position	**GH-6** [morellic acid, **8**]	**GH-9** [isomorellic acid, **9**]	**GH-10** [isomorellinol, **10**]
1	157.3	157.3	15 7.4
2	103.2	103.2	103.1
3	161.2	161.1	161.0
4	108.1	108.3	108.4
4a	157.6	157.6	157.7
4b	90.9	90.7	90.4
5	83.9	83.7	84.5
6	203.3	203.0	203.3
7	46.9	46.9	47.0
8	135.4	135.4	134.4
8a	133.4	133.3	33.8
9	179.0	178.9	180.3
9a	100.5	100.5	100.7
10	115.4	115.4	115.5
11	126.0	136.2	126.3
12	78.6	78.7	78.7
13	28.3	28.3	28.4
14	28.4	28.4	28.3
15	21.6	21.6	21.6
16	122.2	122.1	121.9
17	131.5	131.8	131.9
18	18.1	18.1	18.2

Table 13 (continued).

position	**GH-6** [morellic acid, **8**]	**GH-9** [isomorellic acid, **9**]	**GH-10** [isomorellinol, **10**]
19	25.7	25.8	25.8
20	29.3	29.0	29.7
21	137.6	136.7	118.2
22	127.9	128.8	138.0
23	170.1	11.4	12.6
24	20.7	171.7	68.0
25	25.2	25.3	25.4
26	49.1	49.1	49.1
27	83.8	83.7	83.4
28	28.8	29.0	29.0
29	29.9	30.0	30.1

Table 14 ^{1}H-NMR spectral data of **GH-10**.

position	**GH-10** [isomorellinol, **10**]
1	12.71 (1H, s)
7	3.54 (1H, dd, 4.6, 6.9)
8	7.47 (1H, d, 6.9)
10	6.65 (1H, d, 9.9)
11	5.56 (1H, d, 9.9)
13	1.46 (3H, s)
14	1.46 (3H, s)
Ha-15	3.29 (1H, dd, 7.4, 14.2)
Hb-15	3.38 (1H, dd, 6.9, 14.2)
16	5.27 (1H, dd, 6.9, 7.4)
18	1.70 (3H, s)
19	1.79 (3H, s)
20	2.66 (2H, d, 7.7)
21	4.80 (1H, t, 7.7)
23	1.07 (3H, s)
Ha-24	3.64 (1H, d, 14.2)
Hb-24	3.72 (1H, d, 14.2)
Ha-25	1.37 (1H, dd, 9.4, 13.4)
Hb-25	2.37 (1H, dd, 4.7, 13.4)
26	2.52 (1H, d, 9.4)
28	1.31 (3H, s)
29	1.74 (3H, s)

Table 15 ^{1}H-NMR spectral data of **GH-2** and **GH-4**.

position	**GH-2** [gambogin, **11**]	**GH-4** [isogambogenal, **1**]
1	12.91 (1H, s)	12.75 (1H, s)
7	3.51 (1H, dd, 4.8, 6.9)	3.55 (1H, dd, 4.5, 6.9)
8	7.45 (1H, d, 6.9)	7.57/7.58 (1H, d, 6.9)
10	6.70 (1H, d, 10.2)	6.67 (1H, d,10.1)
11	5.48 (1H, d, 10.2)	5.47/5.48 (1H, d,10.1)
Ha-13	1.63 (1H, overlapped)	1.65 (1H, s)
Ha-13	1.77 (1H, overlapped)	1.77 (1H, s)
14	2.07 (2H, m)	2.04 (2H, m)
15	5.22 (1H, m)	5.08 (1H, m)
17	1.58 (3H, s)	1.57/1.60 (3H, s)
18	1.68 (3H, overlapped)	1.66 (3H, s)
19	1.42 (3H, overlapped)	1.40/1.44 (3H, s)
20	3.35 (2H, m)	3.25 (2H, m)
21	5.09 (1H, m)	5.10 (1H, m, overlapped)
23	1.77 (3H, s)	1.75 (3H, s)
24	1.68 (3H, s)	1.68 (3H, s)
Ha-25	2.59 (2H, d, 7.8)	2.70 (1H, dd, 7.0, 15.3)
Hb-25		2.75 (1H, dd. 7.0, 15.3)
26	4.44 (1H, m)	6.34/6.42 (1H, t, 7.0)
28	1.39 (3H, overlapped)	1.33/1.35 (3H, s)
29	1.05 (3H, s)	9.24/9.25 (3H, s)

Table 15 (continued).

position	**GH2** [gambogin, **11**]	**GH4** [isogambogenal, **1**]
Ha-30	1.39 (1H, overlapped)	1.40 (1H, overlapped)
Hb-30	2.35 (1H, d, 7.8)	2.38 (1H, dd, 4.7, 13.6)
31	2.50 (1H, d, 6.3)	2.58 (1H, d, 9.5)
33	1.27 (3H, s)	1.27 (3H, s)
34	1.72 (3H, s)	1.75 (3H, s)

Table 16 ^{13}C-NMR spectral data of **GH-2** and **GH-4**.

position	**GH-2** [gambogin, **11**]	**GH-4** [isogambogenal, **1**]
1	158.0	157.7
2	102.6	103.0
3	160.9	161.7
4	107.8	107.7
4a	157.6	157.3
4b	90.5	90.8
5	84.6	839.0
6	203.1	203.1
7	46.9	46.8
8	133.7	135.5
8a	133.6	133.4
9	179.5	178.7
9a	100.5	100.5
10	116.0	115.8
11	124.7	125.0
12	81.0	81.5
13	41.8	41.9
14	22.7	22.8
15	122.2	121.9
16	131.9	132.0
17	17.6	17.6
18	25.6	25.6

Table 16 (continued).

position	**GH-2** [gambogin, **11**]	**GH-4** [isogambogenal, **1**]
19	17.2	27.4
20	21.7	21.7
21	123.6	123.6
22	132.0	131.9
23	18.2	18.1
24	25.6	25.6
25	28.8	29.7
26	117.8	146.4
27	135.7	140.1
28	16.7	8.6
29	25.7	194.5
30	25.4	25.3
31	49.2	49.0
32	83.1	83.3
33	29.1	29.0
34	30.1	29.9

Table 17 ^{1}H-NMR spectral data of **GH-7** and **GH-12**.

position	**GH-7** [gambogic acid, **12**]	**GH-12** [isogambogic acid, **13**]
1	12.81 (1H, s)	12.70 (1H, s)
7	3.50 (1H, dd, 4.7, 6.9)	3.51 (1H, dd, 4.8, 6.8)
8	7.55 (1H, d, 6.9)	7.55 (1H, d, 6.8)
10	6.63 (2H, d, 10.1)	6.67 (2H, d, 10.2)
11	5.44 (1H, d, 10.1)	5.46 (1H, d, 10.2)
Ha-13	1.62 (1H, overlapped)	1.62 (1H, overlapped)
Hb-13	1.79 (1H, overlapped)	1.79 (1H, overlapped)
14	2.04 (2H, m)	2.06 (2H, m)
15	5.09 (1H, m)	5.09 (1H, m)
17	1.56 (3H, s)	1.56 (3H, s)
18	1.06 (3H, s)	1.66 (3H, s)
19	1.36 (3H, s)	1.38 (3H, s)
Ha-20	3.16 (1H, m)	3.28 (2H, t, 7.6)
Hb-20	3.32 (1H, m)	
21	5.07 (1H, m)	5.14 (1H, m)
23	1.74 (3H, s)	1.74 (3H, s)
24	1.66 (3H, s)	1.66 (3H, s)
Ha-25	2.88 (1H, dd, 7.5, 15.6)	2.60 (1H, d, 6.6)
Hb-25	2.99 (1H, dd, 7.3, 15.6)	2.63 (1H, d, 6.6)
26	6.09 (1H, dd, 7.3, 7.5)	6.47 (1H, t, 6.6)
28	-	1.36 (3H, s)
29	1.75 (3H, s)	-

Table 17 (continued).

position	**GH-7** [gambogic acid, **12**]	**GH-12** [isogambogic acid, **13**]
Ha-30	1.40 (1H, overlapped)	1.40 (1H, overlapped)
Hb-30	2.33 (1H, dd, 4.6, 13.7)	2.34 (1H, dd, 4.8, 13.6)
31	2.55 (1H, d, 4.6)	2.53 (1H, d, 9.3)
33	1.31 (3H, s)	1.30 (3H, s)
34	1.71 (3H, s)	1.71 (3H, s)

Table 18 ^{13}C-NMR spectral data of **GH-7** and **GH-12**.

position	**GH-7** [gambogic acid, **12**]	**GH-12** [isogambogic acid, **13**]
1	157.6	157.4
2	102.7	102.3
3	161.3	161.4
4	107.6	107.9
4a	157.6	157.6
4b	90.9	90.7
5	83.7	83.7
6	203.3	203.0
7	46.8	46.9
8	135.3	135.3
8a	133.3	133.5
9	178.9	179.0
9a	100.4	100.4
10	115.9	115.9
11	124.7	124.8
12	81.1	81.3
13	41.7	41.9
14	22.7	22.7
15	122.3	123.8
16	131.7	131.8
17	17.6	17.6
18	29.6	25.7

Table 18 (continued).

position	**GH-7** [gambogic acid, **12**]	**GH-12** [isogambogic acid, **13**]
19	26.9	27.5
20	20.5	21.6
21	122.3	122.2
22	131.4	131.9
23	18.1	18.2
24	25.7	25.6
25	29.3	29.0
26	137.9	136.5
27	127.6	128.9
28	171.3	11.5
29	20.7	171.0
30	25.2	25.3
31	49.0	49.1
32	83.8	83.7
33	28.9	29.7
34	29.9	30.0

Table 19 ^{1}H-NMR spectral data of **GH-3** and **GH-15**.

position	**GH-15** [gambogenin, **14**]	**GH-3** [isogambogenin, **15**]
1	12.82 (1H, s)	12.83 (1H, s)
3	6.65 (1H, s)	6.65 (1H, s)
7	3.55 (1H, dd, 4.5, 7.4)	3.54 (1H, dd, 4.7, 6.9)
8	7.58 (1H, d, 7.4)	7.59 (1H, d, 6.9)
10	3.39 (2H, d, 6.6)	3.38 (2H, d, 6.6)
11	5.24 (1H, t, 7.2)	5.24 (1H, t, 7.7)
13	2.13 (1H, m)	2.11 (1H, m)
14	2.13 (2H, m)	2.11 (2H, m)
15	5.09 (1H, t, 5.9)	5.08 (1H, t, 5.9)
17	1.62 (3H, s)	1.62 (3H, s)
18	1.72 (3H, s)	1.70 (3H, s)
19	1.83 (3H, s)	1.83 (3H, s)
20	3.35 (2H, overlapped)	3.33 (2H, d, 6.4)
21	5.20 (1H, t, 5.8)	5.14 (1H, t, 6.4)
23	1.53 (3H, s)	1.71 (3H, s)
24	1.78 (3H, s)	1.77 (3H, s)
25	2.89 (1H, dd, 7.4, 15.3)	2.71 (1H, d, 7.2)
26	6.07 (1H, dd, 7.4, 10.3)	6.39 (1H, t, 7.2)
28	9.57 (1H, s)	1.33 (3H, s)
29	1.33 (3H, s)	9.24 (1H, s)
Ha-30	1.40 (1H, overlapped)	1.40 (1H, overlapped)
Hb-30	2.38 (1H, dd, 4.5, 13.5)	2.38 (1H, dd, 4.7, 13.5)

Table 19 (continued).

position	**GH-15** [gambogenin, **14**]	**GH-3** [isogambogenin, **15**]
31	2.55 (1H, d, 9.3)	2.59 (1H, d, 9.3)
33	1.33 (3H, s)	1.33 (3H, s)
34	1.72 (3H, s)	1.73 (3H, s)

Table 20 ^{13}C-NMR spectral data of **GH-3** and **GH-15**.

position	**GH-15** [gambogenin, **14**]	**GH-3** [isogambogenin, **15**]
1	163.8	160.4
2	107.4	107.5
3	163.4	163.9
4	106.5	106.7
4a	156.0	155.9
4b	90.7	90.6
5	83.3	83.5
6	203.1	203.1
7	46.9	46.9
8	135.7	135.7
8a	133.5	133.5
9	179.2	179.0
9a	100.7	100.6
10	21.2	21.2
11	121.2	121.1
12	139.7	139.8
13	39.7	39.7
14	26.3	26.3
15	123.7	123.7
16	132.0	132.0
17	25.7	25.7
18	17.7	17.7

Table 20 (continued).

position	**GH-15** [gambogenin, **14**]	**GH-3** [isogambogenin, **15**]
19	16.3	16.3
20	22.1	22.2
21	121.7	121.7
22	134.0	134.0
23	18.1	18.1
24	25.4	25.7
25	29.1	29.1
26	146.5	146.5
27	140.2	140.3
28	194.5	8.7
29	18.1	194.5
30	25.3	25.1
31	49.0	49.1
32	83.9	83.7
33	29.0	29.9
34	29.0	29.1

Table 21 ^{1}H-NMR spectral data of **GH-8** and **GH-11**.

position	**GH-8** [gambogenic acid, **16**]	**GH-11** [isogambogenic acid, **17**]
1	12.84 (1H, s)	12.82 (1H, s)
7	3.51 (1H, dd, 4.6, 6.9)	3.52 (1H, dd, 4.5, 6.9)
8	7.56 (1H, d, 6.9)	7.58 (1H, d, 7.0)
10	3.30 (2H, brd, 6.6)	3.39 (2H, overlapped)
11	5.22 (1H, t, 6.6)	5.25 (1H, t, 7.0)
Ha-13	1.67 (1H, overlapped)	1.69 (1H, overlapped)
Hb-13	2.07 (1H, overlapped)	2.09 (1H, overlapped)
14	2.07 (2H, overlapped)	2.09 (2H, overlapped)
15	5.07 (1H, t, 5.7)	5.08 (1H, t, 5.7)
17	1.60 (3H, s)	1.61 (3H, s)
18	1.69 (3H, s)	1.69 (3H, s)
19	1.79 (3H, s)	1.82 (3H, s)
20	3.30 (2H, brd, 6.6)	3.38 (2H, overlapped)
21	5.11 (1H, t, 6.6)	5.16 (1H, t, 6.9)
23	1.75 (3H, s)	1.76 (3H, s)
24	1.74 (3H, s)	1.72 (3H, s)
Ha-25	2.90 (1H, dd, 7.2, 15.3)	2.66 (1H, dd, 7.2, 15.3)
Hb-25	3.10 (1H, dd, 8.1, 15.3)	2.66 (1H, dd, 8.3, 15.3)
26	5.86 (1H, dd, 7.2, 8.1)	6.61 (1H, dd, 7.2, 8.3)
28	-	1.37 (3H, s)
29	1.74 (3H, s)	-

Table 21 (continued).

position	**GH-8** [gambogenic acid, **16**]	**GH-11** [isogambogenic acid, **17**]
Ha-30	1.40 (1H, overlapped)	1.40 (1H, overlapped)
Hb-30	2.34 (1H, dd, 4.6, 13.4)	2.35 (1H, dd, 4.5, 13.4)
31	2.52 (1H, d, 8.9)	2.54 (1H, d, 9.2)
33	1.31 (3H, s)	1.31 (3H, s)
34	1.70 (3H, s)	1.72 (3H, s)

Table 22 ^{13}C-NMR spectral data of **GH-8** and **GH-11**.

position	**GH-8** [gambogenic acid, **16**]	**GH-11** [isogambogenic acid, **17**]
1	163.6	163.6
2	107.6	107.6
3	160.4	160.4
4	106.5	106.5
4a	155.9	156.0
4b	90.5	90.5
5	83.9	83.7
6	203.4	203.1
7	46.9	46.9
8	135.2	135.5
8a	133.6	133.5
9	179.1	179.1
9a	100.7	100.7
10	21.1	21.2
11	121.4	121.3
12	139.0	139.2
13	26.4	26.4
14	39.7	39.7
15	123.9	123.9
16	131.9	131.9
17	25.7	25.7
18	18.0	18.0

Table 22 (continued).

position	**GH-8** [gambogenic acid, **16**]	**GH-11** [isogambogenic acid, **17**]
19	16.2	16.2
20	22.0	22.1
21	122.0	122.0
22	133.9	133.9
23	17.7	17.7
24	25.5	25.7
25	29.5	29.7
26	137.0	136.8
27	128.2	128.7
28	170.5	11.5
29	20.7	171.3
30	25.3	25.3
31	49.0	49.0
32	83.9	83.6
33	28.9	28.9
34	29.8	29.9

Table 23 ^{1}H-NMR spectral data of **GH-13** and **GH-14**.

position	**GH-13** [isogamboginaic acid A, **2**]	**GH-14** [isogamboginaic acid B, **3**]
1	12.68 (1H, s)	12.56 (1H, s)
7	3.52 (1H, dd, 4.5, 6.9)	3.50 (1H, m)
8	7.55 (1H, d, 6.9)	7.55 (1H, d, 7.2)
10	3.09 (1H, d, 9.6)	3.13 (1H, d, 9.6)
11	2.59 (1H, dd, 7.3, 9.6)	2.50 (1H, dd, 6.6, 9.6)
Ha-13	1.68 (1H, overlapped)	1.65 (1H, overlapped)
Hb-13	1.89 (1H, overlapped)	1.88 (1H, overlapped)
14	1.39 (2H, overlapped)	1.40 (2H, overlapped)
15	2.41 (1H, q, 7.3)	2.40 (1H, q, 6.6)
17	1.41 (3H, s)	1.43 (3H, s)
18	0.80 (3H, s)	0.78 (3H, s)
19	1.37 (3H, s)	1.39 (3H, s)
20	3.27 (1H, d, 7.5)	3.32 (1H, d, 6.6)
21	5.15 (1H, t, 7.5)	5.15 (1H, t, 6.6)
23	1.66 (3H, s)	1.67 (3H, s)
24	1.75 (3H, s)	1.77 (3H, s)
Ha-25	2.58 (1H, dd, 4.2, 15.5)	2.65 (2H, d, 7.2)
Hb-25	2.75 (1H, dd, 8.5, 15.5)	
26	6.57 (1H, dd, 4.2, 8.5)	6.53 (1H, t, 7.2)
28	1.31 (3H, s)	-
29	-	1.35 (3H, s)

Table 23 (continued).

position	**GH-13** [isogamboginaic acid A, **2**]	**GH-14** [isogamboginaic acid B, **3**]
Ha-30	1.40 (1H, overlapped)	1.40 (1H, overlapped)
Hb-30	2.35 (1H, dd, 4.5, 13.4)	2.35 (1H, dd, 4.8, 13.5)
31	2.53 (1H, d, 9.4)	2.55 (1H, d, 9.6)
33	1.74 (3H, s)	1.75 (3H, s)
34	1.31 (3H, s)	1.32 (3H, s)

Table 24 ^{13}C-NMR spectral data of **GH-13** and **GH-14**.

position	**GH-13** [isogamboginaic acid A, **2**]	**GH-14** [isogamboginaic acid B, **3**]
1	161.2	161.2
2	105.3	105.4
3	161.4	161.4
4	108.9	109.0
4a	155.2	155.2
4b	90.3	90.3
5	83.7	83.7
6	203.2	203.2
7	46.8	46.9
8	134.9	135.0
8a	133.7	133.7
9	178.9	178.9
9a	100.2	100.5
10	35.4	35.1
11	37.1	37.2
12	85.6	85.8
13	39.0	39.0
14	25.8	25.7
15	46.5	46.4
16	39.1	39.0
17	17.7	17.8
18	27.6	27.5

Table 24 (continued).

position	**GH-13** [isogamboginaic acid A, **2**]	**GH-14** [isogamboginaic acid B, **3**]
19	33.7	33.6
20	21.9	21.9
21	122.4	122.4
22	131.5	131.3
23	25.8	25.8
24	18.2	18.2
25	29.1	29.1
26	137.0	136.7
27	128.1	128.6
28	11.4	11.6
29	170.5	170.5
30	25.3	25.6
31	49.1	49.0
32	83.7	83.7
33	29.9	30.0
34	29.1	29.0

Table 25 ^{1}H-NMR spectral data of **GH-17**.

position	**GH-17** [gamboginolic acid, **4**]
1	12.92 (1H, s)
7	3.55 (1H, dd, 4.2, 7.0)
8	7.53 (1H, d,7.0)
10	3.27 (2H, d, 7.0)
11	5.27 (1H, d, 7.0)
13	2.00 (1H, m)
14	2.08 (1H, m)
15	5.11 (2H, t, 6.4)
17	1.60 (11H, s)
18	1.68 (3H, s)
19	1.78 (3H, s)
Ha-20	3.11 (3H, dd, 9.2, 14.5)
Hb-20	3.18 (2H, dd, 6.3, 14.5)
21	4.75 (1H, dd, 6.3, 9.2)
23	1.48 (3H, s)
24	1.31 (3H, s)
Ha-25	2.85 (1H, dq, 2.2, 14.4)
Hb-25	3.85 (1H, dd, 12.5, 14.4)
26	5.35 (1H, dd, 2.2, 12.5)
28	-
29	1.55 (3H, brs)

Table 25 (continued).

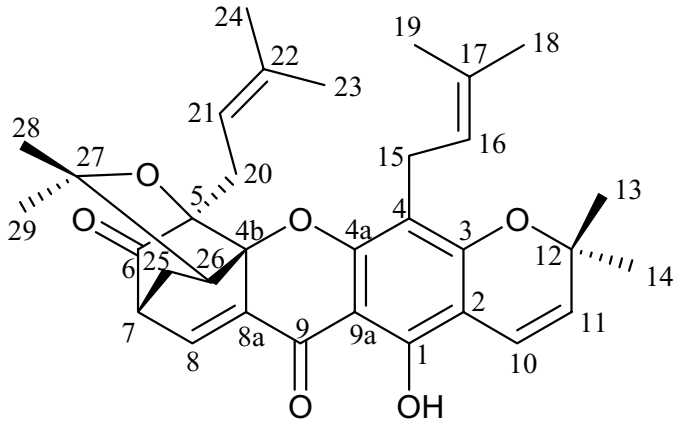
position	**GH-17** [gamboginolic acid, **4**]
30-Ha	1.39 (1H, dd, 4.2, 13.6)
30-Hb	2.37 (1H, dd, 4.2, 13.6)
31	2.45 (1H, d, 9.6)
33	1.34 (3H, s)
34	1.69 (3H, s)

Table 26 ^{13}C-NMR spectral data of **GH-17**.

position	**GH-17** [gamboginolic acid, **4**]
1	163.2
2	105.0
3	167.9
4	103.4
4a	168.5
4b	90.3
5	84.5
6	200.2
7	46.7
8	134.3
8a	133.7
9	178.2
9a	100.6
10	21.4
11	121.6
12	135.6
13	39.7
14	26.7
15	124.4
16	131.3
17	17.7
18	16.2

Table 26 (continued).

position	**GH-17** [gamboginolic acid, **4**]
19	25.3
20	26.7
21	90.3
22	73.8
23	26.7
24	24.5
25	30.3
26	134.9
27	129.9
28	168.5
29	20.9
30	25.3
31	49.0
32	83.7
33	29.3
34	30.0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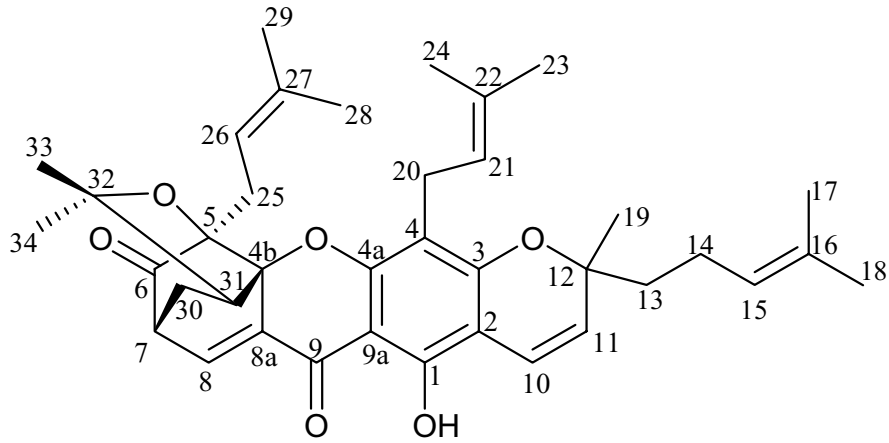
O
OH

GH-1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O
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14
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11
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10
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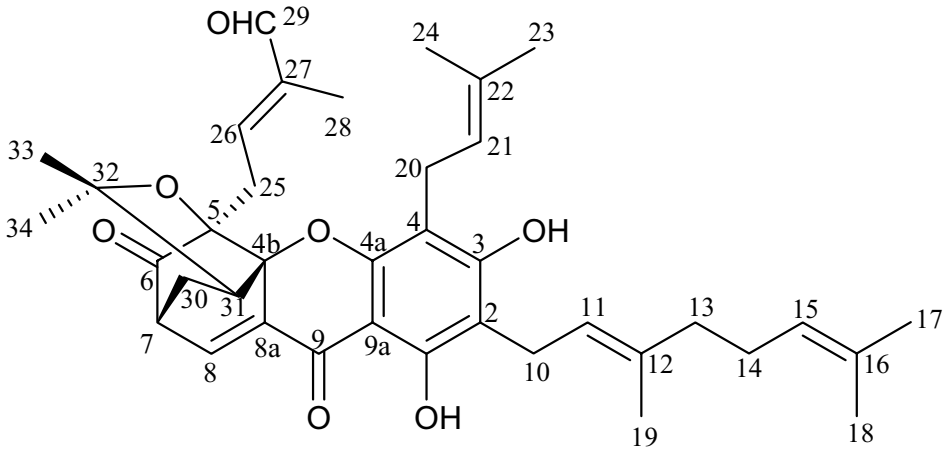
GH-2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4a
6
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31
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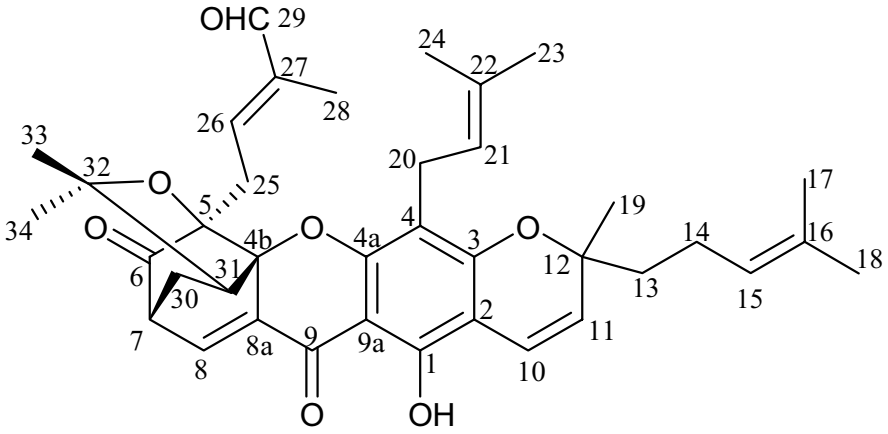
8
O
OH
19
18

GH-3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3
O
14
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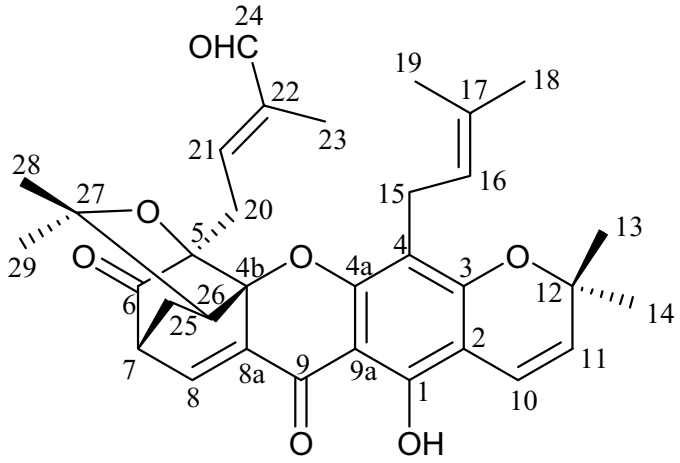
GH-4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4
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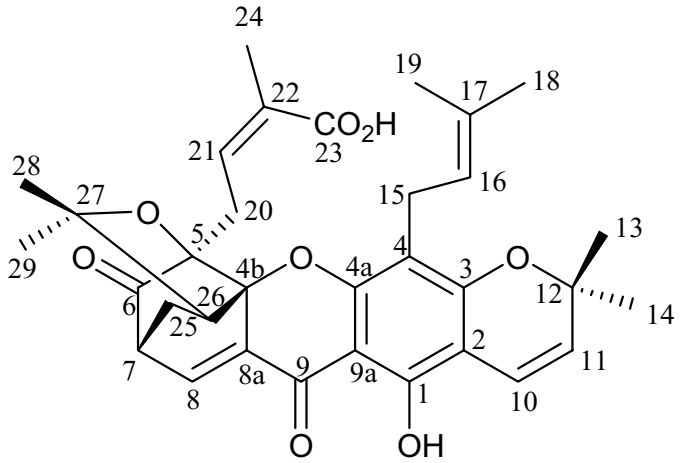
O
OH

GH-5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4a
4
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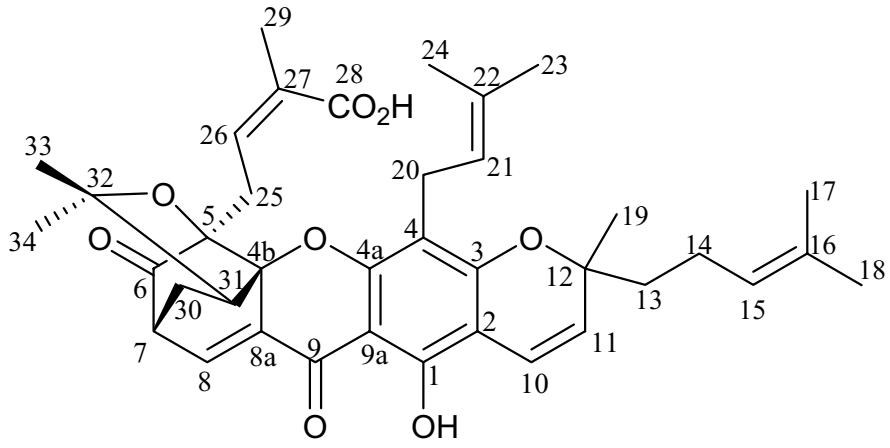
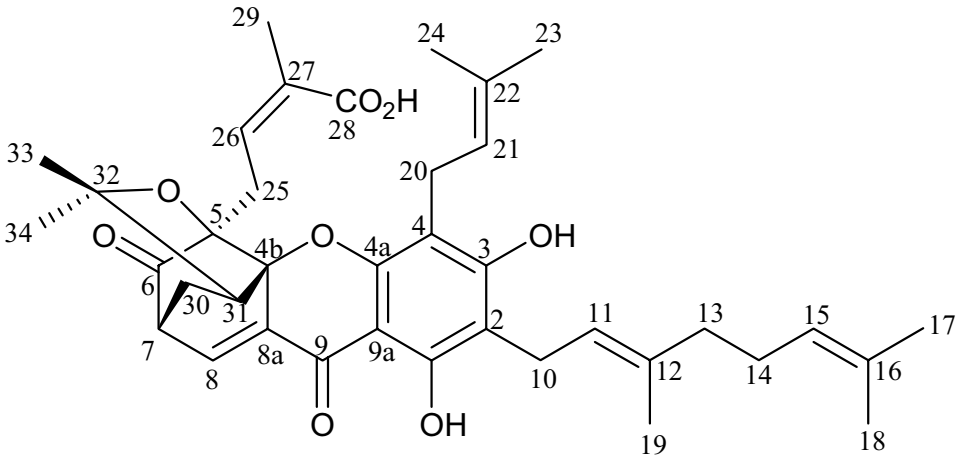
10
O
OH

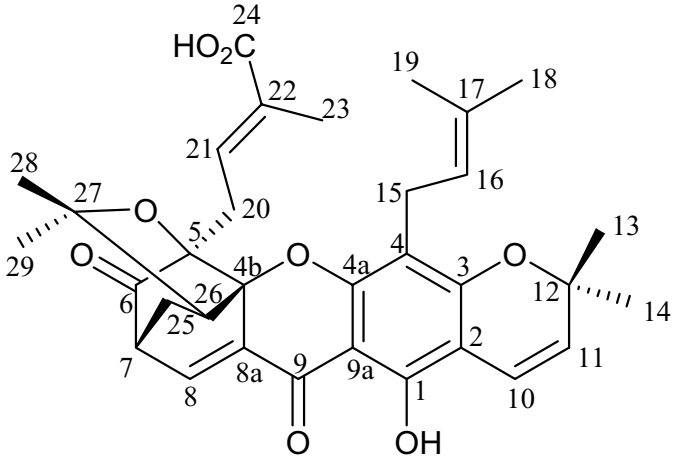
GH-6



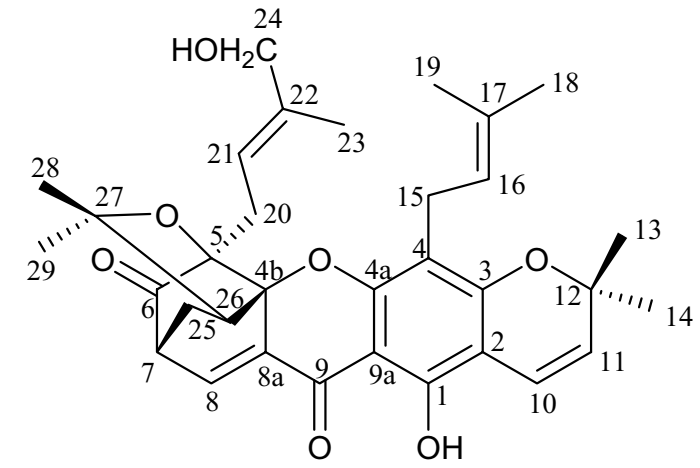
GH-7



GH-8



GH-9



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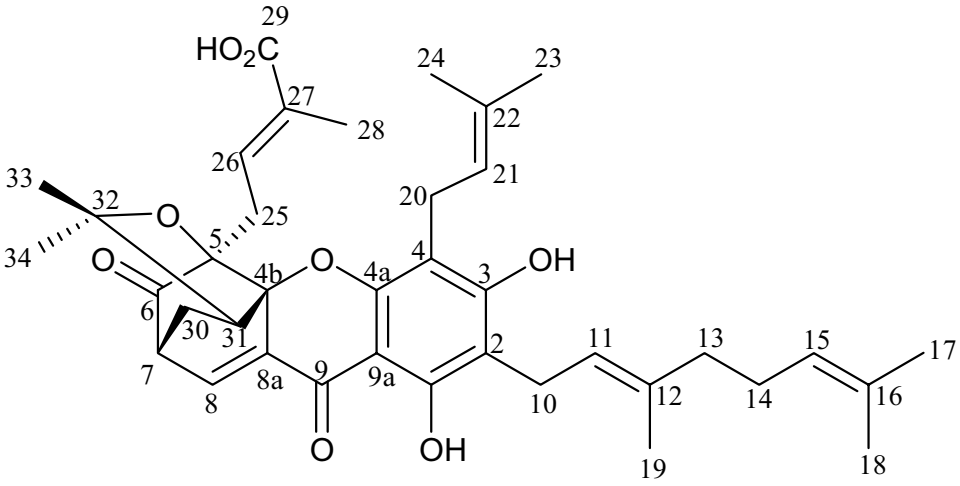

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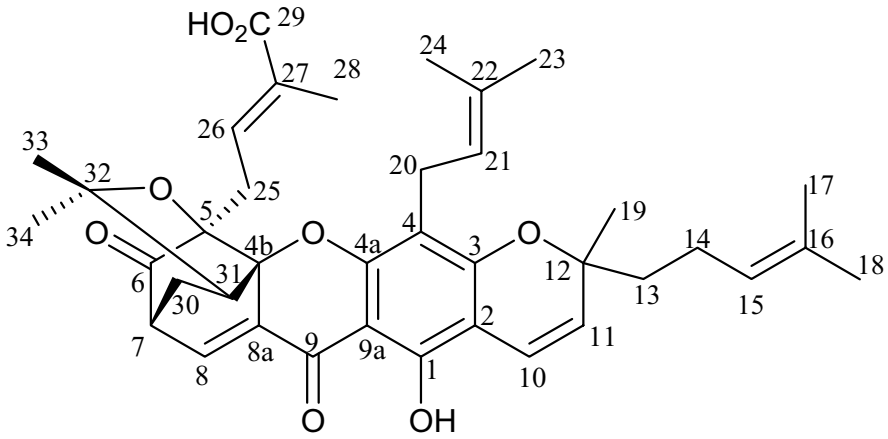

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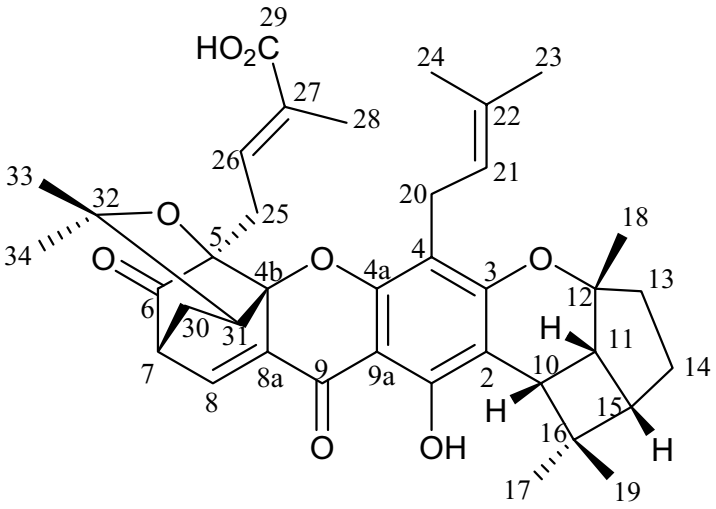

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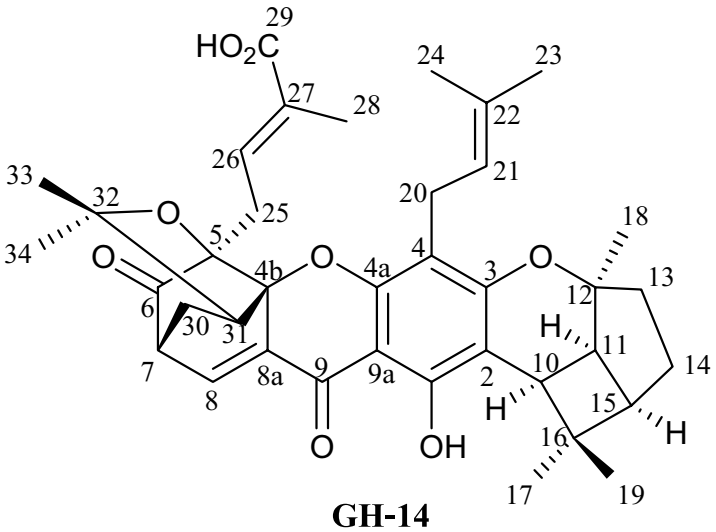
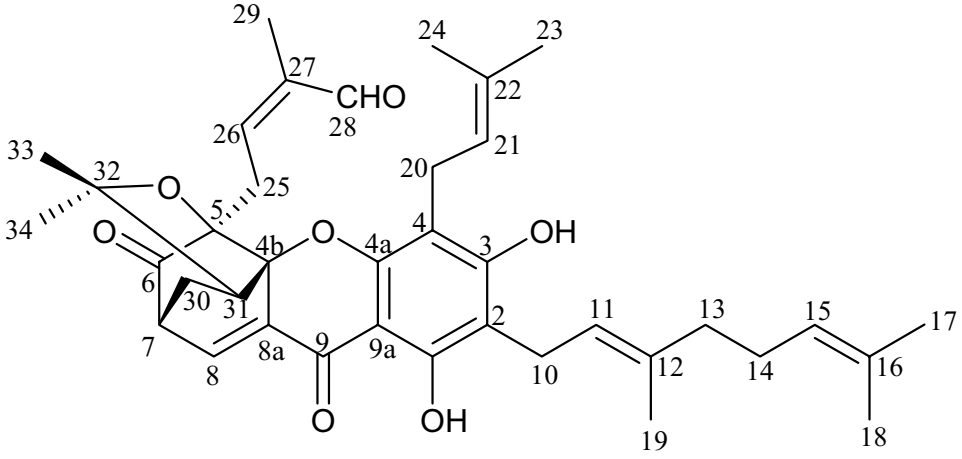
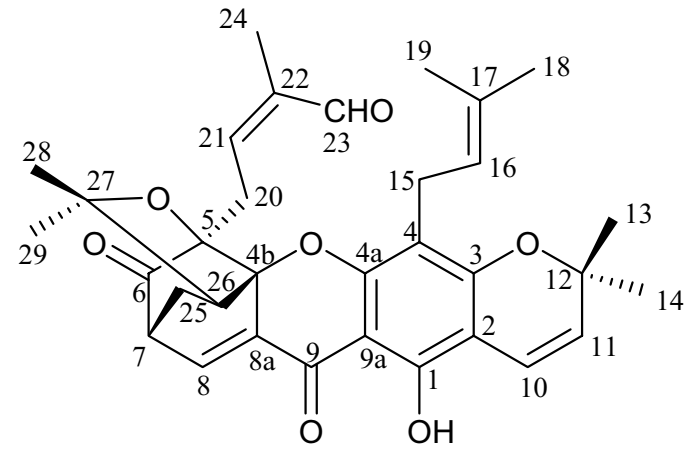


GH-14



GH-15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O
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O
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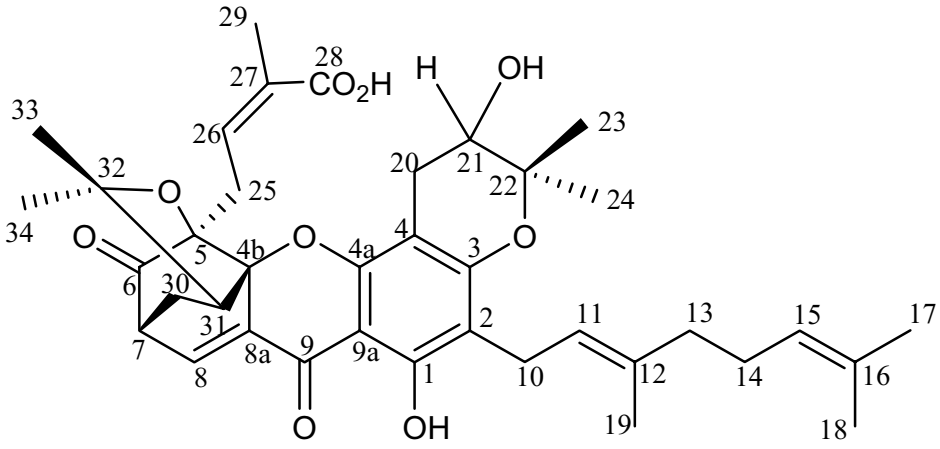
GH-16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8a
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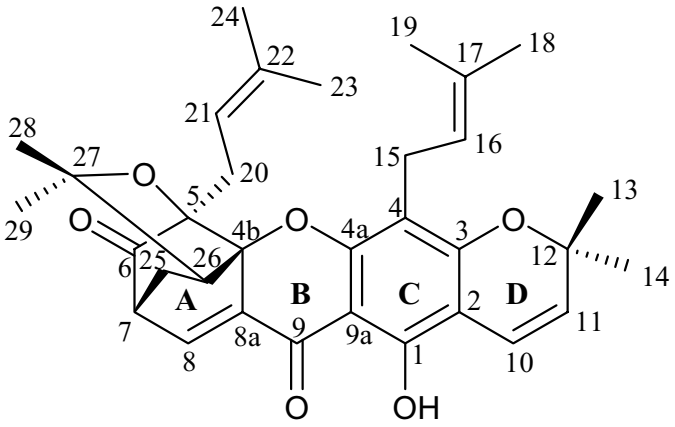
GH-17

CHAPTER 3

RESULT AND DISCUSSION

The crude CH_2Cl_2 extracts from the resin of *G. hanburyi* were separated by chromatographic methods to yield four new compounds; isogambogenal (**1**) isogamboginaic acid A (**2**), isogamboginaic acid B (**3**) and gamboginolic acid (**4**) and fourteen known compounds, deoxymorellin (**5**), morellin (**6**) isomorellin (**7**), morellic acid (**8**), isomorellic acid (**9**), isomorellinol (**10**), gambogin (**11**), gambogic acid (**12**), isogambogic acid (**13**), gambogenin (**14**), isogambogenin (**15**), gambogenic acid (**16**) and isogambogenic acid (**17**). The structures were elucidated by spectroscopic analysis including 2D NMR techniques and comparison of their spectral data with those previously reported in the literatures.

GH-1



5 (deoxymorellin)

GH-1 was isolated as an orange oil, which was shown to be optically active ($[\alpha]_D^{30.9}$-346°, *c* = 0.10, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3425 cm^{-1} and the bands of the carbonyl groups at 1735 and 1685 cm^{-1}.

^{1}H-NMR spectrum (**Table 10**) of **GH-1** contained a singlet of the hydrogen bonded phenolic hydroxy group at δ 12.97. The 2,2-dimethyl dihydropyran ring (ring D) was indicative by two doublets of one hydrogen each at δ 6.66 (*J* = 9.9 Hz, H-10) and 5.54 (*J* = 9.9 Hz, H-11) and a singlet of two methyl groups at δ 1.46 (13-CH_3 and 14-CH_3). An olefinic proton appeared as a doublet at δ 7.45 (*J* = 6.9 Hz, H-8), a doublet of doublets of a methine proton at δ 3.51 (*J* = 4.5, 6.9 Hz, H-7), a methylene group at δ 1.40 (overlapped signal, Ha-25) and 2.34 (dd, *J* = 4.5, 15.0 Hz, Hb-25), a methine proton at δ 2.50 (d, *J* = 9.3 Hz, H-26) and two methyl groups at δ 1.30 (s, 28-CH_3) and 1.74 (s, 29-CH_3) were assigned to the protons of the caged-ring A. Two olefinic protons at δ 5.23 (t, *J* = 6.6 Hz, H-16) and 4.44 (t, *J* = 7.8 Hz, H-21), two methylene groups at δ 3.35 (m, H-15) and 2.58

(d, *J* = 7.2 Hz, H-20) and four methyl groups at δ 1.69 (18-CH_3), 1.62 (19-CH_3), 1.39 (23-CH_3) and 1.04 (24-CH_3) were observed and assigned to the two isoprene units on C-4 and C-5, respectively.

The ^{13}C-NMR spectral data of **GH-1** (**Table 11**) contained six quaternary aromatic carbons at δ 157.8 (C-1), 102.9 (C-2), 160.6 (C-3), 106.4 (C-4), 157.5 (C-4a) and 100.7 (C-9a), five olefinic methine carbons at δ 133.8 (C-8), 115.5 (C-10), 126.2 (C-11), 122.2 (C-16) and 117.8 (C-21), three olefinic quaternary carbons at δ 133.7 (C-8a), 131.6 (C-17) and 134.9 (C-22), three methylene carbons at δ 21.6 (C-15), 29.0 (C-20) and 25.4 (C-25), two methine carbons at δ 46.9 (C-7) and 49.2 (C-26), four oxy-quaternary carbons at δ 90.5 (C-4b), 84.6 (C-5), 78.4 (C-12) and 83.1 (C-27), eight methyl carbons at δ 28.8 (C-13 and C-14), 25.8 (C-18), 18.1 (C-19), 16.7 (C-23), 25.5 (C-24), 29.1 (C-28) and 30.1 (C-29) and two carbonyl carbons at δ 203.5 (C-6) and 179.6 (C-9). The ^{13}C-NMR spectral data of **GH-1** were assigned by a combination of DEPT, 2D HMQC and 2D HMBC experiments.

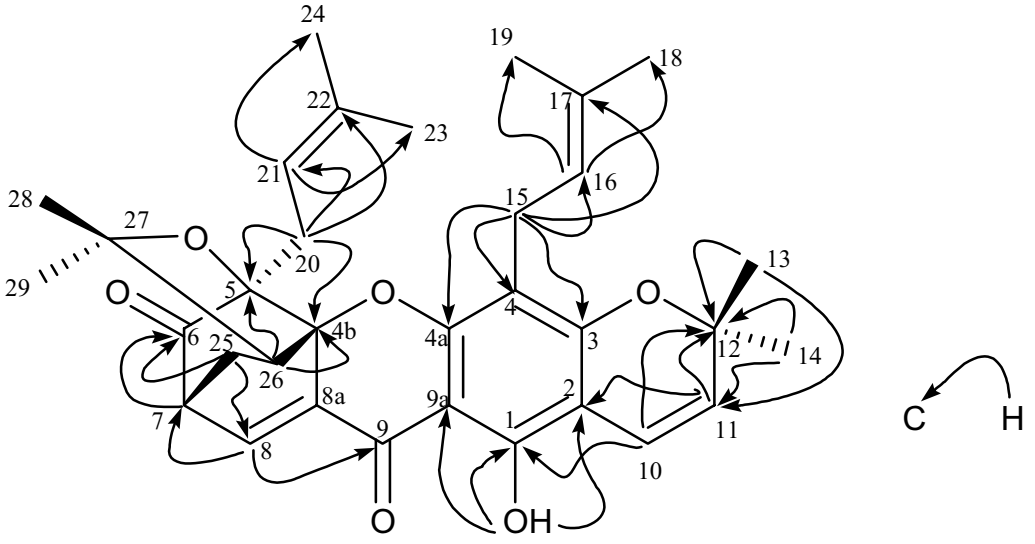
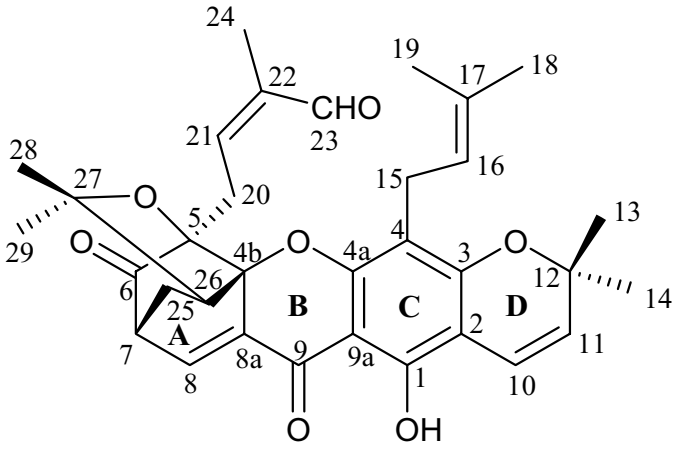


Figure 3 Selected 2D HMBC correlations of **GH-1.**

The position of the phenolic hydroxyl group at C-1 in **GH-1** was established by the 2D HMBC correlations (**Figure 3**). The phenolic hydroxyl group at δ 12.97 had long-range correlations to C-1 (δ 157.8), C-2 (δ 102.9) and C-9a (δ 100.7). The HMBC correlations were observed between H-10 (δ 6.66) and C-1 (δ 157.8) and C-12 (δ 78.4) and between H-11 (δ 5.54) and C-2 (δ 102.9) and C-12 (δ 78.4) implying that the 2,2-dimethyldihydropyran ring connected to the aromatic ring C at C-2 and C-3. The two isopentenyl units were attached to C-4 and C-5 were established by HMBC correlations between H-15 (δ 3.35) and C-4 (δ 106.4), C-3 (δ 160.6) and C-4a (δ 157.5) and between H-20 (δ 2.58) and C-5 (δ 84.6) and C-4b (δ 90.5), respectively. In the HMBC spectrum correlations between C-9 (C=O, δ 179.6) and H-8 (δ 7.45) and between C-7 (δ 46.9) and H-8 (δ 7.45) were observed. In addition, C-6 (C=O, δ 203.5) had correction to H-7 (δ 3.51) and Hab-25 (δ 1.40 and 2.34). On the basis of the above evidences, **GH-1** was characterized as deoxymorellin (**5**).

GH-16

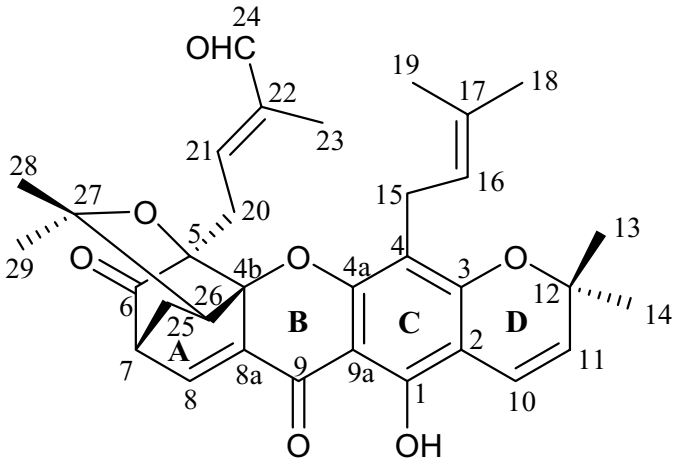


6 (morellin)

GH-16 was isolated as a yellow solid, which was shown to be optically active ($[\alpha]_D^{25.6}$-320°, $\underline{c}$ = 0.10, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3389 cm^{-1} and two bands of the carbonyl groups at 1735 and 1684 cm^{-1}.

The NMR spectra (^1H and ^{13}C) (**Tables 10** and **11**) of **GH-16** were similar to those of **GH-1** (deoxymorellin, **5**) except **GH-16** had an additional signal of an aldehyde group (C-23) [δ_H 9.59 (s), δ_C 194.5] and lack of the signal of one methyl group at δ 1.04 (3H, s). The significant upfield shift of an olefinic proton H-21 (δ 6.07) was observed in the ^1H-NMR of **GH-16** and the signal of C-24 appeared upfield at δ 16.7. This suggested that an olefinic bond between C-21 and C-22 was *cis*-configuration. Compound **GH-16** was thus characterized as morellin (**6**).

GH-5

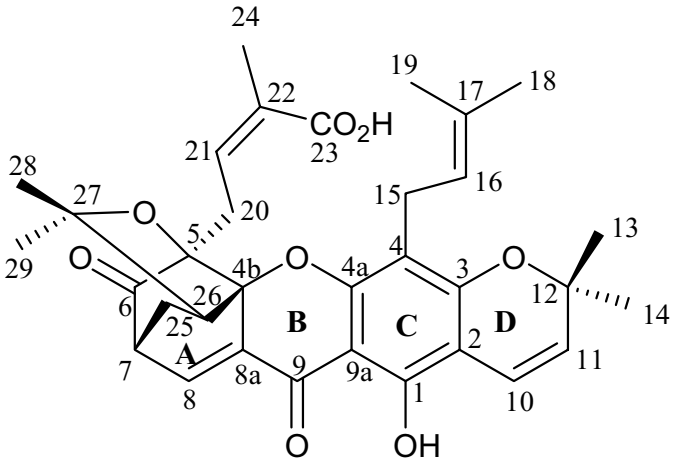


7 (isomorellin)

GH-5 was isolated as a yellow resin, m.p. 84-86^{O}C, which was shown to be optically active ($[\alpha]_D^{26.5}$-435°, *c* = 0.10, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3409 cm^{-1} and two bands of carbonyl groups at 1736 and 1686 cm^{-1}.

The NMR spectra (^{1}H and ^{13}C) (**Tables 10** and **11**) of **GH-5** were similar to those of **GH-16** (morellin, **6**), except the signal of H-21 in the ^{1}H-NMRspectrum of **GH-5** appeared downfield at δ 6.41 (t, *J* = 6.3 Hz) comparing to that of morellin (δ 6.07). In addition, in the ^{13}C-NMR spectrum of **GH-5**, the signal of C-23 appeared upfield at δ 8.6. This suggested that an olefinic bond between C-21 and C-22 in **GH-5** was *trans*-configuration. Comparison the spectra data (^{1}H-, ^{13}C-NMR and MS) of **GH-5** with those previously reported [8], **GH-5** was thus determined to be isomorellin (**7**).

GH-6

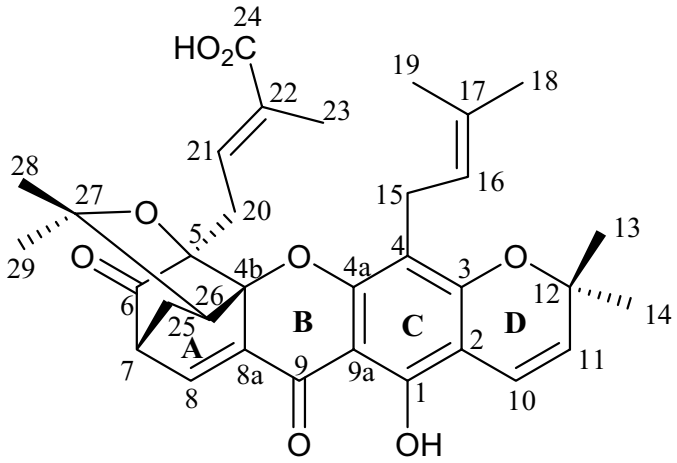


8 (morellic acid)

GH-6 was isolated as a yellow solid, m.p. 90-92^{O}C. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3383 cm^{-1} and the carbonyl groups at 1735 and 1688 cm^{-1}.

The NMR spectra (^{1}H and ^{13}C) (**Tables 12** and **13**) of **GH-6** were similar to those of **GH-16** (morellin, **6**) except **GH-6** had the carboxy carbon (C-23, δ 170.1) instead of an aldehyde carbon (δ 194.5), the olefinic proton (H-21) of **GH-6** appeared upfield at δ 6.08 (t, J = 6.8 Hz), therefore the double bond between C-21 and C-22 was determined to be *cis*-configuration. Compound **GH-6** was thus assigned as morellic acid (**8**).

GH-9

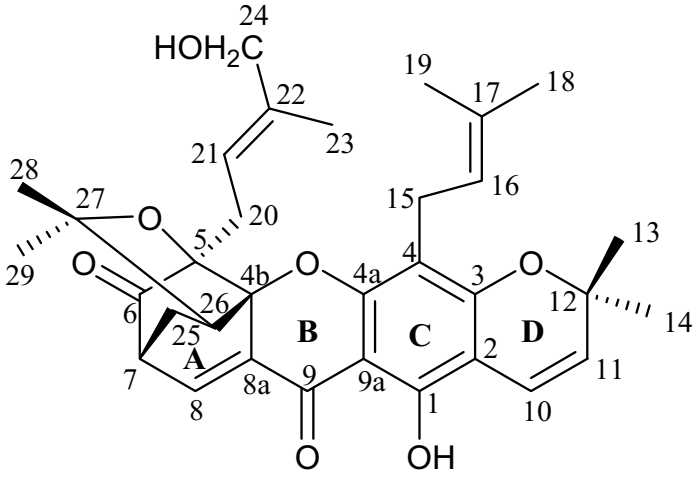


9 (isomorellic acid)

GH-9 was isolated as a yellow solid, which was shown to be optically active ($[\alpha]_D^{25.6}$ -287°, *c* = 0.08, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3384 cm^{-1} and the carbonyl groups at 1738 and 1687 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra (**Tables 12** and **13**) of **GH-9** were very similar to those of **GH-6** (morellic acid, **8**), except the signal of H-21 in the ^{1}H-NMR spectrum of **GH-9** appeared downfield at δ 6.60 (dd, *J* = 8.4, 15.5 Hz) comparing to that of morellic acid (δ 6.08). In addition, in the ^{13}C-NMR spectrum of **GH-9**, the signal of C-23 appeared upfield at δ 11.4 comparing to that of C-24 of morellic acid (δ_C 20.7). These indicate that the double bond between C-21 and C-22 was *trans*-configuration. Compound **GH-9** was thus determined to be isomorellic acid (**9**).

GH-10



10 (isomorellinol)

GH-10 was isolated as a yellow resin, m.p. 66-68 ^{O}C, which was shown to be optically active ($[\alpha]_D^{25.6}$-412°, *c* = 0.10, MeOH). The compound gave a parent ion by HR-MS at *m/z* 546, corresponding to a molecular formula $C_{33}H_{38}O_7$. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3525 cm^{-1} and the carbonyl groups at 1737 and 1645 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra (**Tables 14** and **13**) of **GH-10** were very similar to those of **GH-9** (isomorellic acid, **9**). The significant upfield shift of H-21 (δ 4.80), when compared with those of isomorellic acid (**9**) (δ 6.60) and the presence of an AB pattern at δ 3.64 and 3.72 (both d, *J* = 14.2 Hz) further implied that a primary alcohol had replaced the carboxy group at C-24. Furthermore, the methylene carbon resonance observed at δ 68.0 suggested the presence of a primary alcohol in the molecule. The chemical shift of C-23 (δ 12.6) in **GH-10** is comparable to that of isomorellic acid (δ 11.4) suggesting that the prenyl group on C-5 of compounds **GH-10** and isomorellic acid (**9**), had the stereochemistry of the

C-21/C-22 double bond as *trans*. 2D HMBC correlation of **GH-10** was shown in **Figure 4**. Comparison of the spectral data (^{1}H-,^{13}C-NMR and MS) of **GH-10** with those previously reported [6], **GH-10** was thus identified as isomorellinol (**10**).

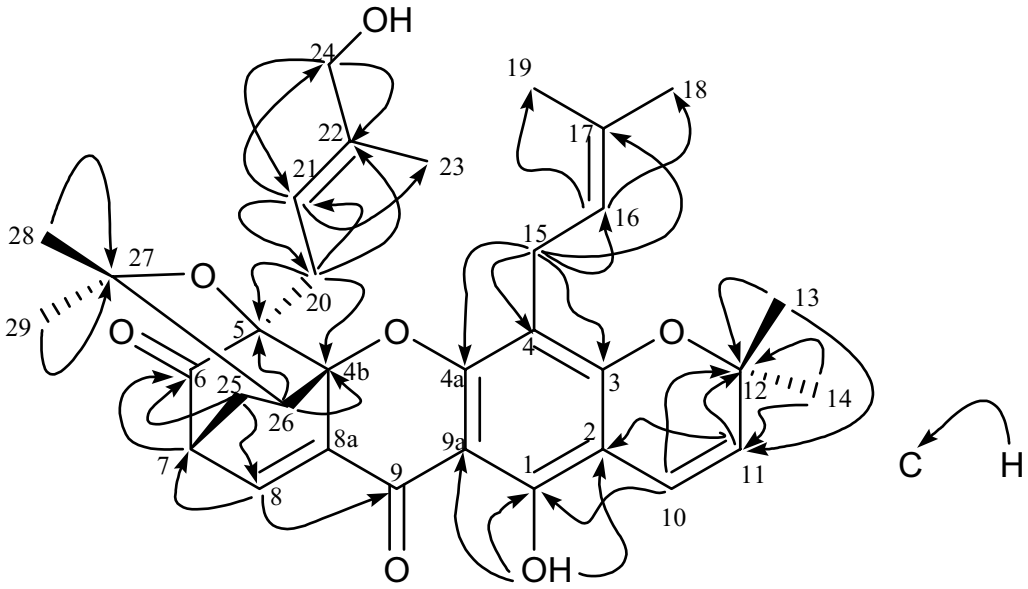
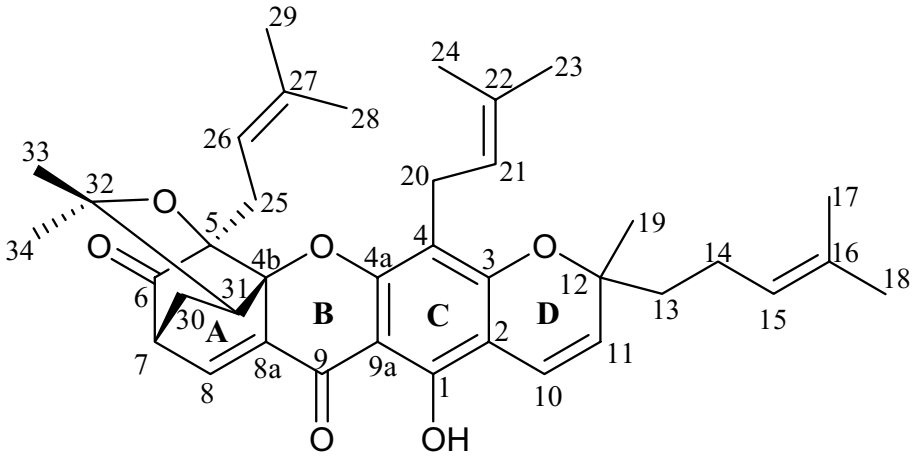


Figure 4 Selected 2D HMBC correlations of **GH-10.**

GH-2



11 (gambogin)

GH-2 was isolated as an orange oil, which was shown to be optically active ($[\alpha]_D^{26.5}$-351°, *c* = 0.10, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3435 cm^{-1} and the carbonyl groups at 1733 and 1682 cm^{-1}.

The ^{1}H NMR spectra (**Table 15**) of **GH-2** were similar to those of **GH-1** (deoxymorellin, **5**) (**Table10**) except that **GH-2** had one isoprene unit (C5 unit) more than that of deoxymorellin (**5**). The isoprene unit (C5 unit) (ring D) of deoxymorellin was replaced by the geranyl unit (C10 unit) in **GH-2**. The ^{1}H-NMR spectrum of **GH-2** contained two additional proton resonances, H-14 (δ 2.07) and H-15 (δ 5.22). In addition, nine methyl resonances were observed in the NMR spectrum of **GH-2**, suggesting the presence of the isoprene unit attached to C-13. In the HMBC spectrum of **GH-2** (**Figure 5**), the methylene protons of H-14 (δ_H 2.07) of the prenyl unit showed cross-peaks with C-13 (δ 41.8) and C-12 (δ 81.0), indicating the attachment of the isoprene unit at C-13. On the basis of the above evidences, **GH-2** was thus identified as gambogin (**11**).

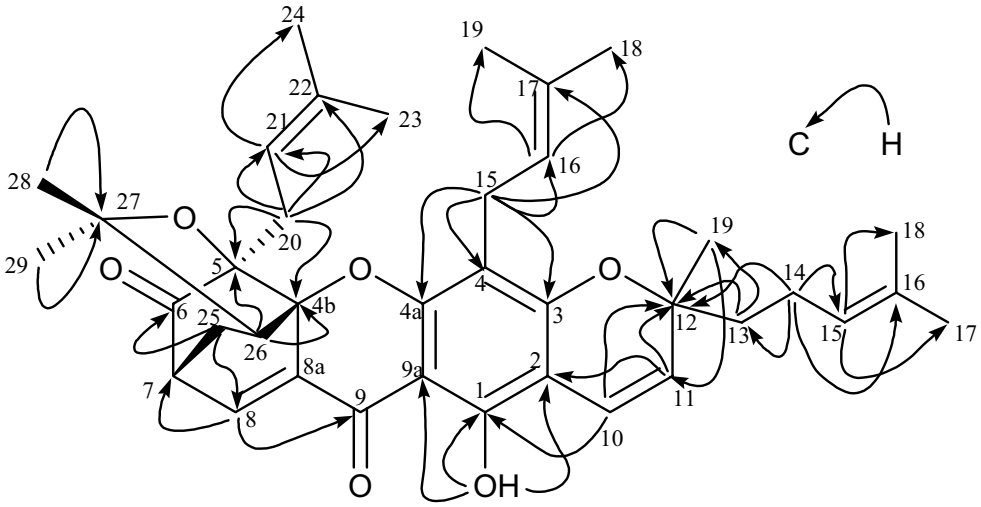
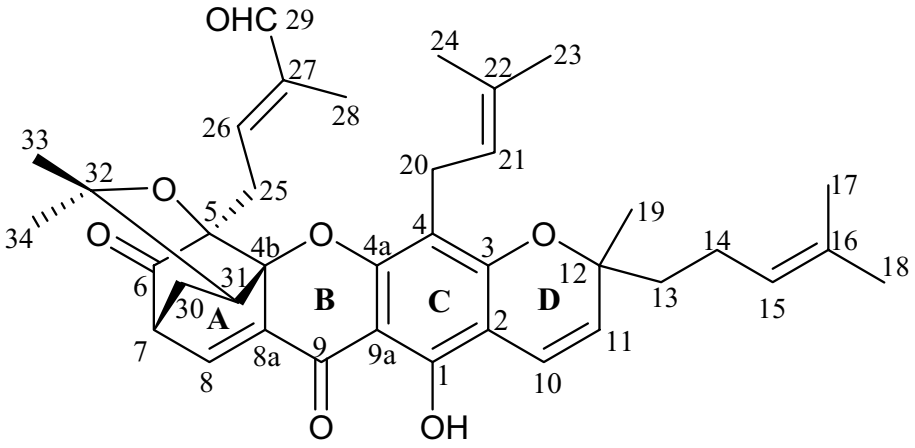


Figure 5 Selected 2D HMBC correlations of **GH-2.**

GH-4

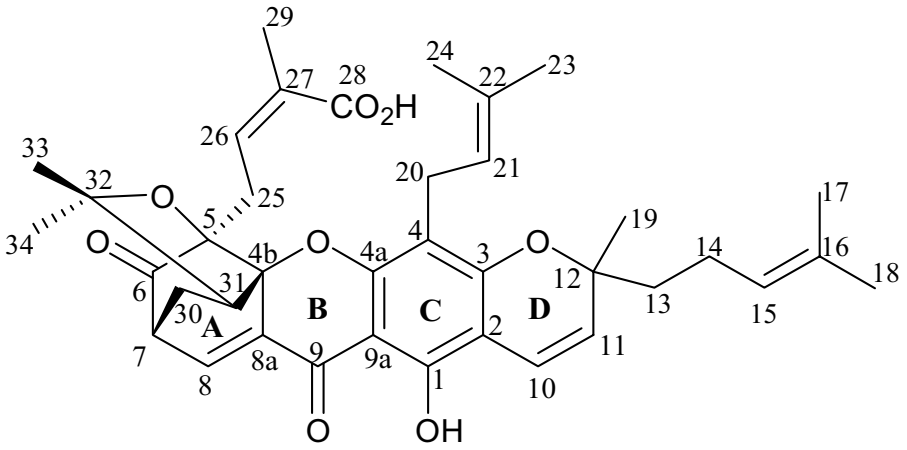


1 (isogambogenal)

GH-4 was isolated as a yellow resin, which was shown to be optically active ($[\alpha]_D^{29.3}$ -361°, *c* = 0.12, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3379 cm^{-1} and the carbonyl groups at 1737 and 1689 cm^{-1}.

The ^{1}H- and ^{13}C-NMR spectra (**Tables 15** and **16**) of **GH-4** were similar to those of **GH-2** (gambogin, **11**) except **GH-4** had an additional signal of the aldehyde group (C-29) [δ_H 9.24/9.25 (s), δ_C 194.5) and lack of the signal of one methyl group at δ 1.05 (3H, s). The significant down field shift of an olefinic proton H-26 (δ 6.34/6.42) was observed in the ^{1}H-NMR spectrum of **GH-4**. In addition, in the ^{13}C-NMR spectrum of **GH-4**, the signal of C-28 appeared upfield at δ 8.6. This suggested that an olefinic bond between C-26 and C-27 was *trans*-configuration. Compound **GH-4** was thus identified as isogambogenal (**1**), which was a new compound.

GH-7

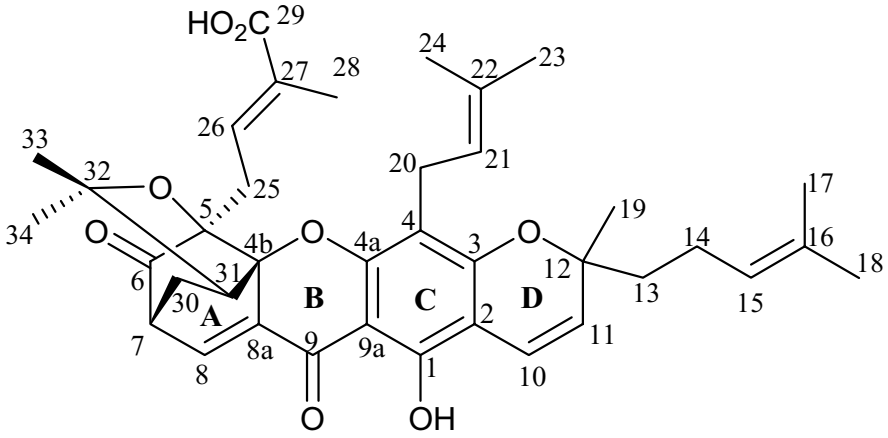


12 (gambogic acid)

GH-7 was isolated as a red resin, m.p. 86-88^{O}C. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3429 cm^{-1} and the carbonyl groups at 1736 and 1692 cm^{-1}.

The NMR spectra (^{1}H and ^{13}C) (**Tables 17** and **18**) of **GH-7** were similar to those of **GH-2** (gambogin, **11**) (**Tables 15** and **16**) except **GH-7** had an additional signal of the carboxy carbon (C-28, δ 171.3) instead of the methyl carbon (δ_C 16.7). In the ^{1}H-NMR spectrum of **GH-7**, the olefinic proton (H-26) of **GH-7** appeared upfield at δ 6.09 (1H, dd, J = 7.3, 7.5 Hz), which was comparable with H-21 (δ 6.08) of morellic acid (**8**) (**Table 12**). The stereochemistry of the C-26/C-27 double bond of **GH-7** was therefore identified as *cis*. Comparison the spectra data (^{1}H-, ^{13}C- NMR and MS) of **GH-7** with those previously reported [6], **GH-7** was thus identified as gambogic acid (**12**).

GH-12

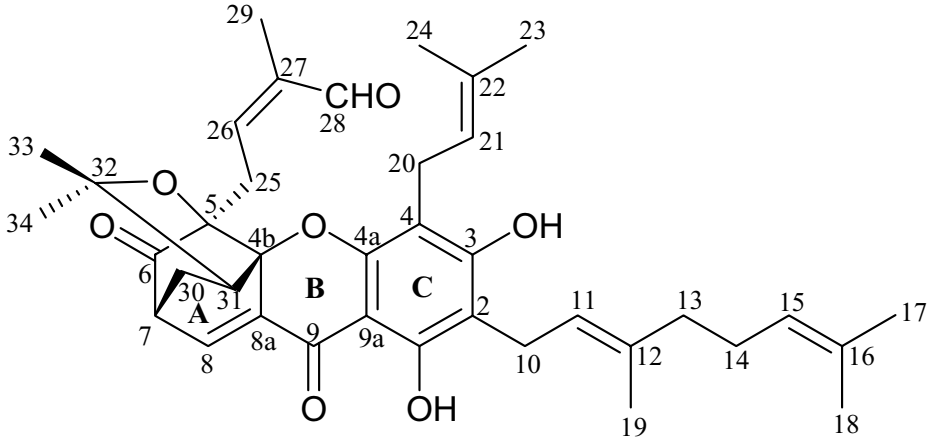


13 (isogambogic acid)

GH-12 was isolated as a yellow resin, m.p. 88-90^{O}C, which was shown to be optically active ($[\alpha]_D^{25.4}$-410°, $\underline{c}$ = 0.10, MeOH). The compound gave a parent ion by HR-MS at *m/z* 628, corresponding to a molecular formula $C_{38}H_{44}O_8$. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3184 cm^{-1} and the carbonyl groups at 1737 and 1687 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra (**Tables 17** and **18**) of **GH-12** were very similar to those of **GH-7** (gambogic acid, **12**), except the signal of H-26 in the ^{1}H-NMR spectrum of **GH-12** appeared downfield at δ 6.47 (1H, t, *J* = 6.6 Hz) comparing to that of **GH-7** (δ 6.09). In addition, in the ^{13}C-NMR spectrum of **GH-12**, the signal of C-28 appeared upfield at δ 11.5 comparing to that of C-29 of **GH-7** (δ_C 20.7). These indicated that the double bond between C-26 and C-27 in **GH-12** was *trans*-configuration. Comparison the spectra data (^{1}H-, ^{13}C- NMR and MS) of **GH-12** with those previously reported [6], **GH-12** was determined to be as isogambogic acid (**13**).

GH-15



14 (gambogenin)

GH-15 was isolated as a yellow solid, which was shown to be optically active ($[\alpha]_D^{25.6}$ -440°, *c* = 0.10, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3338 cm^{-1} and the carbonyl groups at 1737 and 1685 cm^{-1}.

Comparison of the ^{1}H- and ^{13}C-NMR spectra data of **GH-15** (**Tables 19** and **20**) with those of **GH-2** (gambogin, **11**) (**Tables 15** and **16**) and **GH-15** showed that two characteristic proton signals of H-10 and H-11 of the pyrane ring D of gambogin (**11**) at δ 6.70 (1H, d, *J* = 10.2 Hz) and 5.48 (1H, d, *J* = 10.2 Hz) were absent in the ^{1}H-NMR spectrum of **GH-15**. An olefinic proton at δ 5.24 (1H, t, *J* = 7.2 Hz, H-11), a methylene groups at δ 3.39 (2H, d, *J* = 6.6 Hz, H-10) and a signal of the hydroxyl group at δ 6.65 (1H, s, 3-OH) were present in the ^{1}H-NMR spectrum of **GH-15**. These suggested that **GH-15** has a geranyl group and a hydroxyl group at C-3 instead of the ether ring in the structure of gambogin (**11**). An olefinic bond between C-11 and C-12 was determined to be *trans*-configuration by the chemical shift of the methyl carbon of 19-CH_3 (δ_C 16.3). The methyl carbon signal of the *cis*-configuration should

appear more downfield, because of the decreasing γ- effect. The olefinic proton (H-26) of **GH-15** appeared upfield at δ 6.07 (1H, dd, *J* = 7.4, 10.3 Hz), therefore the double bond between C-26 and C-27 was determined to be *cis*-configuration. In the HMBC spectrum of **GH-15** (**Figure 6**), the methylene protons H-10 (δ 3.39) showed correlations with C-1 (δ 163.8), C-2 (δ 107.4), C-11 (δ 121.2) and C-19 (δ 16.3) and the olefinic proton H-11 (δ 5.24) showed correlations with C-10 (δ 21.2) and C-19 (δ 16.3). On the basis of the above evidence, **GH-15** was thus characterized as gambogenin (**14**).

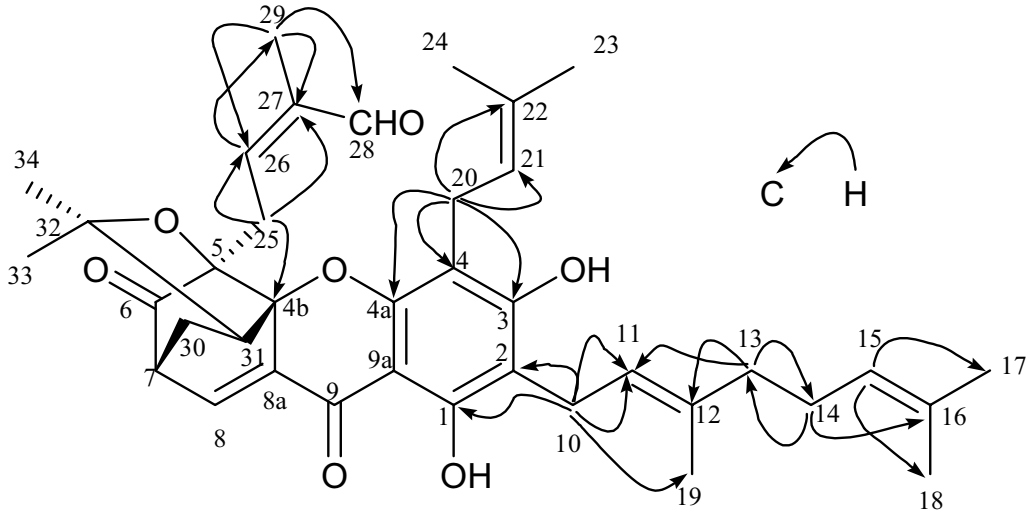
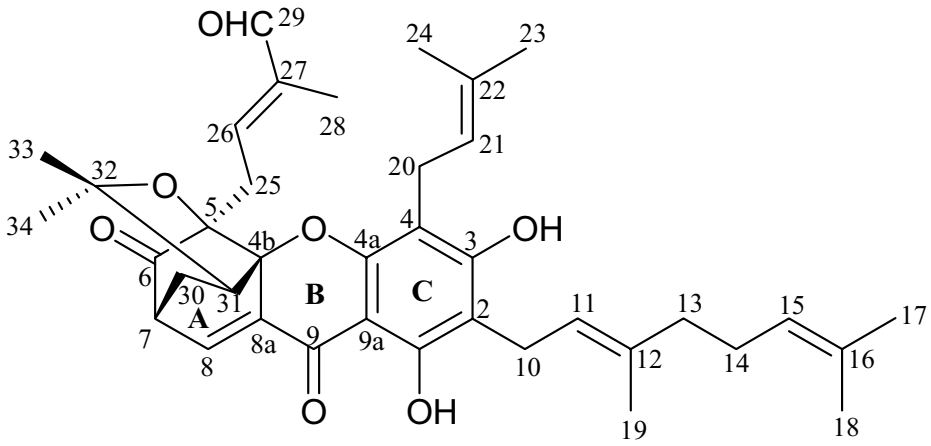


Figure 6 Selected 2D HMBC correlations of **GH-15.**

GH-3

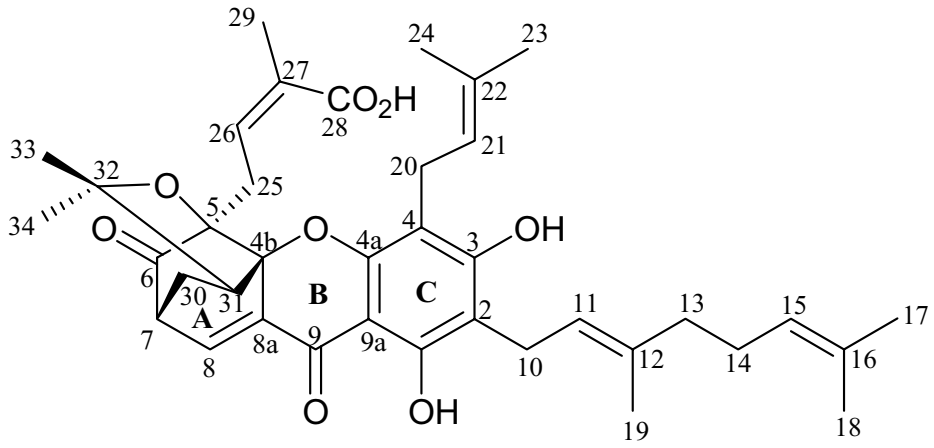


15 (isogambogenin)

GH-3 was isolated as a yellow resin, which was shown to be optically active ($[\alpha]_D^{25.4}$-436°, *c* = 0.09, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3383 cm^{-1} and the carbonyl groups at 1737 and 1686 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra (**Tables 19** and **20**) of **GH-3** were very similar to those of **GH-15** (gambogenin, **15**), except the signal of H-26 in the ^{1}H-NMR spectrum of **GH-3** appeared downfield at δ 6.39 (1H, t, *J* = 7.2 Hz) as compared to that of **GH-15** (δ 6.07). In addition, in the ^{13}C-NMR spectrum of **GH-3**, the signal of C-28 appeared upfield at δ_C 8.7 comparing to that of C-29 of gambogenin (**15**) (δ_C 18.1). These suggested that the double bond between C-26 and C-27 was *trans*-configuration in **GH-3**. On the basis of the above evidences, **GH-3** was thus determined to be isogambogenin (**15**).

GH-8

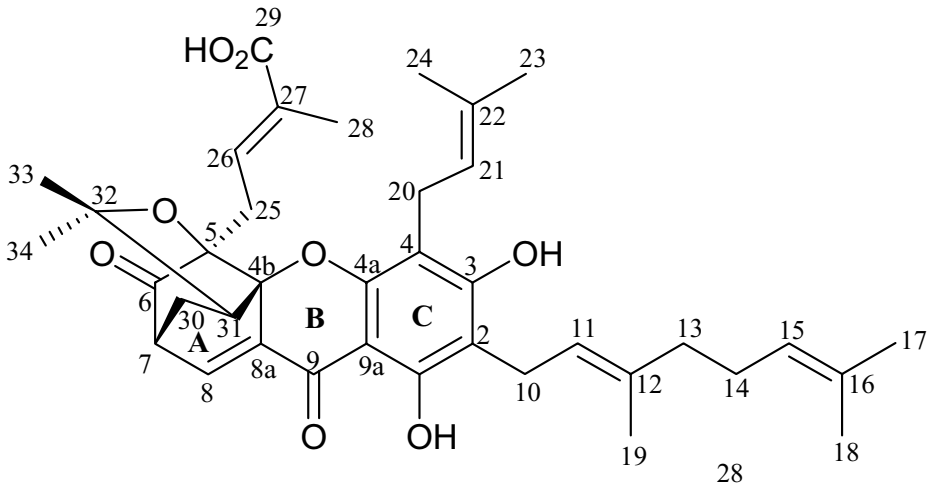


16 (gambogenic acid)

GH-8 was isolated as a yellow resin, m.p. 77-78^{O}C, which was shown to be optically active ($[\alpha]_D^{25.4}$-529°, $\underline{c}$ = 0.15, MeOH). The compound gave a parent ion by HR-MS at *m/z* 628, corresponding to a molecular formula $C_{38}H_{46}O_8$. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3383 cm^{-1} and the carbonyl groups at 1739 and 1689 cm^{-1}.

The NMR spectra (^{1}H and ^{13}C) (**Tables 21** and **22**) of **GH-8** were similar to those of gambogenin (**14**) (**Tables 19** and **20**) except **GH-8** had the carboxy carbon (C-28, δ_C 170.5) instead of an aldehyde carbon (δ_C 194.5) and the olefinic proton (H-26) of **GH-8** appeared upfield at δ 5.86 (1H, dd, *J* = 7.2, 8.1 Hz), which was comparable with that of gambogenin (**15**) appeared at δ 6.07. The double bond between C-26 and C-27 was therefore determined to be *cis*-configuration. On the basis of the evidences and upon comparison the spectral data of **GH-8** with those previously reported [10], compound **GH-8** was thus assigned as gambogenic acid (**16**).

GH-11

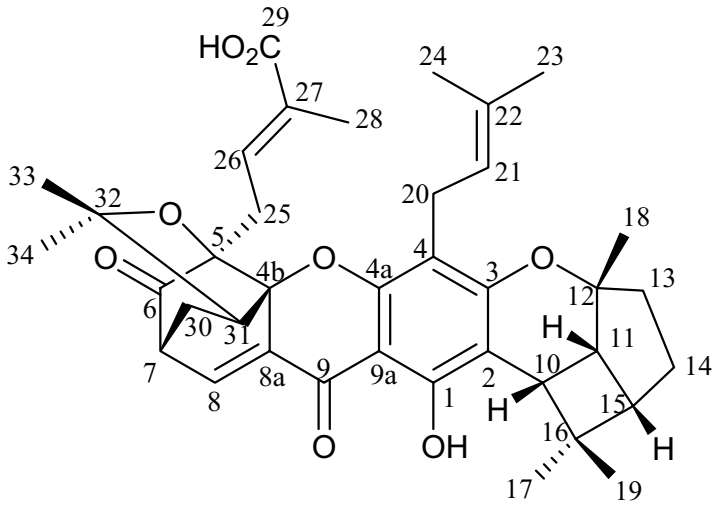


17 (isogambogenic acid)

GH-11 was isolated as a yellow resin, m.p. 80-82^{O}C, which was shown to be optically active ($[\alpha]_D^{25.6}$ -398 °, *c* = 0.10, MeOH). The compound gave a parent ion by HR-MS at *m/z* 628, corresponding to a molecular formula $C_{38}H_{46}O_8$. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3379 cm^{-1} and the carbonyl groups at 1738 and 1689 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra (**Tables 21** and **22**) of **GH-11** were very similar to those of **GH-8** (gambogenic acid **16**), except the signal of H-26 in the ^{1}H-NMR spectrum of **GH-11** appeared downfield at δ 6.61 (1H, dd, *J* = 7.2, 8.3 Hz)) comparing to that of **GH-8** (δ 5.86). In the ^{13}C-NMR spectrum of **GH-11**, the signal of C-28 appeared upfield at δ 11.5 comparing to that of C-29 of gambogenic acid (δ_C 20.7). These indicated that the double bond between C-26 and C-27 in **GH-11** was *trans*-configuration. Together the spectral data previously reported [14], **GH-11** was thus determined to be isogambogenic acid (**17**).

GH-13



2 (isogamboginaic acid A)

GH-13 was isolated as a yellow solid. The compound gave a parent ion by HR-MS at *m*/*z* 628, corresponding to a molecular formula $C_{38}H_{46}O_8$. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 2952 cm^{-1} and the carbonyl groups at 1737 and 1690 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra (**Tables 23** and **24**) of **GH-13** were very similar to those of **GH-12** (isogambogic acid, **13**), except the NMR signals from 10- to 19-positions. The ^{1}H-NMR spectrum of **GH-13** showed the proton signals of three methyl groups at δ 0.80 (s, Me-17), 1.41 (s, Me-18) and 1.37 (s, Me-19), two methylene functions at δ 1.68 (Ha-13), 1.89 (Hb-13) and 1.39 (H-14), and three methine groups at δ 3.09 (d, *J* = 9.6 Hz, H-10), 2.59 (dd, *J* = 7.3, 9.6 Hz, H-11) and 2.41 (q, *J* = 7.3 Hz, H-15) instead of the signals due to H-10 (δ 6.63, d, *J* = 10.1 Hz) and H-11 (δ 5.44, d, *J* = 10.1 Hz) and a prenyl group at C-13 of isogambogic acid (**13**). The ^{13}C-NMR spectrum of **GH-13** showed the signals of

the methyl carbons at δ 17.7 (C-17), 27.6 (C-18) and 33.7 (C-19), two methylene carbons at δ 39.0 (C-13) and 25.8 (C-14) and three methine carbons δ 35.4 (C-10), 37.1 (C-11) and 46.5 (C-15). The NMR signals (^{1}H and ^{13}C) were assigned by detail analysis of the 2D NMR (COSY, DEPT, HMQC and HMBC) spectra.

In the COSY spectrum of **GH-13** (**Figure 7**), a proton at δ 2.59 (H-11) showed coupling with two resonances at δ 3.09 (H-10) and 2.41 (H-15). The latter resonance showed further coupling to the resonance at δ 1.39 (H-14). The 2D HMBC correlations of **GH-13** (**Figure 8**) were observed between H-10 (δ 3.09) and C-11 (δ 37.2), C-12 (δ 85.8) and C-19 (δ 33.6) and between H-11 (δ 2.59) and C-14 (δ 25.7) and C-15 (δ 46.4). The long-range correlations between Hab-13 (δ 1.68 and 1.89) and C-11 (δ 37.2) and C-12 (δ 85.8), between H-14 (δ 1.39) and C-11 (δ 37.2), C-13 (δ 39.0) and C-15 (δ 25.7) and between H-15 (δ 2.41) and C-11 (δ 37.2) and C-19 (δ 33.6) were also observed.

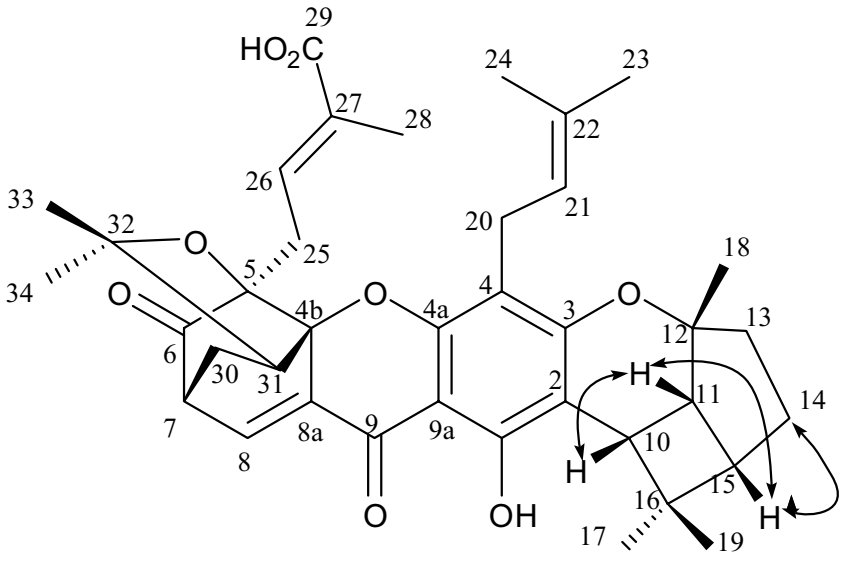


Figure 7 COSY correlations of **GH-13**.

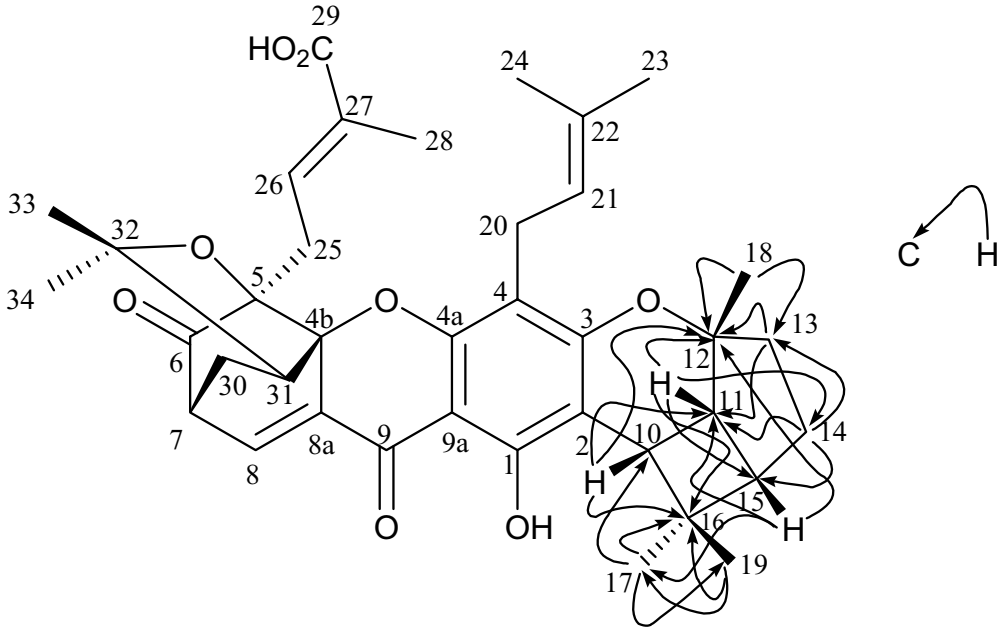


Figure 8 Selected 2D HMBC correlations of **GH-13**.

The relative stereochemistry of **GH-13** was derived from the ^{1}H NOE correlations (**Figure 9**). The significant NOE were observed between H-11 (δ 2.59), H-10 (δ 3.09) and CH_3-18 (δ 1.41); H-15 (δ 2.41), H-11 (δ 2.59), Ha-13 (δ 1.68) and CH_3-19 (δ 1.37); CH_3-19 (δ 1.37), CH_3-17 (δ 0.80), H-10 (δ 3.09) and H-15 (δ 2.41) and CH_3-17 (δ 0.80), CH_3-19 (δ 1.37), H-14 (δ 1.39) and CH_3-28 (δ 1.31). Thus H-10, H-11, H-15, CH_3-18 and CH_3-19 had the β-configurations while the C-17 methyl and the prenyl group at C-5 occupy the α-face (relatively). On the basis of the above evidences, thus structure **GH-13** was identified for isogamboginaic acid A (**2**). Isogamboginaic acid A (**2**) was a new compound.

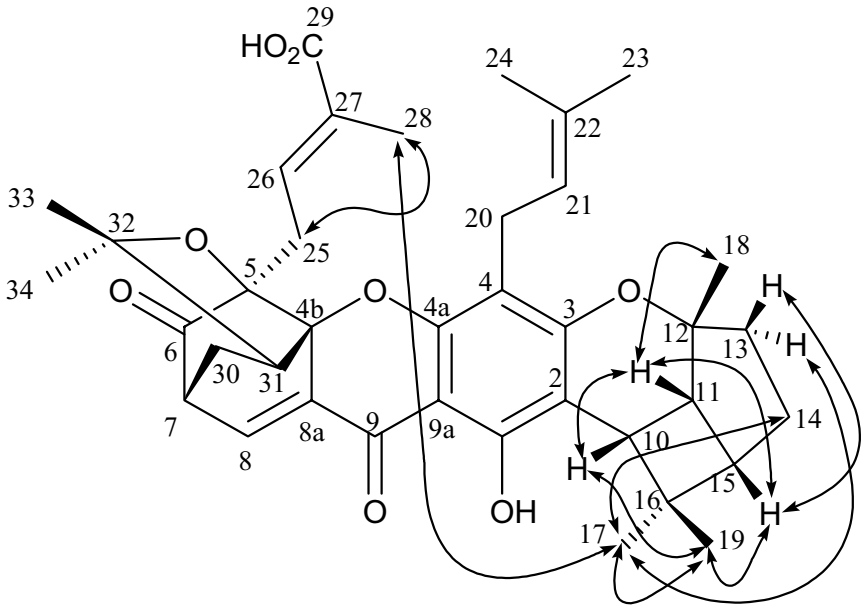
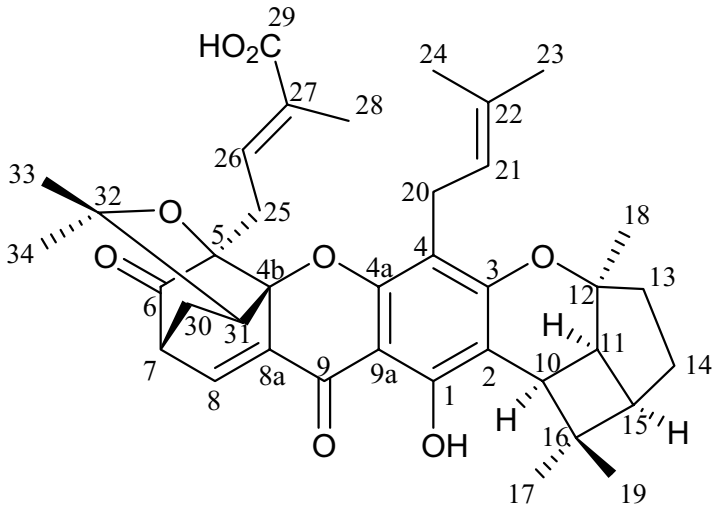


Figure 9 Correlation in the NOE spectrum of **GH-13**.

GH-14

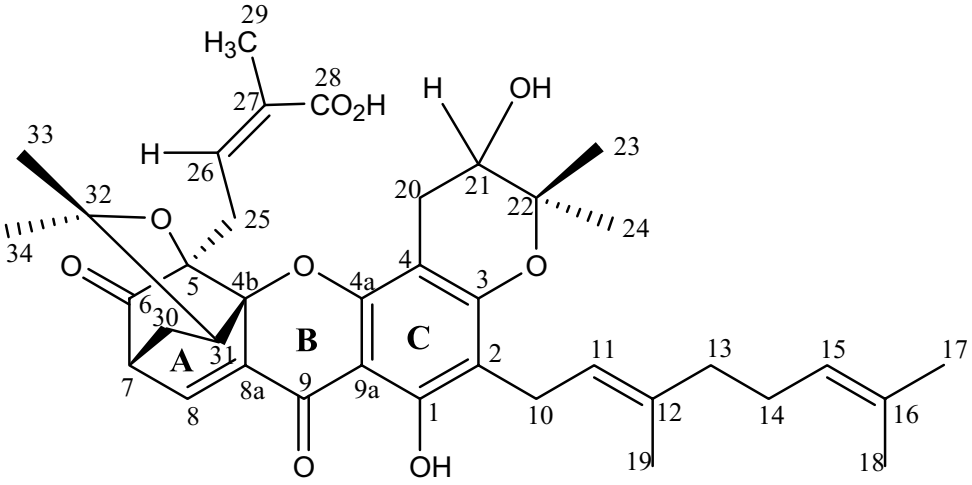


3 (isogamboginaic acid B)

GH-14 was isolated as a yellow resin. The compound gave a parent ion by HR-MS at *m/z* 628, corresponding to a molecular formula $C_{38}H_{46}O_8$. Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 2952 cm^{-1} and the carbonyl groups at 1739 and 1688 cm^{-1}.

The ^{1}H-NMR and ^{13}C-NMR spectra (**Tables 23** and **24**) of **GH-14** were very similar to those of **GH-13** (isogamboginaic acid A, **2**). This suggested that the skeleton structure of **GH-14** was similar to **GH-13** but the relative stereochemistry of **GH-14** at C-10, C-11, C-12 and C-15 were not yet determined. It was suspected that the stereochemistry at C-10, C-11, C-12 and C-15 may be opposited to those of isogamboginaic acid A (**2**). Structure **GH-14** was thus tentatively identified for isogamboginaic acid B (**3**).

GH-17



4 (gamboginolic acid)

GH-17 was isolated as a yellow resin, which was shown to be optically active ($[\alpha]_D^{28.7}$-266°, $\underline{c}$ = 0.08, MeOH). Its IR spectrum showed absorption bands corresponding to the hydroxyl group at 3429 cm^{-1} and the groups at 1736 and 1699 cm^{-1}.

GH-17 was determined to have the molecular formula $C_{38}H_{46}O_9$ by its HRMS ($\underline{m}/\underline{z}$ 669.3039 $[M+Na]^+$), which suggested that **GH-17** has one oxygen atom more than that of the known gambogenic acid (**16**). The NMR spectral data (**Tables 25** and **26**) of **GH-17** was similar to those of gambogenic acid (**16**) (**Tables 21** and **22**). Except in regard to the signals of the substituents at C-3 and C-4. In **GH-17**, proton signals appeared at δ 1.48 (3H, s, H-23), 1.31 (3H, s, H-24), 4.75 (1H, dd, *J* = 6.3, 9.2 Hz, H-21), 3.11 (1H, dd, *J* = 9.2, 14.5 Hz, Ha-20) and 3.18 (1H, dd, *J* = 6.3, 14.5 Hz, Hb-20) and carbon signals at δ 26.7 (C-23), 24.5 (C-24), 90.3 (C-21), 26.7 (C-20) and 73.7 (C-22) due to the presence of 2,2-dimethyl-3-hydroxytetrahydrochromene ring located between C-3 and C-4. Since

the coupling constants between H-21 and Ha-20 and Hb-20 were 9.2 and 6.3 Hz, therefore the hydroxyl group at C-21 must be equatorial.

The 2D HMBC data (**Figure 10**) revealed three- and two-bonds correlations between the proton signals of H-23 (δ 1.48) and H-24 (δ 1.31) and C-22 (δ_C 73.8) and C-21 (δ_C 90.3), between H-21 (δ 4.75) and C-22 (δ_C 73.8) and between Hab-20 (δ 3.11 and 3.18) and C-21 (δ_C 90.3), C-4 (δ_C 103.4), C-4a (δ_C 168.5) and C-3 (δ_C 167.9). The olefinic proton (H-26), upfield shifted, appeared at δ 5.35(1H, dd, *J* = 2.2, 12.5 Hz). Furthermore, H-26 gave enhancement with 29-Me in the NOEDIFF spectrum. This indicated the *cis*-configuration of the double bond between C-26 and C-27. The ^{1}H- and ^{13}C-NMR data of **GH-17** were clearly assigned on the basic of the 2D NMR spectral data, thus structure **GH-17** was identified for gamboginolic acid (**4**). Gamboginolic acid (**4**) was a new compound.

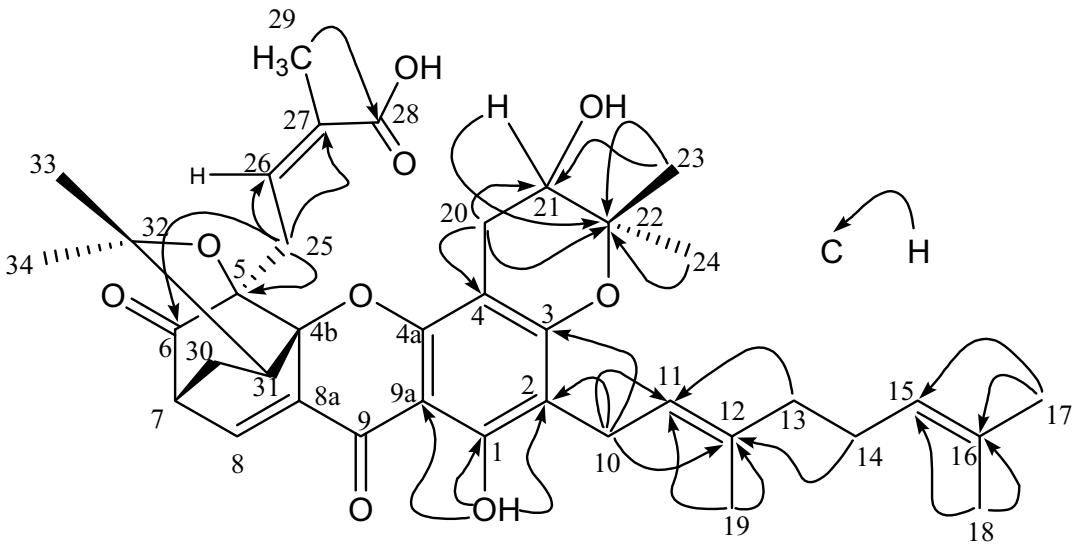


Figure 10 Selected 2D HMBC correlations of **GH-17.**

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APPENDICES

δ	=	chemical shift relative to tetramethylsilane (TMS)
ε	=	molar absorptivity coefficient
λ_{max}	=	maximum wavelength
ν_{max}	=	absorption frequencies
μm	=	micrometer
brs	=	broad singlet
d	=	doublet
dd	=	doublets of doublet
dq	=	doublets of quartet
$CDCl_3$	=	deuterochloroform
$CeSO_4$	=	cerium sulfate
CH_2Cl_2	=	dichloromethane
CH_3CN	=	acetonitile
COSY	=	correlation Spectroscopy
DEPT	=	Distortionless Enhancement by Polarization Transfer
DPPH	=	2, 2-Diphenyl-1-picrylhydrazyl radical
EI MS	=	Electron-Ionization Mass Spectrometry
EtOAc	=	ethylacetate
eV	=	Electron Volt
g	=	gram
H_2SO_4	=	sulfuric acid
HMBC	=	Heteronuclear Multiple Bond Correlation
HMQC	=	Heteronuclear Multiple Quantum Coherence

HPLC	=	High Performance Liquid Chromatography
Hz	=	hertz
INEPT	=	Insensitive Nuclei Enhanced by Polarization Transfer
IR	=	Infrared
J	=	coupling constant
m	=	multiplet
MeOH	=	methanol
MIC	=	Minimum Inhibitory Concentration
MHz	=	Megahertz
mg	=	milligram
mL	=	mililiter
mm	=	millimeter
NMR	=	Nuclear Magnetic Resonance
NOE	=	Nuclear Overhauser Effects
NOESY	=	Nuclear Overhauser Enhancement Spectroscopy
PLC	=	Preparative Layer Chromatography
ppm	=	part per million
q	=	quartet
ROESY	=	Rotating frame Overhauser Enhancement Spectroscopy
RP	=	reverse phase
s	=	singlet
TLC	=	Thin Layer Chromatography
t	=	triplet
UV	=	Ultraviolet-Visible

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