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Triterpenoids

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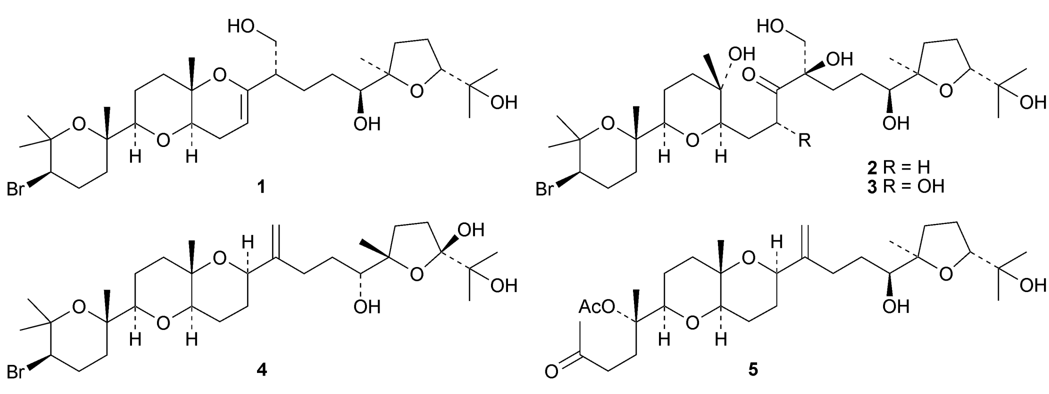
This review covers the isolation and structure determination of triterpenoids including squalene derivatives, lanostanes, holostanes, cycloartanes, cucurbitanes, dammaranes, euphanes, tirucallanes, tetranortriterpenoids, quassinoids, lupanes, oleananes, friedelanes, ursanes, hopanes, onoceranes and saponins; 308 references are cited.

1 Introduction

Interest in the biological activities of triterpenoids continues with reviews on their anti-inflamatory,[1,2] antiviral,[3] antitumour,[4–6] anti-HIV[7] and insecticidal[8] activities and for treatment of metabolic and vascular diseases.[9] Surveys have appeared describing the triterpenoids isolated from *Anemone raddeana*,[10] *Poria cocos*,[11] *Lantana*[12] and *Simaba*[13] species and Pinaceae[14] and Meliaceae[15] families. Triterpenoid saponins show a range of biological activities[16] and this has generated interest in their biosynthesis[17] and improvement of yields from natural sources.[18] Reviews covering triterpenoid saponins from *Camellia*[19] and *Polygala*[20] species and the Theaceae[21] and Caryophyllaceae and Illecebraceae[22] families have appeared.

2 The squalene group

15-Dehydroxythyrsenol A **1**, prethyrsenol A **2** and 13-hydroxyprethyrsenol A **3** are new cytotoxic squalene derivatives from *Laurencia viridis*.[23] The related compounds 22-hydroxy-15(28)-dehydrovenustatriol **4**, secodehydrothyrsiferol **5**, iubol **6** and 1,2-dehydropseudodehydrothysiferol **7** have also been isolated from *Laurencia viridis* by the same group.[24] Squalene-1,10,24,25,30-pentol **8**, which shows moderate anti-



mycobacterial activity, has been reported from the leaves and twigs of *Rhus taitensis*.[25] The biochemistry and molecular biology of squalene has been reviewed.[26]

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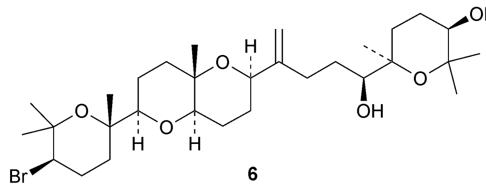

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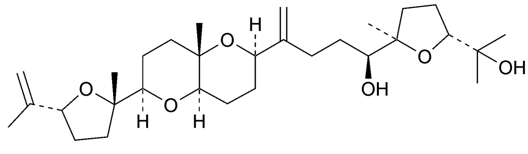

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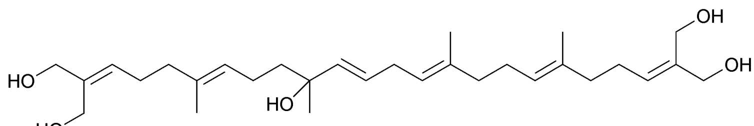

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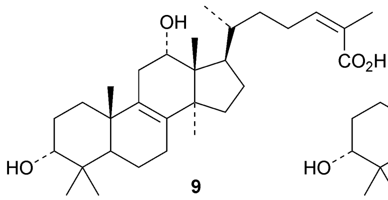
3 The lanostane group

Schiglauzic acid **9** and schiglaucyclozic acid **10** are new lanostanes from the stems of *Schisandra glaucescens*.[27] The structures of both compounds were confirmed by X-ray analyses. The three lanostanes **11**, **12** and **13**, from the leaves of *Abies spectabilis*, are accompanied by the mariesane derivative **14** and the 18(13→17)-*abeo*-lanostane **15**.[28] The rearranged lanostane **16** and 24,25,26-trihydroxylanost-7-en-3-one **17** have been isolated from *Abies nephrolepis*.[29] The tetradecanoyl ester **18** is a constituent of *Euphorbia sapinii*.[30]

Bioactive lanostane derivatives from fungi include **19** and **20** from *Poria cocos*[31] and 24,25,26-trinor-3-oxolanosta-7,9(11)-dien-24-oic acid **21**[32] and methyl ganoderate A acetonide **22** and butyl ganoderate H **23**[33] from *Ganoderma lucidum*. The epoxyganoderic acid **24** is also a constituent of *Ganoderma lucidum*.[34] The biological properties of triterpenoids from *Poria cocos*[35] and *Ganoderma lucidum*[36] have been reviewed.



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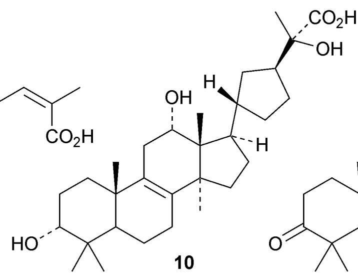

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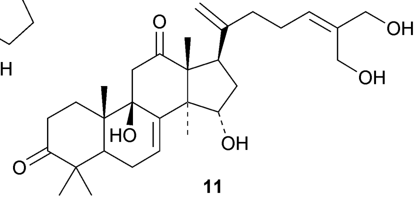

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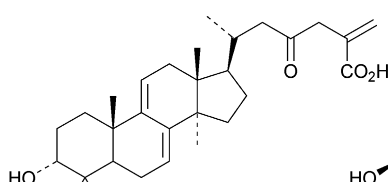

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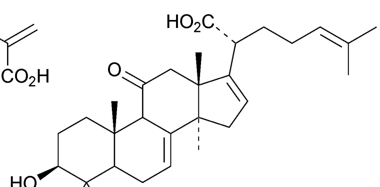

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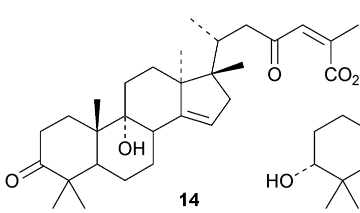

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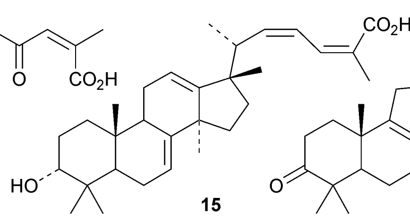

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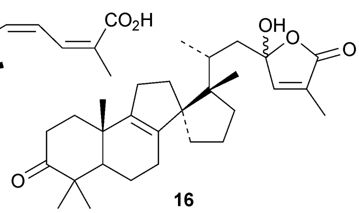

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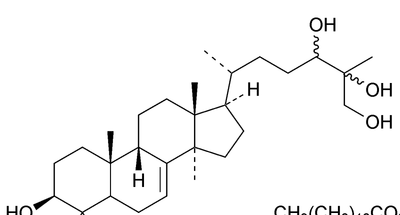

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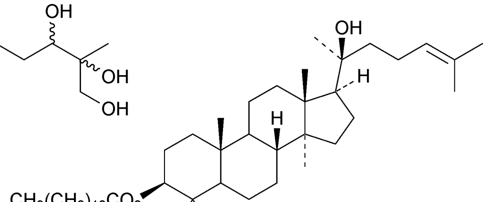

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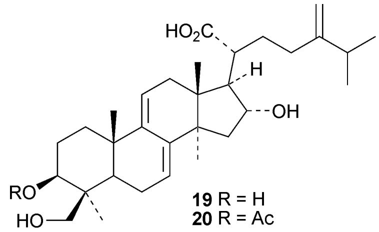
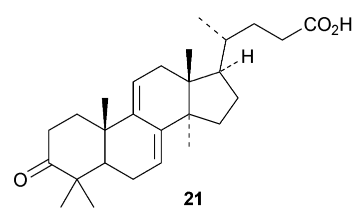


19 R = H
20 R = Ac



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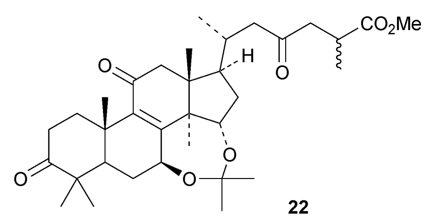

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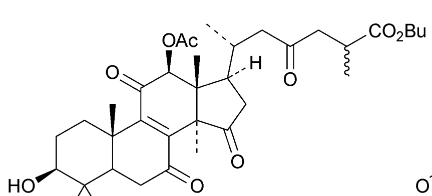

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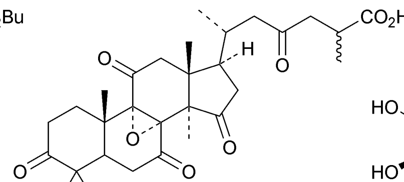

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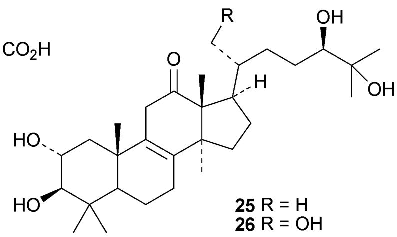
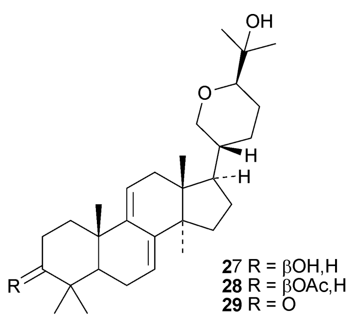
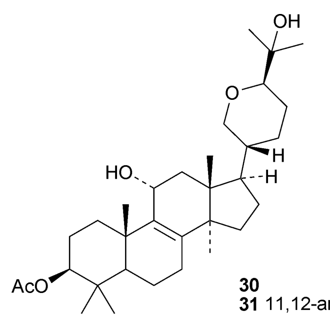


25 R = H
26 R = OH

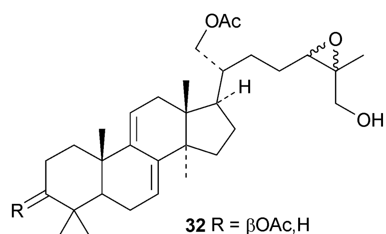
Fasciculols H **25** and I **26** are constituents of the Chinese mushroom *Naematoloma fasciculare*.[37] The entomopathogenic fungus *Hypocrella* sp. BCC 14524 is the source of the lanostanes hypocrellols A–G **27–33**.[38] Xylariacins A **34**, B **35** and C **36** have been isolated from *Xylarialeum* sp. A45, an endophytic fungus isolated from *Annona squamosa*.[39] Inonotsutriols D **37** and E **38** have been reported from the white rot fungus *Inonotus obliquus*.[40]



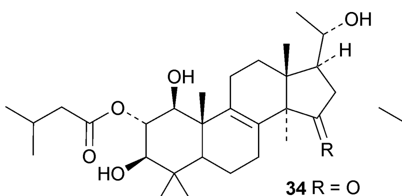
27 R = βOH,H
28 R = βOAc,H
29 R = O



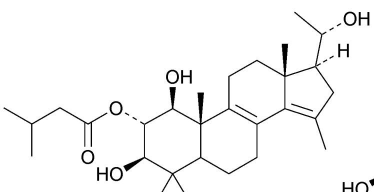
30
31 11,12-anhydro



32 R = βOAc,H
33 R = O



34 R = O
35 R = βOH,H



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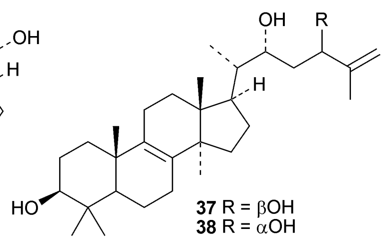
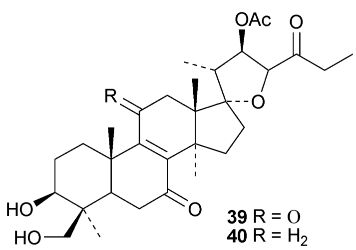
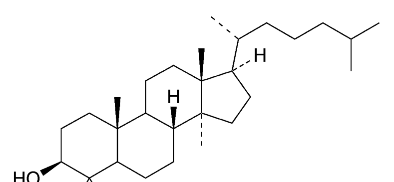


37 R = βOH
38 R = αOH



39 R = O
40 R = H_2



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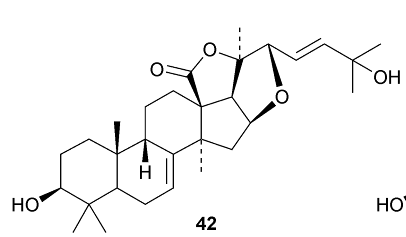

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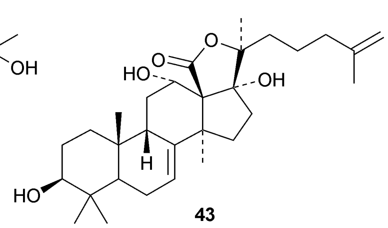

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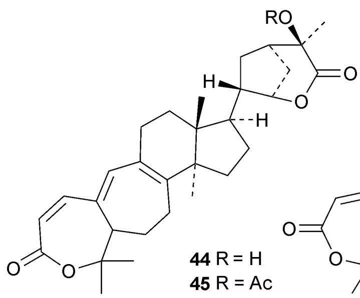
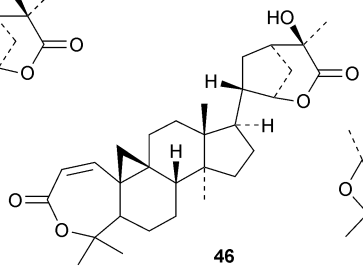
Erylosides R_1, T_1, T_2, T_3, T_4, T_5 and T_6 are lanostane saponins with known genins from the Caribbean sponge *Erylus formosus*.[41] Of the five new saponins, scillanostasides A–E, isolated from the bulbs of *Scilla scilloides*, only A and B have new genins **39** and **40**.[42] Lanostan-3β-ol **41** is a new genin of a diglucuronoside from the flowers of *Punica granatum*.[43]

Cucumariosides H_5, H_6, H_7 and H_8 are new holostane glycosides from the sea cucumber *Eupentacta fraudatrix*.[44] Cucumarioside H_8 has a new genin **42** with an unusual 16,22-epoxide. Patagonicosides B and C, sulphated glycosides from the sea cucumber *Psolus patagonicus*, display antifungal activity.[45] Patagonicoside B has the new genin **43**. Two new



44 R = H
45 R = Ac



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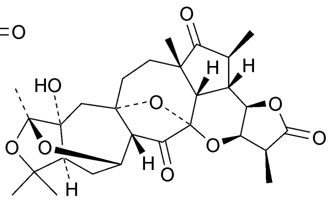

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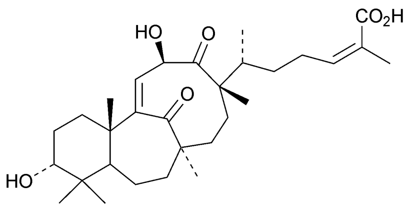

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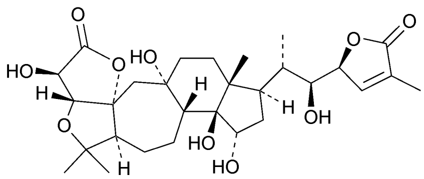

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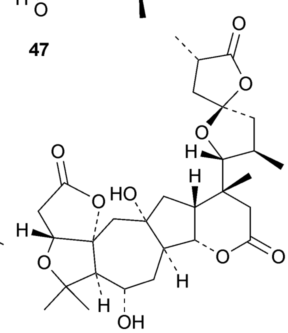

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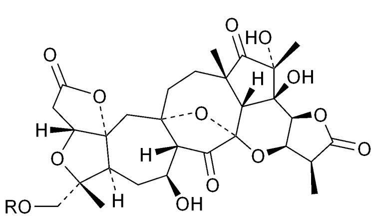
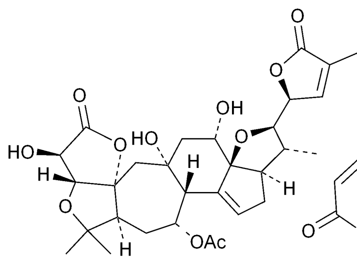


51 R = H
52 R = Ac



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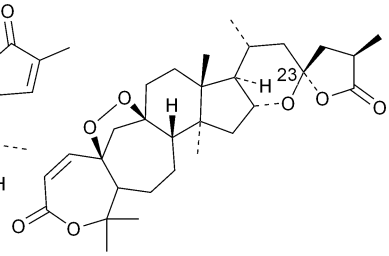
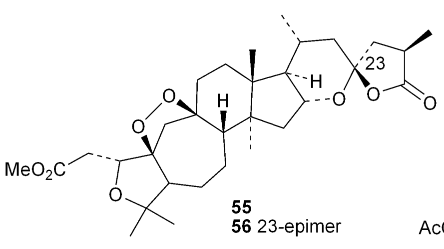
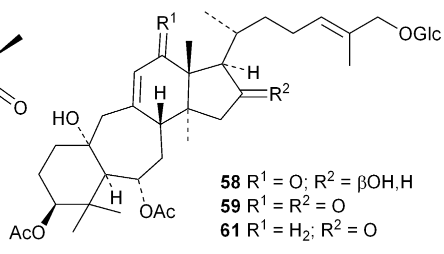


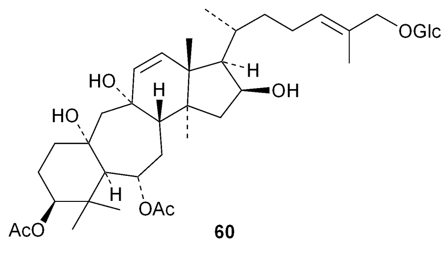
54
57 23,25-diepimer



55
56 23-epimer



58 R^1 = O; R^2 = βOH,H
59 $R^1 = R^2$ = O
61 $R^1 = H_2$; R^2 = O



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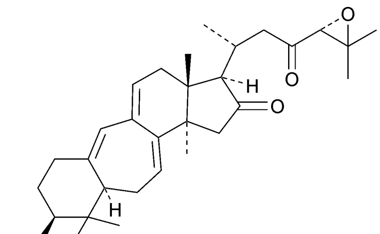

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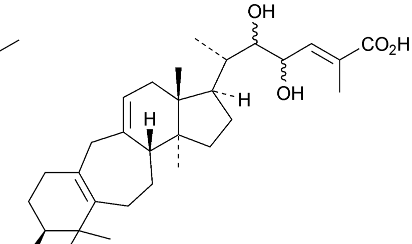

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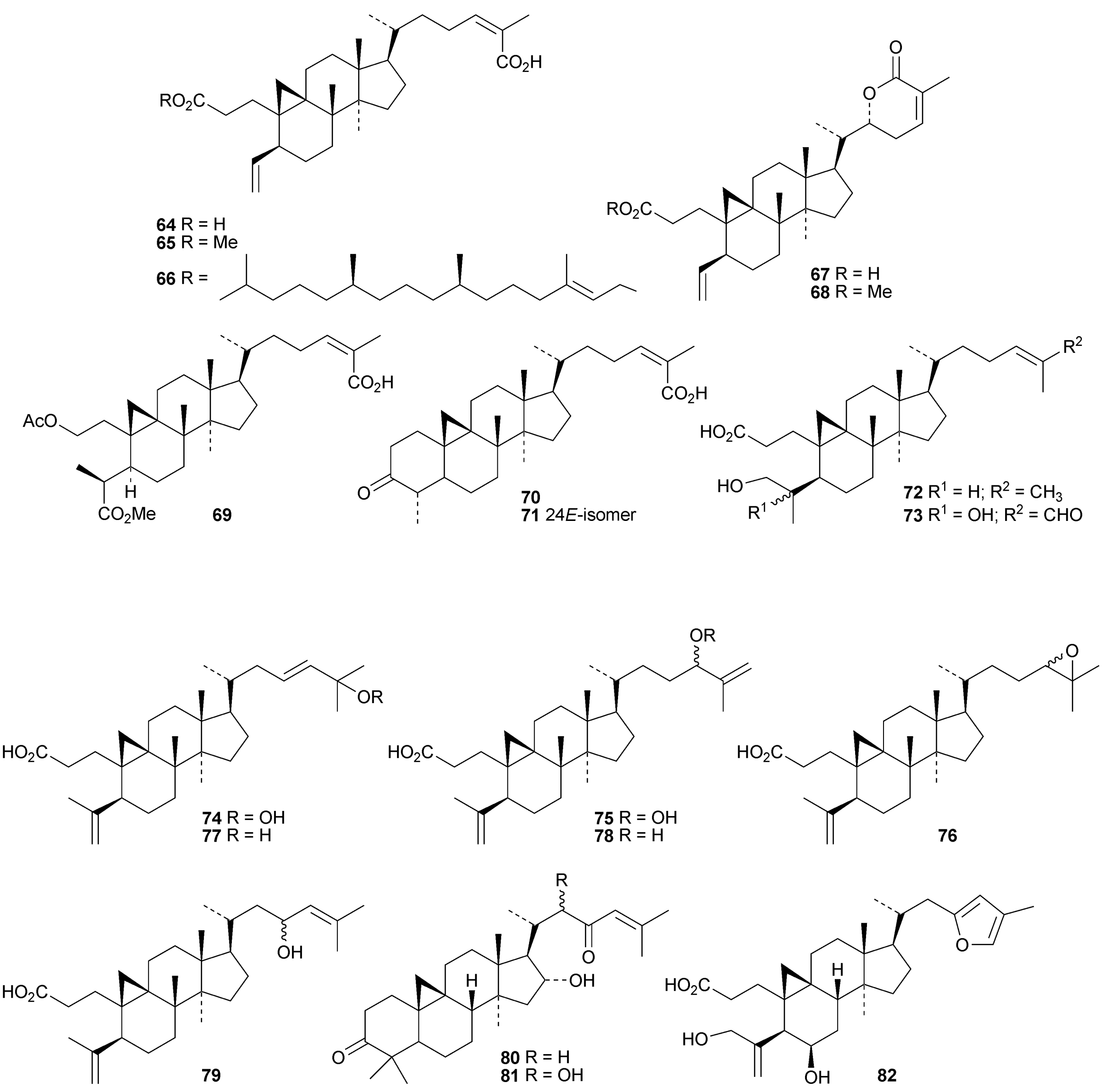
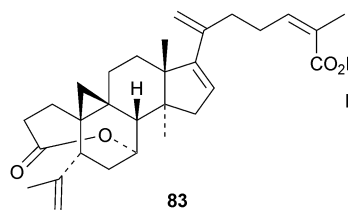
glycosides with known genins, liouvillosides A_4 and A_5, have been isolated from the sea cucumber *Staurocucumis liouvillei*.[46]

Interesting new compounds from *Schisandra* species include henrischinins A–C **44–46** from *Schisandra henryi* with an oxabicyclo[3.2.1]octane moiety in the side chain,[47] the bisnorderivative schinarisanlactone A **47** from *Schisandra arisanensis*[48] and the tricyclic derivative schiglautone A **48** from the stems of *Schisandra glaucescens*.[49] The structure of henrischinin B **45** was confirmed by X-ray analysis. 2β-Hydroxymicrandilactone C **49**,[50] schintrilactone C **50**[51] and wilsoniadilactones D–F **51–53**[52] are new constituents of *Schisandra chinensis*, *Schisandra sphenanthera* and *Schisandra wilsoniana*, respectively. Four new peroxylactones, pseudodarolides Q_2 **54**, T_1 **55** and T_2 **56**[53] and 25-epi-pseudolarolide Q **57**,[54] have been isolated from *Pseudolarix kaempferi*. Huangqiyenins G–J **58–61** are new saponins from *Astragalus membranaceus*.[55] The xyloside cimipodocarpaside **62** has been reported from *Cimifuga racemosa*.[56] The myxomycete *Tubulifera arachnoidea* afforded the new 9,10-secocycloartane tubiferic acid **63**.[57]

Sinocalycanchinensins A–H **64–71** are 29-norcycloartanes from the leaves of *Sinocalycanthus chinensis*.[58] Sinocalycanchinensins A–E **64–68** are 3,4-*seco*-derivatives while sinocalycanchinensin F **69** has a 2,3-cleaved ring A. Other 3,4-cleaved cycloartanes include gardenoins I **72** and J **73** from the exudates of *Gardenia thailandica*[59] and coccinetanes B–G **74–79** from *Kadsura coccinea*.[60] Secopisonic acid from *Pisonia umbellifera*[61] and gardenoin H from the apical buds of *Gardenia obtusifolia*[62] are identical with coccinetane E **77**. Gardenoins E–G **80–82** are other constituents of *Gardenia obtusifolia*.[62] Angustific acid A **83**, from *Kadsura angustifolia*, has an unusual bridged lactone.[63] It is accompanied by angustific acid B **84** and angustifodilactones A **85** and B **86**. The compounds are reported to have anti-HIV activity.

In separate studies ten new cycloartanes and glycosides **87–96**[64] and three new glycosides, two (**97** and **98**) with new genins,[65] have been reported from *Cimifuga foetida*. Six new glycosides **99–104** have been isolated from the rhizome of *Cimifuga heracleifolia*[66] and two, tareciliosides L and M with new genins





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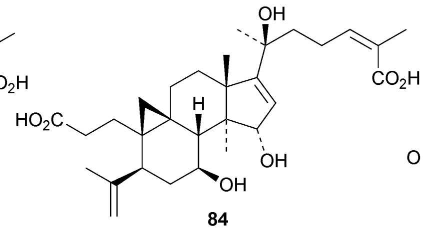

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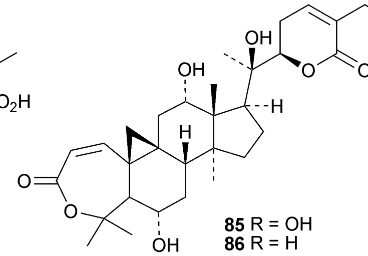
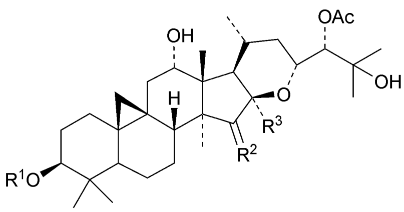
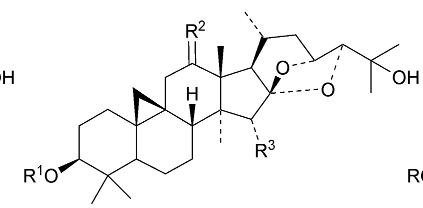
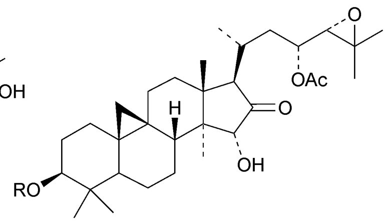


85 R = OH
86 R = H



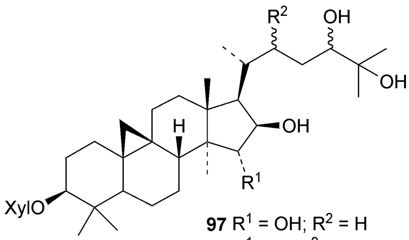




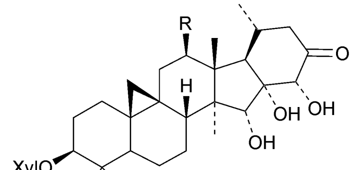
87 R^1 = 2-*O*-Ac-Ara; R^2 = O; R^3 = H
88 R^1 = Ara; R^2 = O; R^3 = H
89 R^1 = 2-*O*-Ac-Ara; R^2 = αOH,H; R^3 = OH;

90 R^1 = H; R^2 = βOH,H; R^3 = OH; 25,26-anhydro
91 R^1 = Ara R^2 = H_2; R^3 = OH; 25,26-anhydro
92 R^1 = H; R^2 = O; R^3 = OH
93 R^1 = H; R^2 = βOH,H; R^3 = H
94 R^1 = 2-*O*-Ac-Ara R^2 = H_2; R^3 = OH; 24*R*
95 R^1 = 2-*O*-Ac-Xyl; R^2 = H_2; R^3 = OH

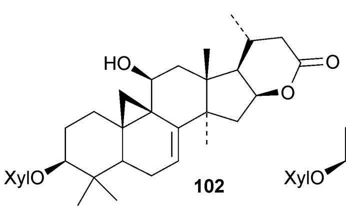
96 R = 2-*O*-Ac-ara



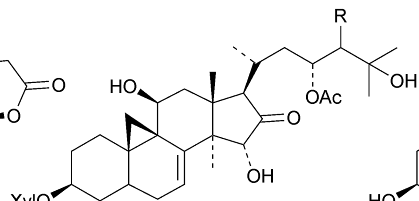
97 R^1 = OH; R^2 = H
98 R^1 = H; R^2 = OH



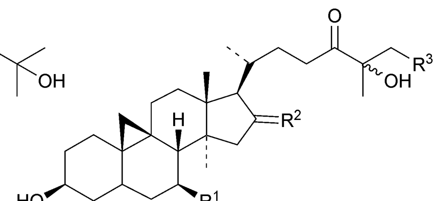
99 R = H
100 R = H; 7,8-didehydro
101 R = OAc; 7,8-didehydro



102



103 R = αOAc
104 R = βOH



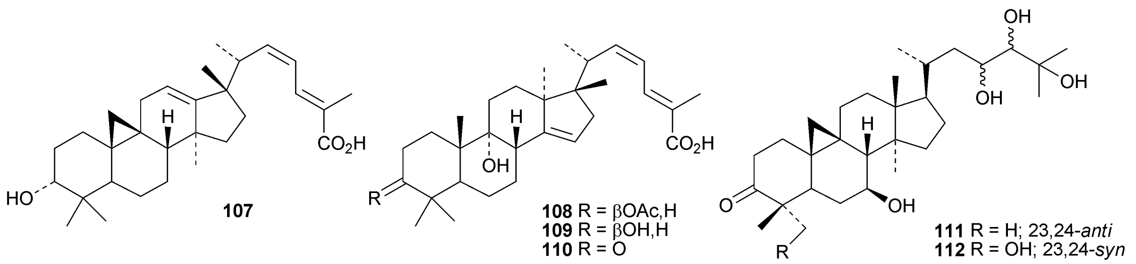
105 R^1 = H; R^2 = βOH,H; R^3 = OH
106 R^1 = OH; R^2 = O; R^3 = H

105 and **106**, from the leaves of *Tarenna gracilipes*.[67] Tareciliosides H–K have known genins.

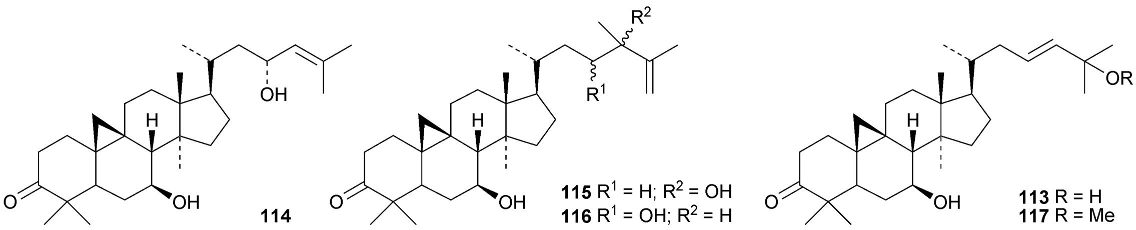
The 18(13 → 17)-abeocycloartane **107** is a constituent of the bark and leaves of *Garcinia benthami*, where it occurs along with the 14,17-friedolanostanes **108–110**.[68] Other new cycloartanes include combretanones A–G **111–117** and combretic acids A **118** and B **119** from *Combretum quadlangulare*,[69] bicusposides D–F **120–122** from *Astragalus bicuspis*,[70] macrostachyosides A **123** and B **124** from *Mallotus macrostachyus*,[71] cycloart-24-ene-2α,3β-diol **125** from the stigma of *Zea mays*[72] and boniatic acids A **126** and B **127** from *Radermachera boniana*.[73] Bonianic acids A **126** and B **127** showed some antitubercular activity. Codonopilates A–C **128–130** are cycloartane esters from *Codonopsis pilosula*.[74]

Novel cycloartane saponins with known genins include askendoside K from *Astragalus taschkendicus*,[75] cicerosides A and B from *Astragalus cicer*,[76] shengmaxinsides A–C from *Cimicifuga simplex*,[77] and unnamed saponins from *Astragalus mucidus*.[78] The biological activities of cycloartane triterpenoids have been reviewed.[79]

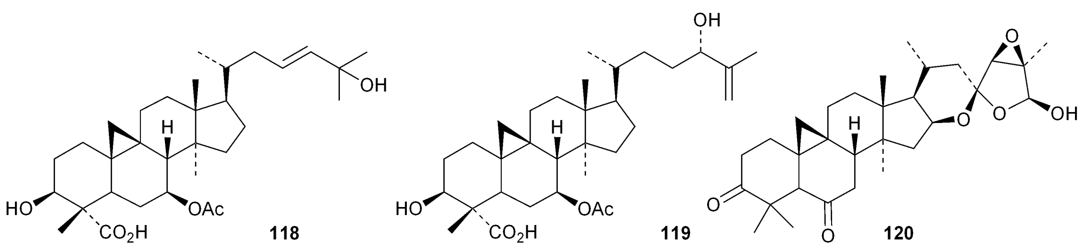
Machilusides A **131** and B **132**, from the stem bark of *Machilus yaoshansis*, are cucurbitane glycosides with an unusual *C*-glycoside moiety.[80] The roots of *Machilus yaoshansis* afforded seven new glycosides **133–139**.[81] These authors also revised the C-24 configurations of several known compounds, including cucurbitacins S and T and colocyhthins A, B and C, from 24*S* to 24*R*. Compounds **140** and **141**, from the roots of *Wilbrandia*



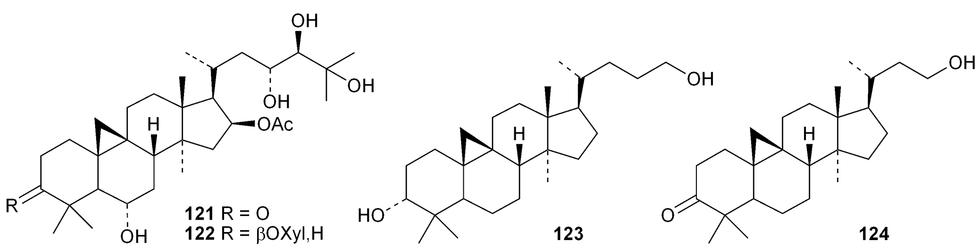
107; 108 R = βOAc,H; 109 R = βOH,H; 110 R = O; 111 R = H; 23,24-*anti*; 112 R = OH; 23,24-*syn*



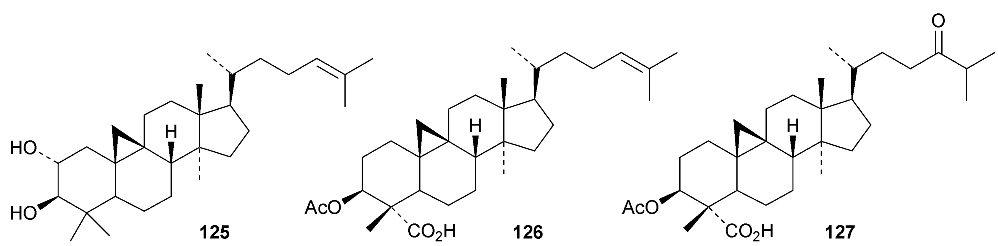
114; 115 R^1 = H; R^2 = OH; 116 R^1 = OH; R^2 = H; 113 R = H; 117 R = Me



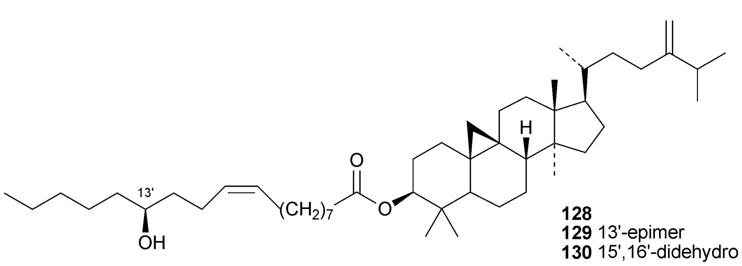
118; 119; 120



121 R = O; 122 R = βOXyl,H; 123; 124

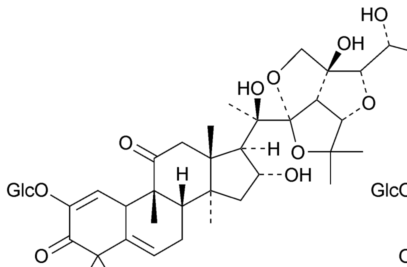


125; 126; 127



128; 129 13'-epimer; 130 15',16'-didehydro

ebracteata, are reported to have cytotoxic activity.[82] New cucurbitanes from *Momordica charantia* include the antioxidants taiwacins A **142** and B **143** from the stems and fruit,[83] **144–148**[84] and **149** and **150**.[85] Compound **148** is a 19-*nor*-derivative with an aromatic ring B. The biological activities of compounds from *Momordica charantia* have been reviewed.[86]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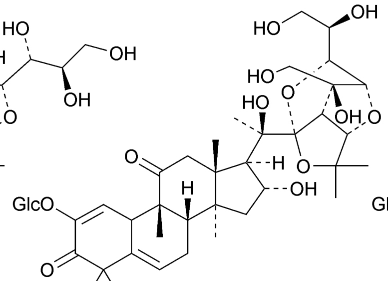
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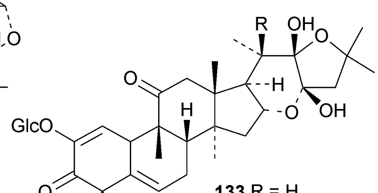
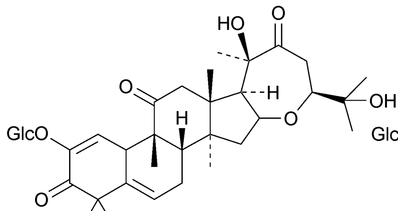

133 R = H
134 R = OH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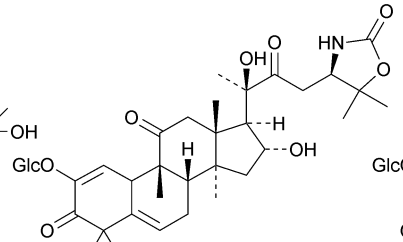
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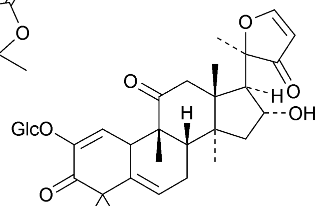
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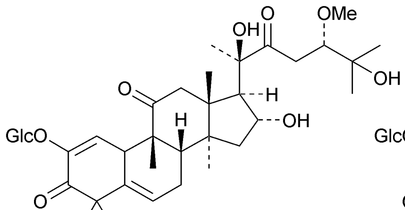
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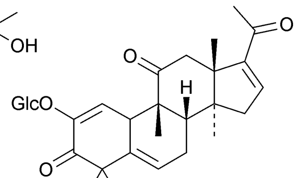
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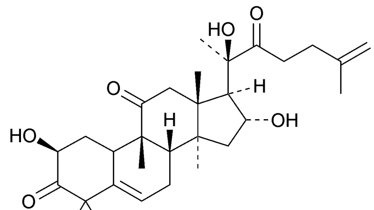
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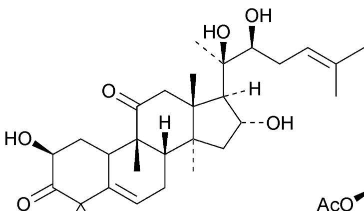
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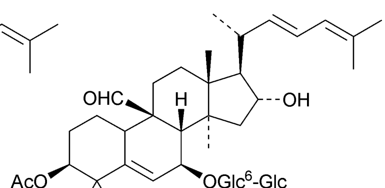
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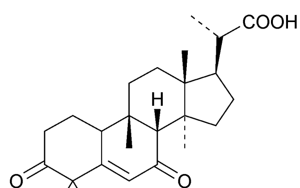
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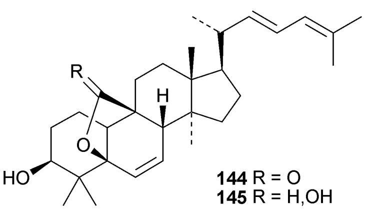
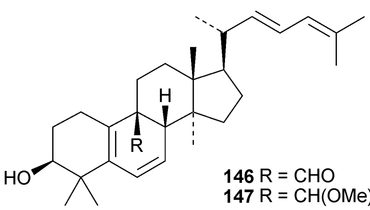
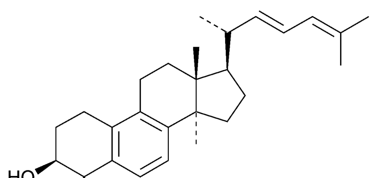

144 R = O
145 R = H,OH


146 R = CHO
147 R = CH(OMe)$_2$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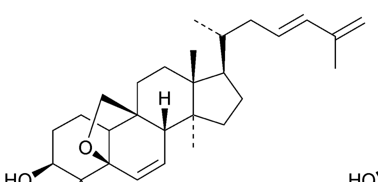
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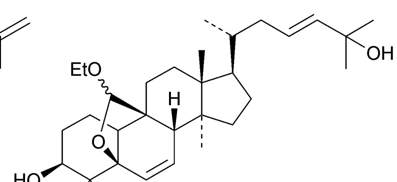
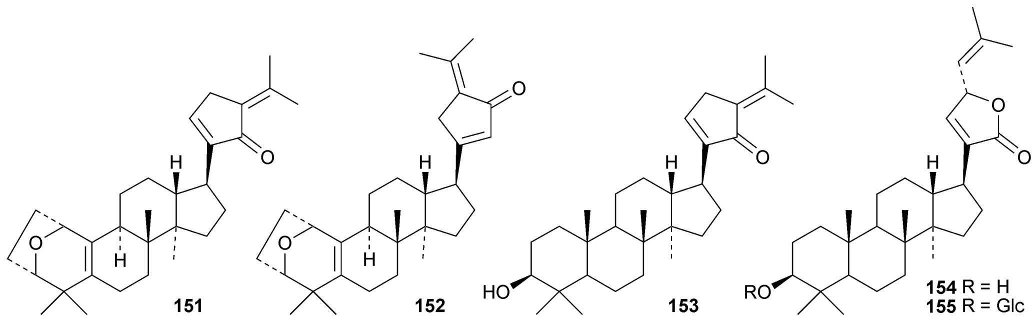

150

4 The dammarane group

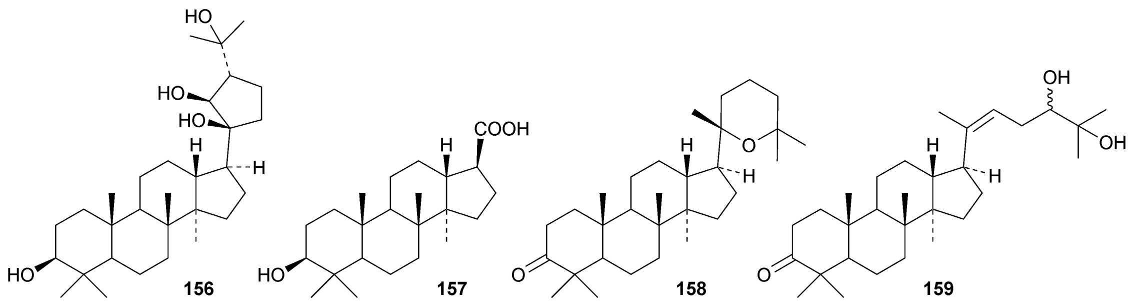
Gypensapogenins A **151** and B **152** are modified dammaranes, with an unusual ring A, from *Gynostemma pentaphyllum*, where they are found with gypensapogenins C **153**, D **154** and the glucoside **155**[87] and the 21,24-cyclo derivative **156** and the nonanordammarane **157**.[88] The structure of gypensaponin A **151** was confirmed by X-ray analysis. Other new dammaranes include gardaubryones A–C **158–160** from *Gardenia aubryi*,[89] **161–163** from the berries of *Panax ginseng*,[90] **164–170** from the floral spikes of *Betula platyphylla* var. *japonica*,[91] the 24-epimers **171** and **172** from the apical buds of *Gardenia collinsae*,[92] dammara-20(22),24-diene-3β,26,27-triol **173** from the leaves and twigs of *Rhus taitensis*[25] and the α-ketol **174** from the exudate of the leaves of *Cerasus yedoensis*.[93] The structure recently proposed for ailexcelone, from *Ailanthus excelsa*, is similar to that of gardaubryone B **159** but its spectroscopic data are inconsistent with this structure, The revised structure, 24,25-dihydroxytirucall-7-en-3-one, has been proposed and the structure of the corresponding 3β-hydroxy-derivative should also be revised.[89]

Four new saponins, operculinosides A–D **175–178**, have been reported from the aerial parts of *Operculina turpethum*.[94] The structure of operculinoside A **175** was confirmed by X-ray analysis. Of the six saponins ginsenosides Re_1- Re_6 have been reported from the root of *Panax ginseng*, only ginsenoside Re_5 **179** has a new genin.[95] Panajaponol, from the roots of *Panax japonicus* var. *major*, is identical to ginsenoside Re_5 **179** but was drawn with the wrong double bond geometry.[96] Reviews on the pharmacological activities of the ginsenosides have appeared.[97,98]

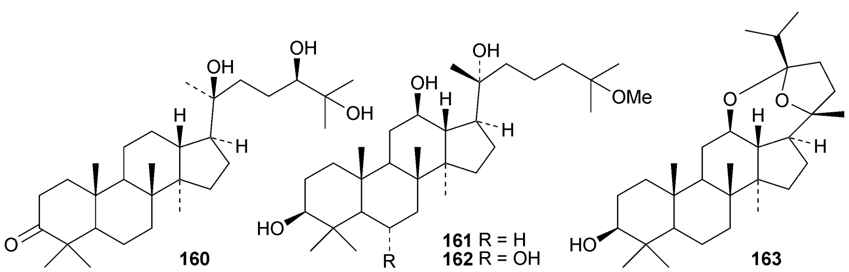
Novel dammarane saponins with known genins include betalnosides B and C from *Betula alnoides*,[99] centellosides A and B and ginsenosides Mc and Y from *Centella asiatica*,[100] ginsenosides Ra_4–Ra_9[101] and 20*R*-ginsenoside ST_2[102] from *Panax*



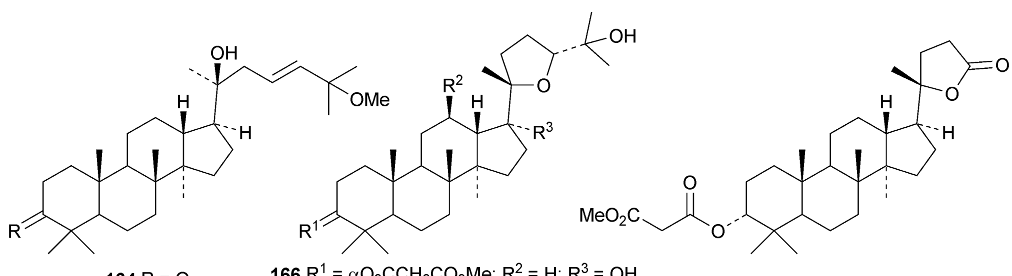
151 152 153 154 R = H 155 R = Glc



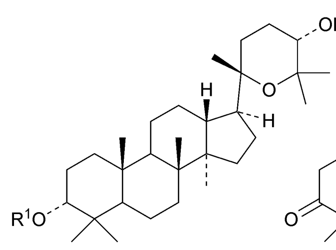
156 157 158 159

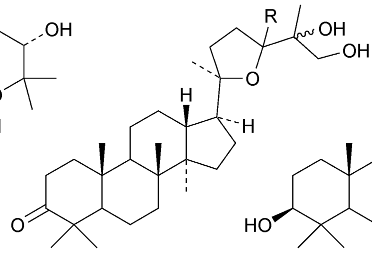


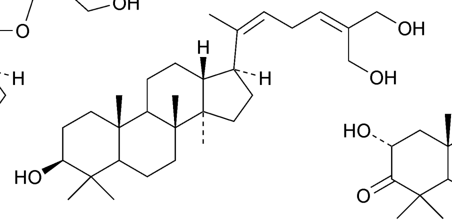
160 161 R = H 162 R = OH 163



164 R = O
165 R = αOH,H
166 R^1 = $\alpha O_2CCH_2CO_2Me$; R^2 = H; R^3 = OH
167 R^1 = O; R^2 = OAc; R^3 = H
168


169 R = H
170 R = $OCCH_2CO_2Me$


171 R = βH
172 R = αH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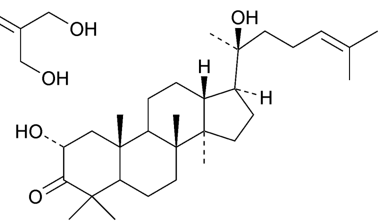
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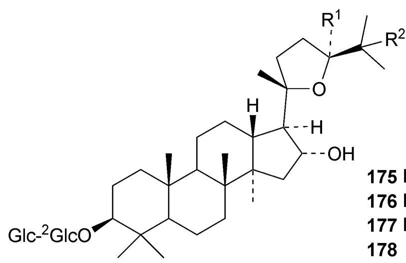
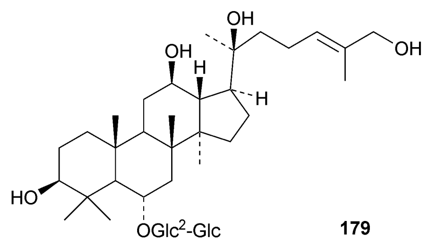
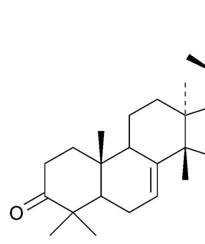
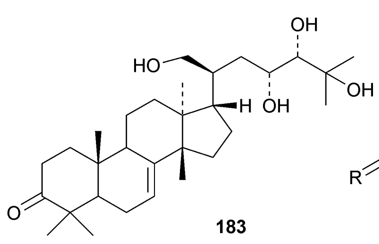

175 $R^1 = CH_2OH$; R^2 = H
176 $R^1 = CH_2OGlc$; R^2 = H
177 R^1 = H; R^2 = OH
178 R^1 = H; R^2 = OGlc


179

ginseng, gypenosides GC1–GC7 from *Gynostemma pentaphyllum*,[103] notoginsenosides SFt_1–SFt_4 from *Panax notoginseng*,[104] pseudoginsenosides G_1 and G_2 from *Panax quinquefolium*,[105] yesanchinosides R_1 and R_2 from *Panax japonicus*[106] and unnamed saponins from *Gynostemma pentaphyllum*.[107]

Toona ciliata var. *pubescens* is the source of the tirucallane derivatives toonapubesins A–G **180–186**.[108] Toonapubesin G **186** has a rearranged side chain. The tirucallanes **187–192**, together with dysoxylumstatins A–C **193–195**, have been reported from *Dysoxylum lukii*.[109] Dysoxylumstatin C **195** is an apotirucallane γ-lactone. Several *nor*-tirucallane derivatives **196–199** have been isolated from *Aphanamixis grandifolia*.[110] Compound **199** was also isolated as dysolenticin G from the twigs and leaves of *Dysoxylum lenticellatum*, a rich source of interesting tirucallane derivatives including dysolenticin A **200**, with its rearranged side chain, and dysolenticins B–F **201–205** and H–J **206–208**.[111] The structures of **200**, **202**, **203**, **205** and **207** were confirmed by X-ray analyses. Other new tirucallane derivatives from *Aphanamixis grandifolia* include aphagranins A–G **209–215**[112] and compounds **216–220**.[113] Several of these compounds look suspiciously like artefacts of the extraction process. *Cornus walteri* is also a good source of new tirucallane derivatives.[114] The constituents of this plant include cornusalterins A–L **221–232**. Ailanthusaltenin A, from the stem bark of *Ailanthus altissima*,[115] is the same as cornusalterin D **224**. Other new tirucallanes include **233** from *Euphorbia sapinii*,[30] **234** from the resin of *Boswellia carterii*,[116] the dihydroxy acid


180
181 24-epimer
182 22,23-diepimer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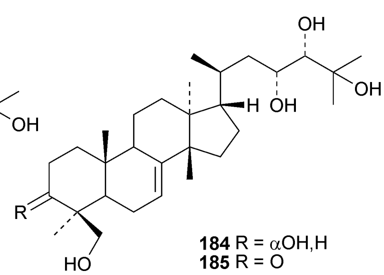
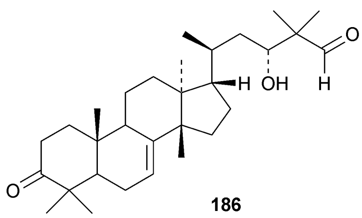

184 R = αOH,H
185 R = O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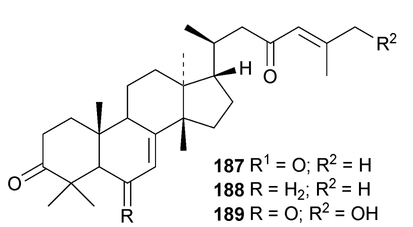
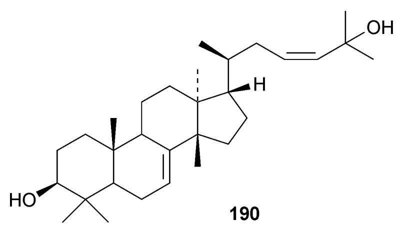

187 R^1 = O; R^2 = H
188 R = H_2; R^2 = H
189 R = O; R^2 = OH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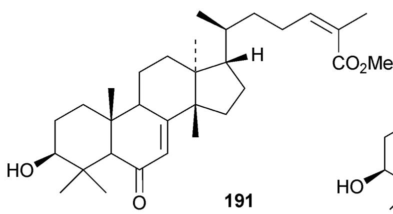

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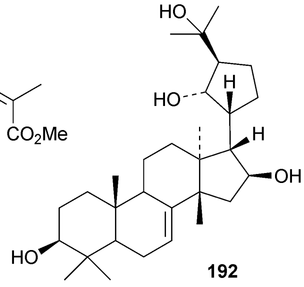

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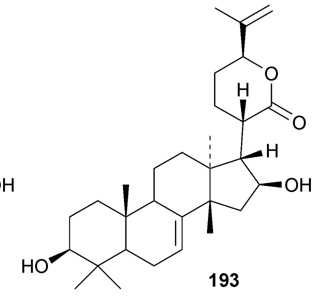

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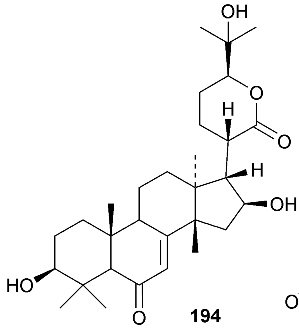

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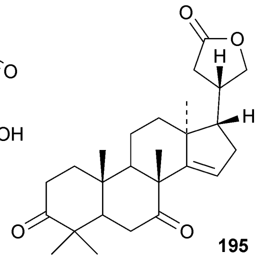

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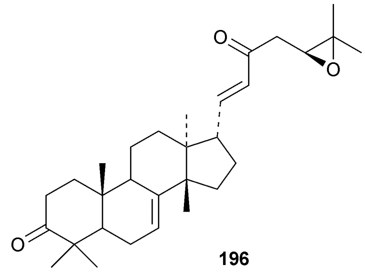

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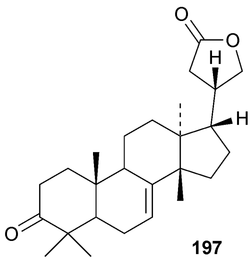

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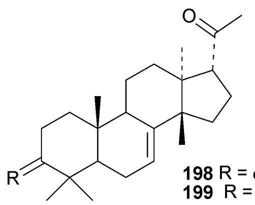
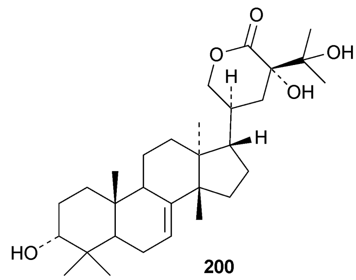


198 R = αOH,H
199 R = O



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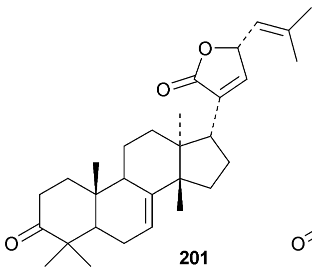

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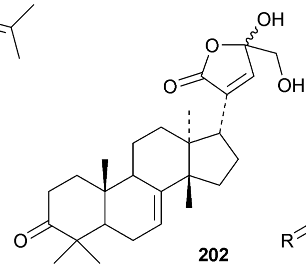

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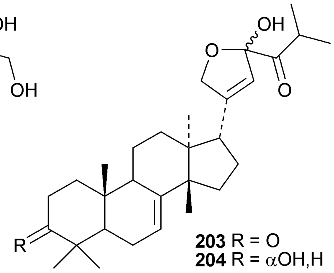
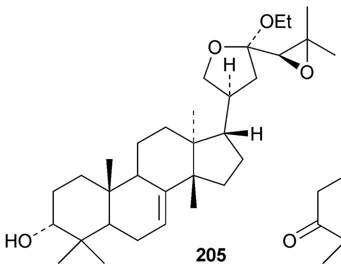


203 R = O
204 R = αOH,H



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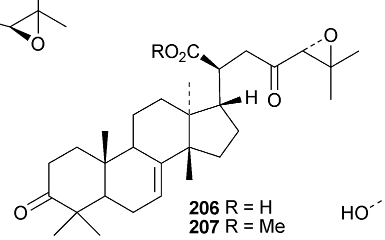
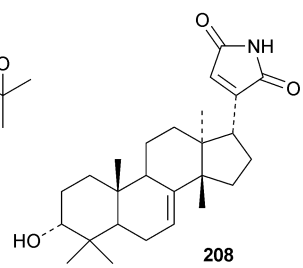


206 R = H
207 R = Me

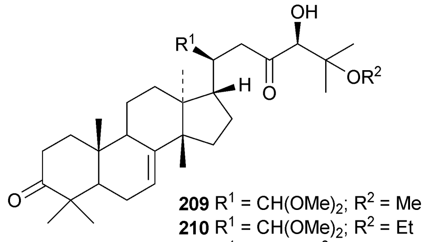


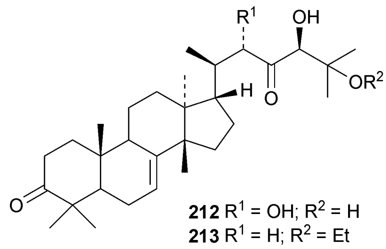
208

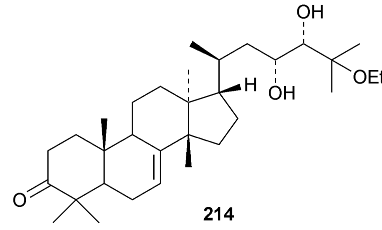
235 from Jordanian propolis[117] and **236** and **237** from *Azadirachta indica*.[118]

Only seven euphane triterpenoids have been reported. They are compounds **238–241** from the bark of *Broussonetia papyrifera*,[119] nepetadiol **242** from *Nepeta suavis*[120] and the 21,24-cycloeuphane **243** and cinamodiol acetate **244** from the bark of *Melia azedarach*.[121]

Cumingianols A–C **245–247** are cycloapotirucallane derivatives from *Dysoxylum cumingianum*.[122] Other constituents include cumingianoside R **248**, a rare glycoside in this series,


209 $R^1 = CH(OMe)_2$; $R^2 = Me$
210 $R^1 = CH(OMe)_2$; $R^2 = Et$
211 $R^1 = CHO$; $R^2 = Et$


212 $R^1 = OH$; $R^2 = H$
213 $R^1 = H$; $R^2 = Et$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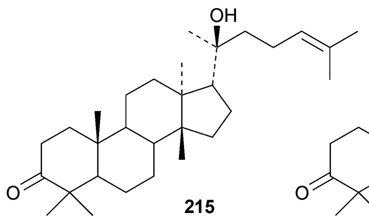
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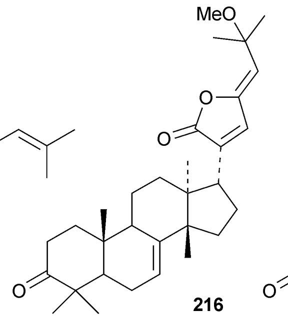
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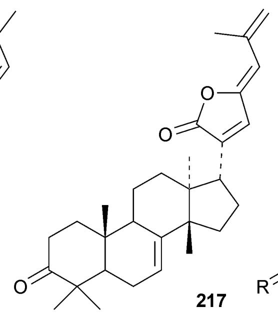
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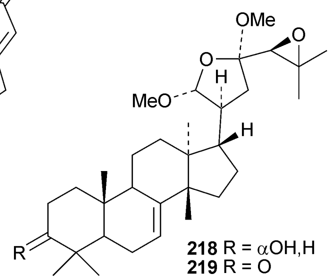
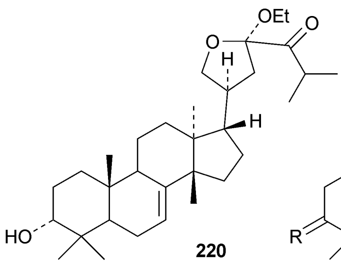

218 R = αOH,H
219 R = O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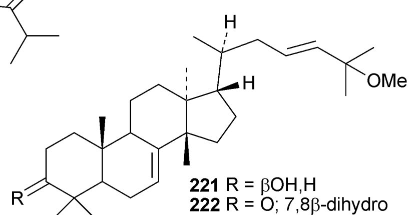
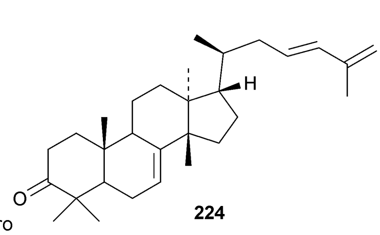

221 R = βOH,H
222 R = O; 7,8β-dihydro
223 R = βOH,H; 7,8β-dihydro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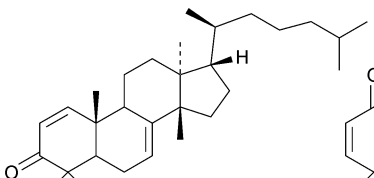
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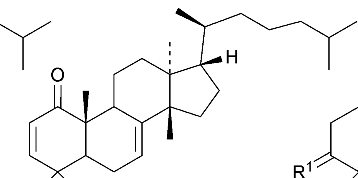
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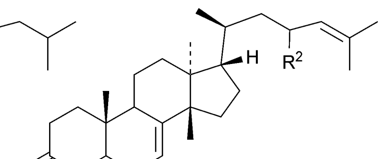
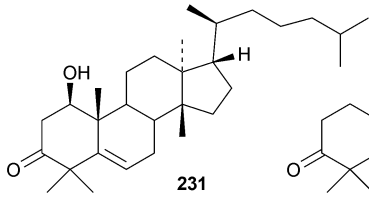

227 R^1 = O; R^2 = αOMe
228 R^1 = O; R^2 = βOMe
229 R^1 = O; R^2 = βOMe; 9,11-didehydro
230 R^1 = βOH,H; R^2 = αOMe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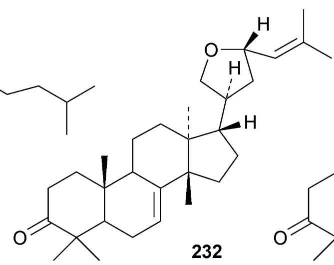
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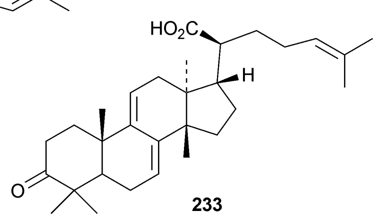
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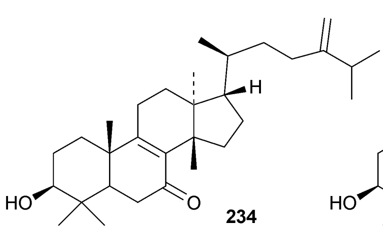
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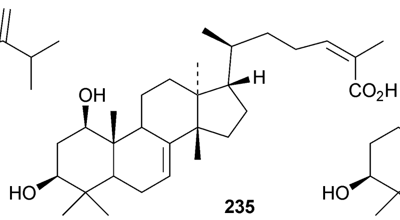
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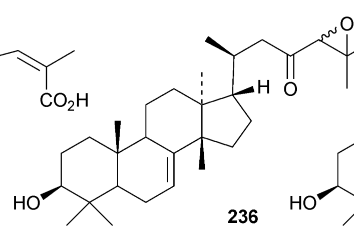
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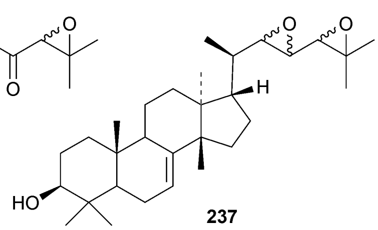
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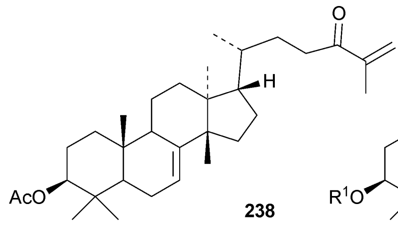
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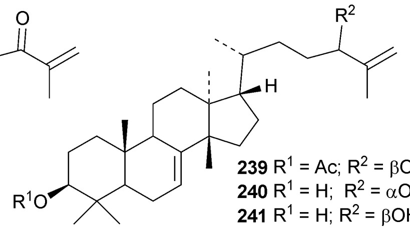
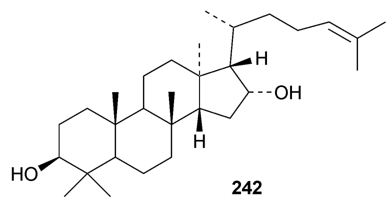

239 R^1 = Ac; R^2 = βOH
240 R^1 = H; R^2 = αOH
241 R^1 = H; R^2 = βOH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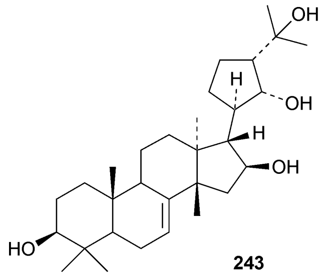
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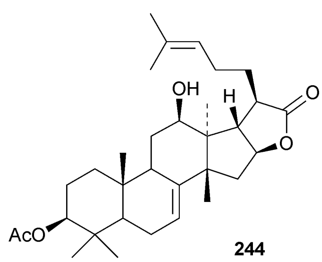
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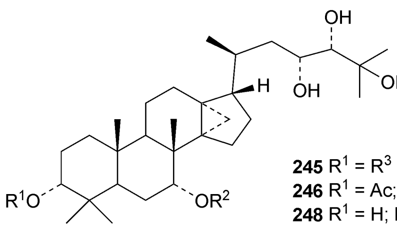
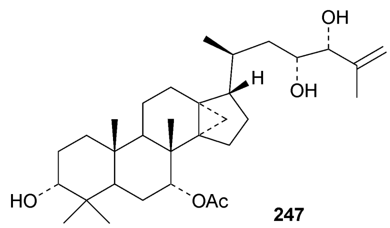

245 R^1 = R^3 = H; R^2 = Ac
246 R^1 = Ac; R^2= R^3 = H
248 R^1 = H; R^2= Glc; R^3 = Me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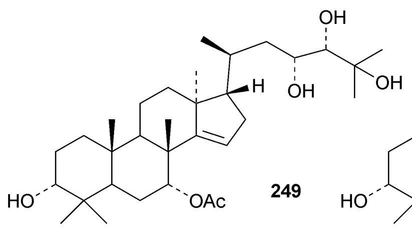
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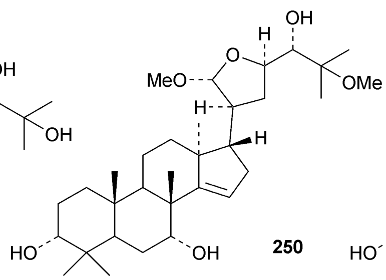
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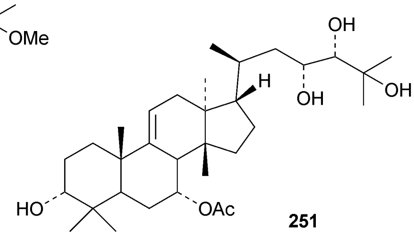

251

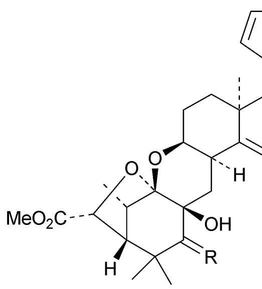
the apotirucallane derivatives, cumingianols D **249** and E **250**, and the tirucallane, cumingianol F **251**.

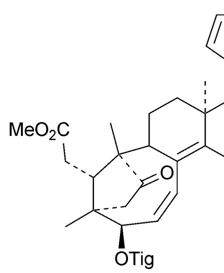
4.1 Tetranortriterpenoids

Reviews have appeared on limonoids from the Meliaceae[123] and from *Trichilia emetica*[124] and on the synthesis of limonoid natural products.[125] Kokosanolides A **252** and C **253** are rearranged limonoids from the seeds and bark of *Lansium domesticum* cv. Kokossan.[126] Other interesting derivatives include chisomicines A **254**, B **255** and C **256** from the bark of *Chisocheton ceramicus*,[127] 5,6-didehydrodesepoxyhaperforin C2 **257** and harrpernoids B **258** and C **259** from the fruit of *Harrisonia perforata*,[128] aphapolynins A **260** and B **261**[129] and aphanamolides A **262** and B **263**[130] from *Aphanamixis polystachya*. The structures of kokosanolide A **252**, chisomicines A–C **254–256** and aphapolyrin A **260** were all confirmed by X-ray analyses.

The lack of a furan ring is the notable feature of the tris-nor derivatives toonapubesic acids A **264** and B **265** from *Toona ciliata* var. *pubescens*.[108] The structure of the methyl ester of toonapubesic acid A was confirmed by X-ray analysis. Ceramicines E–I **266–270** constitute a series of 1-oxo derivatives from *Chisocheton ceramicus*.[131] The structure of the previously published ceramicine B **271** has been confirmed by X-ray analysis. Meliarachins A–K **272–282** are further limonoids from the twigs and leaves of *Melia azedarach*.[132]

Dasylactones A **283** and B **284** are degraded derivatives from *Dictamnus dasycarpus*.[133] Raputiolide **285** is a ring-A cleaved limonoid from *Raputia heptaphylla*.[134] *Toona ciliata* var. *henryi* is a rich source of ring-B cleaved derivatives, affording toonacilianins A–L **286–297**.[135] Toonacilianins K **296** and L **297** are 29-nor derivatives. Two further 29-nor derivatives, toonaciliatins N **298** and O **299** have been reported from *Toona ciliata* var. *yunnanensis*, where they occur along with toonaciliatin P **300**.[136]


252 R = O
253 R = H_2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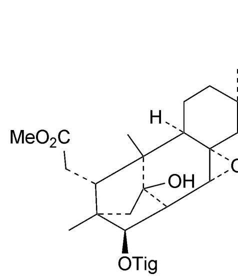
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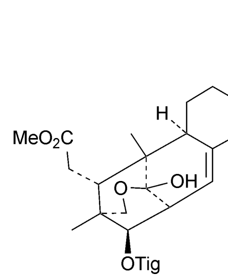
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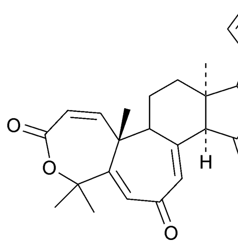
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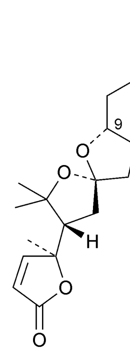
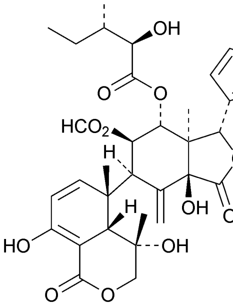

258
259 9-epimer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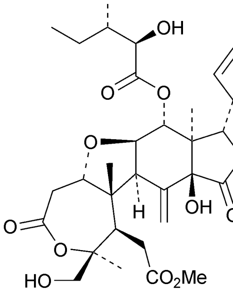
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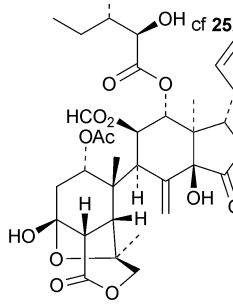
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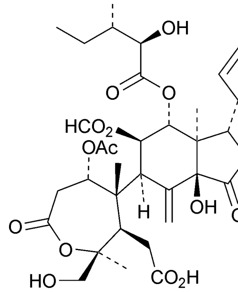
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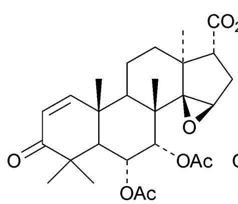
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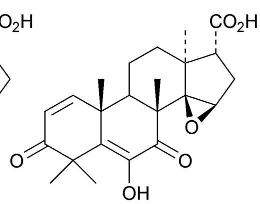
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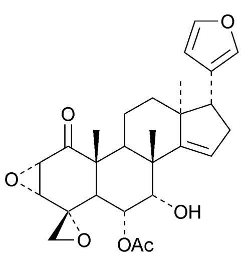
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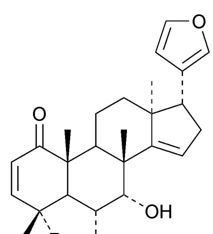
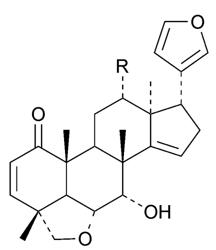
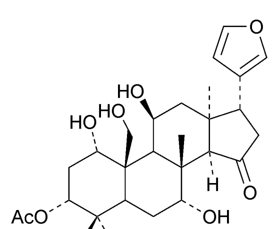
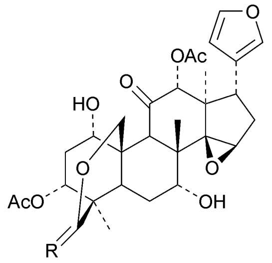

267 R = CHO
268 R = CO_2Me

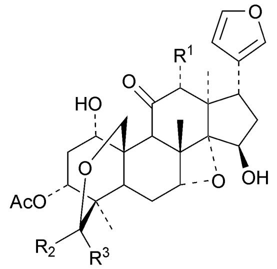

269 R = OTig
270 R = OAc
271 R = H


272

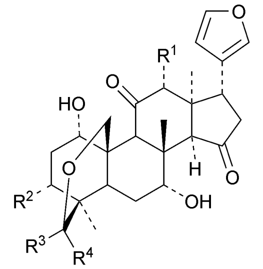
Three methyl angolensate derivatives **301–303** have been found in the root bark of *Entandrophragma angolense*, where they occur with the gedunin derivatives **304** and **305**.[137] Compound **301** is the same as moluccensin O which was published in 2010. Thaimoluccensin A **306** is an andirobin derivative from the seeds of *Xylocarpus moluccensis*.[138] Although its structure was confirmed by X-ray analysis the wrong relative configuration was published in the original paper.



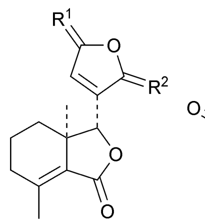
273 R = O
274 R = OMe,H



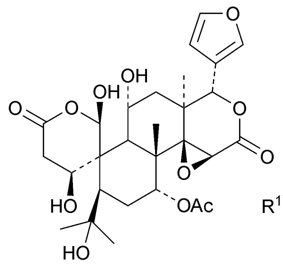
275 R[1] = OAc; R[2] = OMe; R[3] = H
276 R[1] = R[3] = OH; R[2] = H
277 R[1] = R[2] = OH; R[3] = H



278 R[1] = R[2] = OAc; R[3] = OMe; R[4] = H
279 R[1] = OAc; R[2] = OH; R[3] = OMe; R[4] = H
280 R[1] = R[2] = OH; R[3] = OMe; R[4] = H
281 R[1] = OH; R[2] = OAc; R[3] = H; R[4] = OMe
282 R[1] = R[2] = OAc; R[3] = H; R[4] = OMe



283 R[1] = O; R[2] = OH,H
284 R[1] = OH,H; R[2] = O



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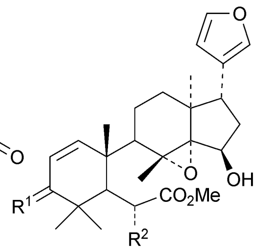
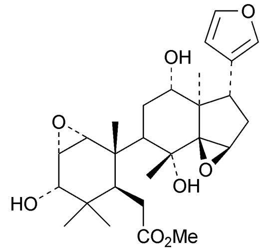


286 R[1] = αOH,H; R[2] = OH
287 R[1] = O; R[2] = OH
288 R[1] = O; R[2] = H



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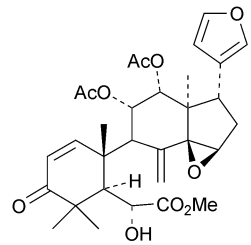

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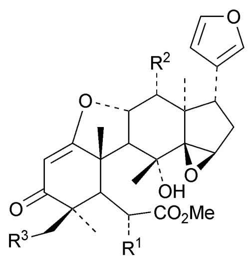
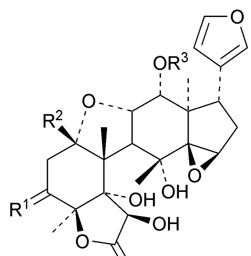
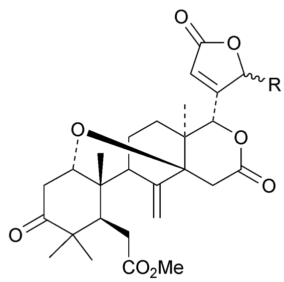


291 R[1] = H; R[2] = OH; R[3] = H
292 R[1] = OAc; R[2] = OH; R[3] = H
293 R[1] = H; R[2] = R[3] = OAc
294 R[1] = OAc; R[2] = OH; R[3] = H; 1β,2-dihydro
295 R[1] = OAc; R[2] = OH; R[3] = OAc; 1β,2-dihydro
300 R[1] = OAc; R[2] = R[3] = H

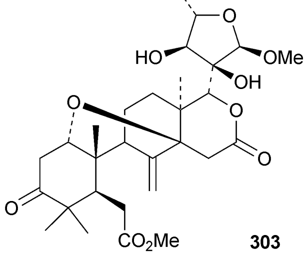


296 R[1] = βOH,H; R[2] = OH; R[3] = H
297 R[1] = αOH,H; R[2] = OH; R[3] = H
298 R[1] = O; R[2] = H; R[3] = Ac
299 R[1] = αOH,H; R[2] = H; R[3] = Ac



301 R = OH
302 R = OMe

Four new ring C cleaved limonoids **307–310** have been isolated from the fruit of *Melia toosendan*, together with the tirucallane derivatives meliasenins S **311** and T **312**.[139] Meliasenin T **312** was also obtained from *Melia azedarach* seeds where it occurs with the tirucallane **313**, the toosendanin esters **314** and **315** and the nimbolinin C derivative **316**.[140] The ring-C cleaved hydroperoxide **317** has been isolated from *Azadirachta indica*.[118]



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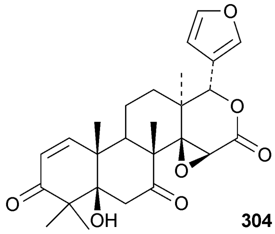

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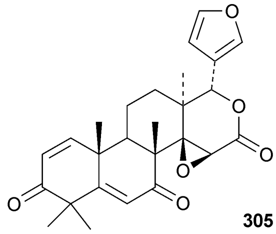

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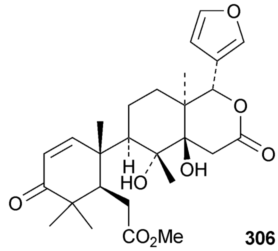

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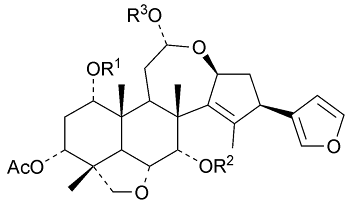
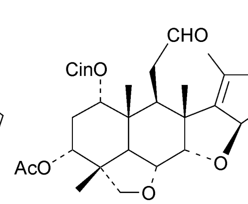


307 R^1 = H; R^2 = Tig; R^3 = Me
308 R^1 = R^2 = Tig; R^3 = Me
309 R^1 = Ac; R^2 = Tig; R^3 = Et
316 R^1 = Bz; R^2 = H; R^3 = Me



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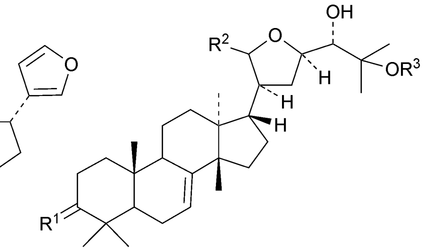
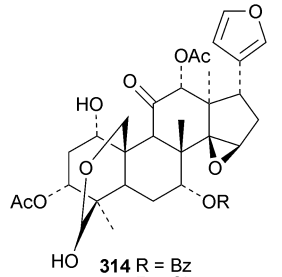
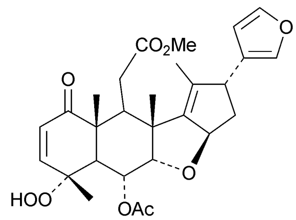


311 R^1 = βOH,H; R^2 = αOMe; R^3 = H
312 R^1 = βOH,H; R^2 = βOMe; R^3 = H
313 R^1 = O; R^2 = αOMe; R^3 = Et



314 R = Bz
315 R = Cin



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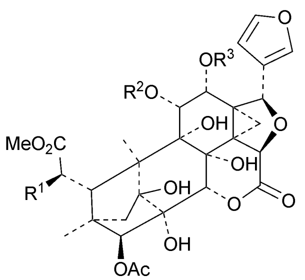
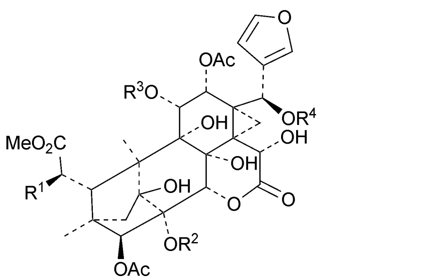
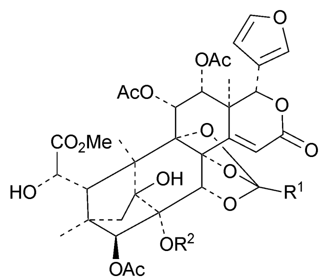


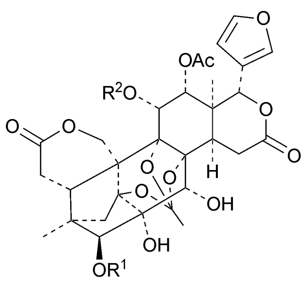
318 R^1 = H; R^2 = $OCCH_2CH_3$; R^3 = Ac
319 R^1 = H; R^2 = $OCCH(CH_3)_2$; R^3 = Ac
320 R^1 = OAc; R^2 = Ac; R^3 = $OCCH(CH_3)_2$
321 R^1 = OAc; R^2 = H; R^3 = $OCCH(CH_3)_2$
322 R^1 = OAc; R^2 = $OCCH(CH_3)_2$; R^3 = Ac
323 R^1 = OAc; R^2 = R^3 = Ac



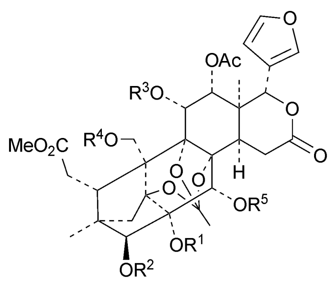
324 R^1 = OAc; R^2 = H; R^3 = Ac; R^4 = $OCCH(CH_3)_2$
325 R^1 = OAc R^2 = H; R^3 = $OCCH(CH_3)_2$; R^4 = Ac
326 R^1 = OAc; R^2 = $OCCH(CH_3)_2$; R^3 = R^4 = Ac
327 R^1 = H; R^2 = H; R^3 = Ac; R^4 = $OCCH(CH_3)_2$



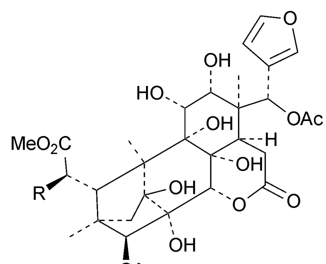
328 R^1 = $CH(CH_2)_3$; R^2 = H
329 R^1 = Me; R^2 = $OCCH(CH_3)_2$



330 R^1 = R^2 = H
331 R^1 = Ac; R^2 = H
332 R^1 = H; R^2 = Ac

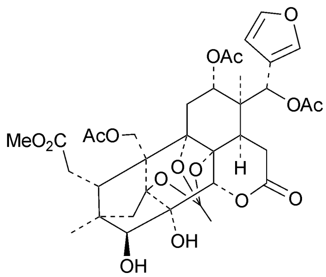


333 R^1 = R^2 = R^4 = R^5 = Ac; R^3 = H
334 R^1 = H; R^2 = R^3 = R^4 = R^5 = Ac
335 R^1 = R^2 = R^5 = H; R^3 = R^4 = Ac
336 R^1 = R^3 = R^5 = H; R^2 = Ac; R^4 = $OCCH(CH_3)_2$



337 R = H
338 R = OAc

The flow of new mexicanolide and phragmalin derivatives continues unabated. *Chukrasia tabularis* var. *velutina* is a particularly rich source. The new derivatives reported from this source include velutabularins A–J **318–327**,[141] tabulalides F–N **328–336**,[142] tabulalins A–E **337–341**,[143] chukvelutilide H **342** and tabularisin R **343**,[144] tabulvelutins A **344** and B **345**[145] and tabulalin F **346**.[146] Many of these compounds are trivial variants of known systems. Velutabularins A–J **318–327** are cyclopropyl derivatives with a modified ring D and tabulvelutin A **344** is a 19-nor derivative. A similar range of phragmalin derivatives, swietenitins N–X **347–357**, has been isolated from the twigs of *Swietenia macrophylla*.[147] The structure of swietenitin N **347** was confirmed by X-ray analysis. The stereochemistry of the known compound 14,15-dihydroepoxyfebrinin B **358** was also established during this study. The leaves of *Trichilia connaroides* produced trichagmalins A–F **359–364** and several acetyl derivatives **365–369**, together with trichanolide **370**.[148] The gedunin andirolide A **371**, the mexicanolides andirolides B–D **372–374** and the phragmalins andirolides E–G **375–377** have been reported from the flowers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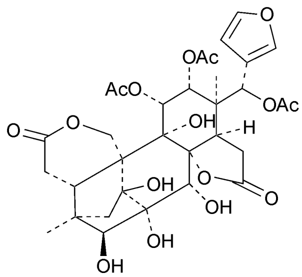
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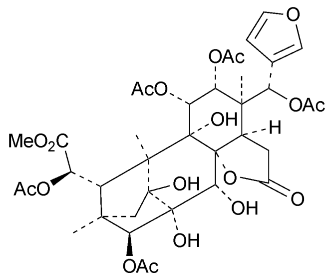
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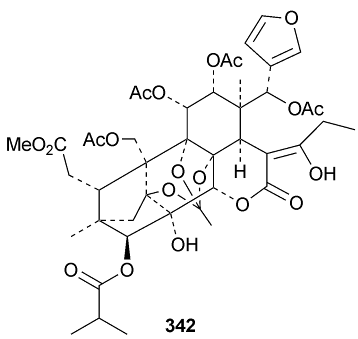
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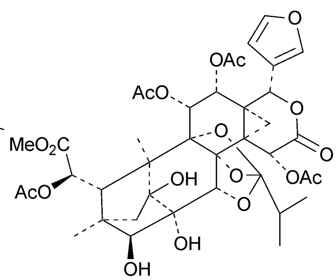
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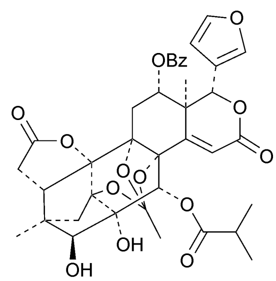
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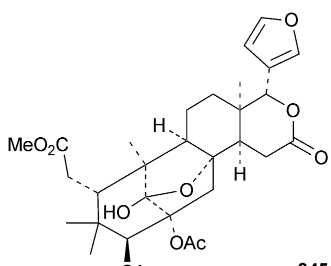
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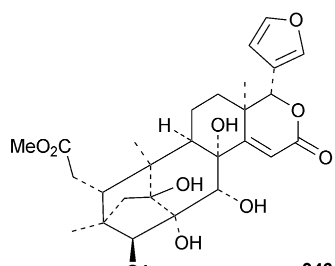
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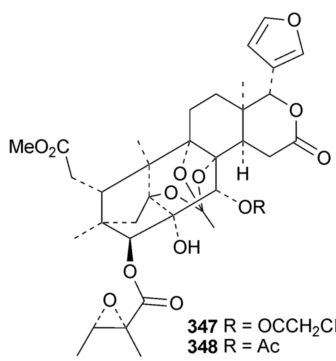
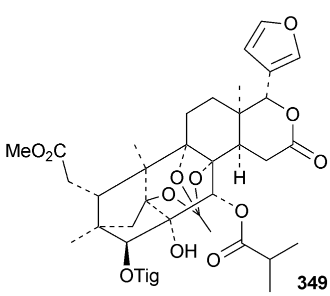

347 R = $OCCH_2CH_3$
348 R = Ac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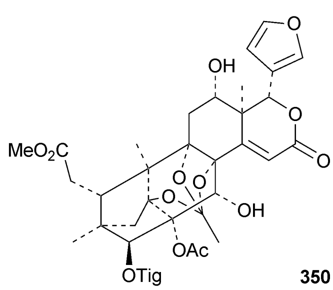
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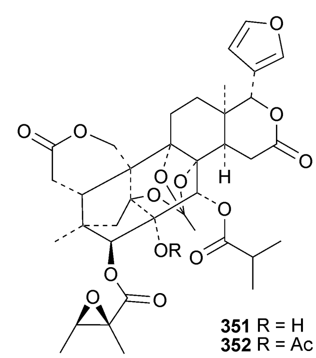
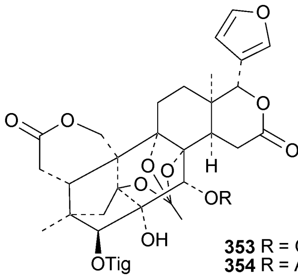
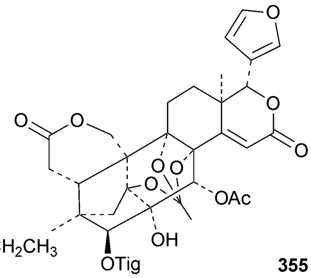

351 R = H
352 R = Ac



353 R = OCCH$_2$CH$_3$
354 R = Ac



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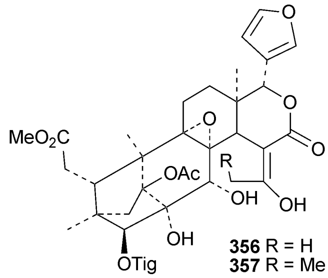
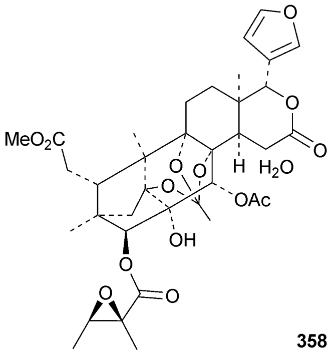


356 R = H
357 R = Me



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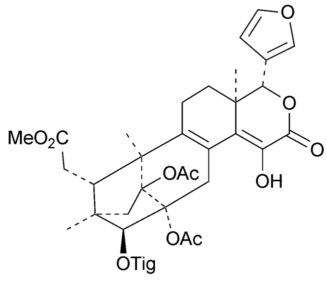

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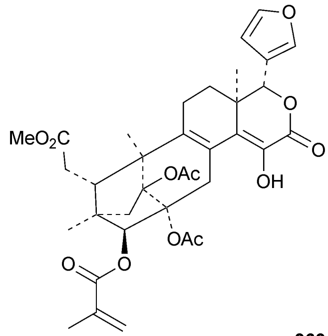

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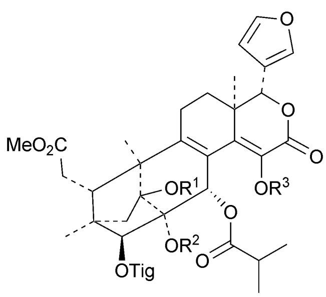
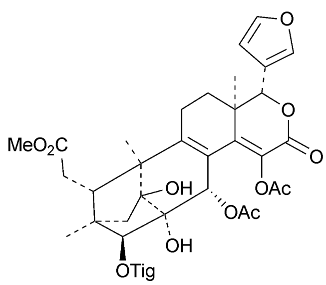


361 R^1 = R^2 = R^3 = H
365 R^1 = R^2 = H; R^3 = Ac
366 R^1 = R^2 = Ac; R^3 = H



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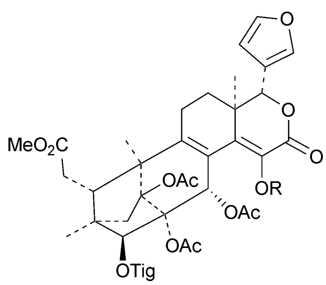
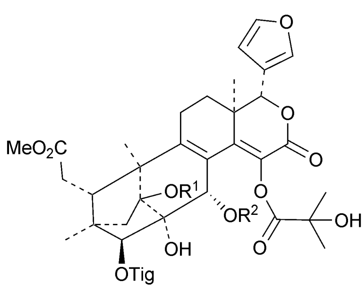
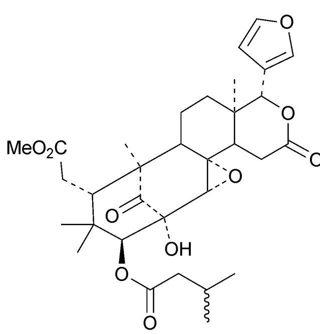


363 R = H
367 R = Ac



364 R^1 = R^2 = H
368 R^1 = H; R^2 = Ac
369 R^1 = R^2 = Ac;



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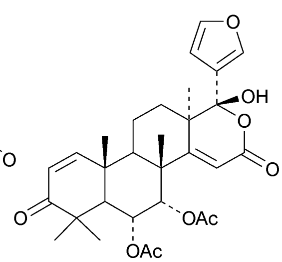
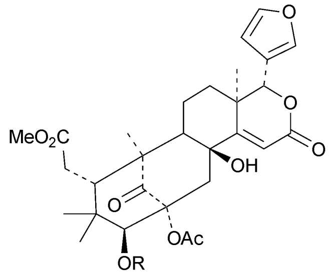
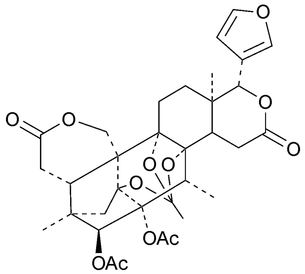


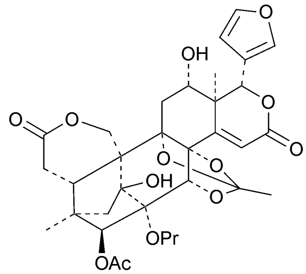
371

of *Carapa guianensis*.[149] The structure of andirolide E **375** was confirmed by X-ray analysis. Other phragmalin derivatives include thaimoluccensins B **378** and C **379** from the seeds of Thai *Xylocarpus moluccensis*[138] and godvarin K **380** from the Godvari mangrove *Xylocarpus moluccensis*.[150]

New quassinoids are few in number. They include 2′-isopicrasin A **381** from the stems of *Picrasma quassinoides*,[151] bruceines K **382** and L **383** from the ripe fruit of *Brucea javanica*,[152] yadanziolides T–V **384–386** from the stems of *Brucea mollis*[153] and nothospondin **387** from *Nothospondias staudtii*.[154]


372 R = Ac
373 R = OCCH(CH$_3$)$_2$
374 R = Tig


375
376 14,15-didehydro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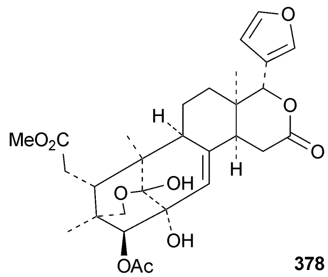
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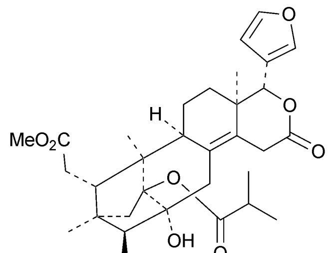
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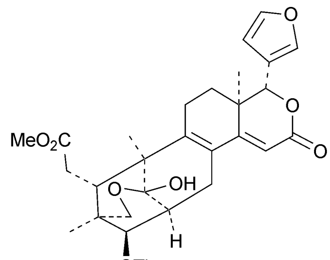
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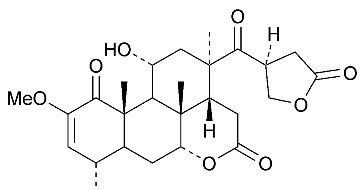
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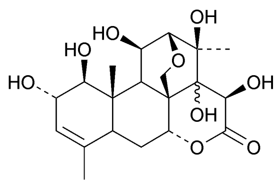
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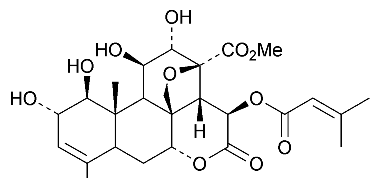
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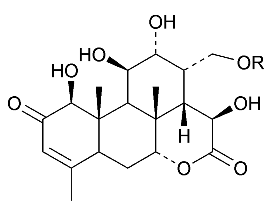
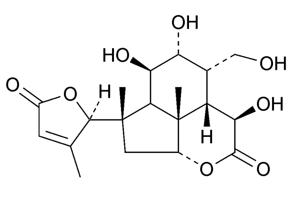

384 R - H
385 R = Glc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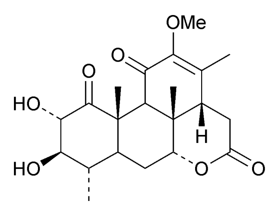
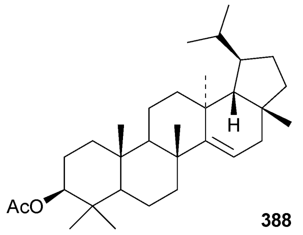

387

5 The lupane group

The pharmacological activities of lupeol[155] and lupane saponins[156] have been reviewed. Lactucenyl acetate **388**, from *Lactuca indica*, has a migrated lupane structure which is identical to the structure originally assigned to tarolupenyl acetate.[157] The structure of tarolupenyl acetate has been revised to lup-19(21)-en-3β-yl acetate **389**. Breynceanothanolic acid **390** is a 25-norceanothic acid derivative from roots of *Breynia fruticosa*.[158] The ring A-*seco* lupane dysoxyhainic acid H **391** is from *Dysoxylum hainanense*.[159] *Liquidambar formosana* is the source of liquidambarone **392** which is 18α,29-epoxy-20*R*-hydroxy-28-norlupan-3-one.[160] Sorbicins A **393** and B **394** are lupane derivatives from *Sorbus cashmiriana*.[161] Olibanum, the gum resin of *Boswellia carterii*, is the source of olibanumols F **395** and G **396**.[162] Other simple lupane derivatives include lupane-3β,18α,19β-triol **397** from *Garcinia tetralata*,[163] lup-12-ene-3β,28-diol **398** from roots of *Diospyros virginiana*,[164] the 3β,19β-dihydroxy derivatives **399** and **400** from *Paragonia pyrimidata*,[165] and the 23,27,28-trioic acid **401** from *Heteropanax fragrans*.[166] Pulsatilla triterpenic acid A **402**, from *Pulsatilla chinensis*, is an acetal of 5-hydroxymethylfurfural and 3β,23-dihydroxylup-20(29)-en-28-oic acid.[167] The caffeate esters **403**[168] and **404**[169] are from *Alnus firma* and *Alangium salviifolium*, respectively, while the palmitate ester **405** is found in leaves of *Rauvolfia vomitoria*.[170] The 21-configuration of **405** has not been established. Seven lupane saponins with known genins have been isolated from *Stryphnodendron fissuratum*.[171]



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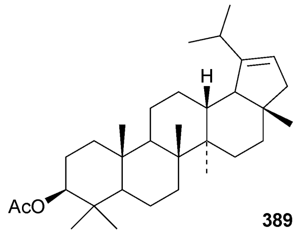

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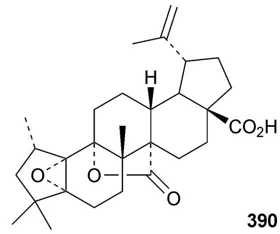

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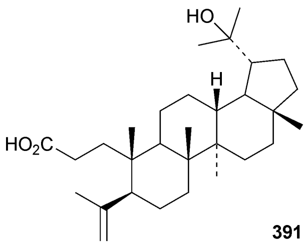

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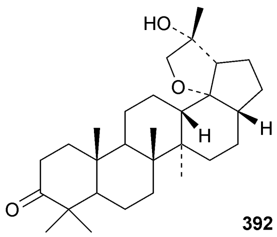

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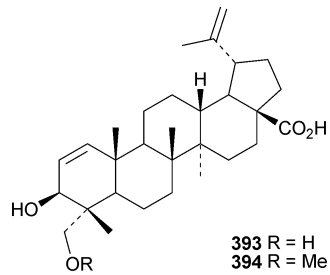
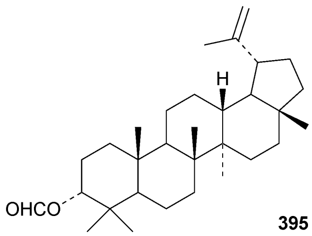


393 R = H
394 R = Me



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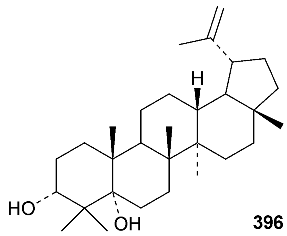

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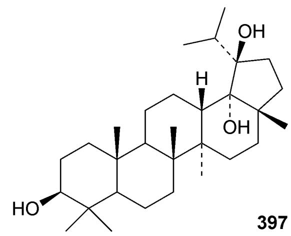

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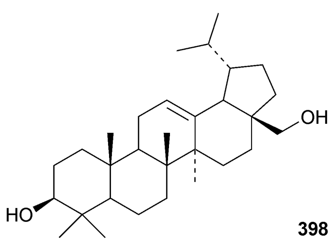

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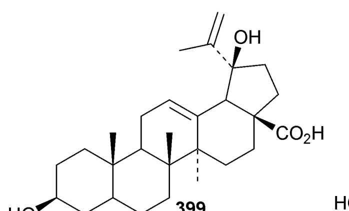
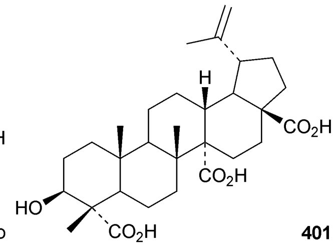


399
400 20,29-dihydro



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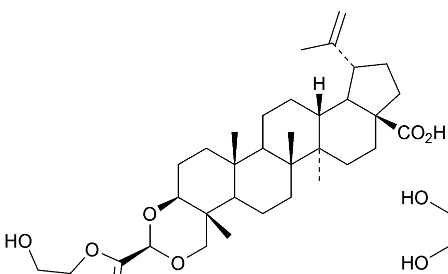

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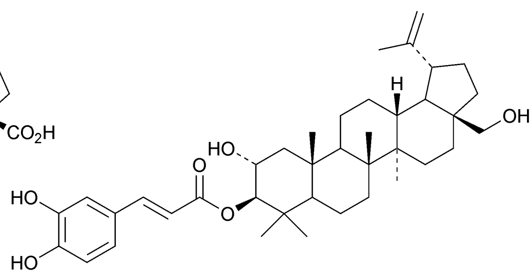

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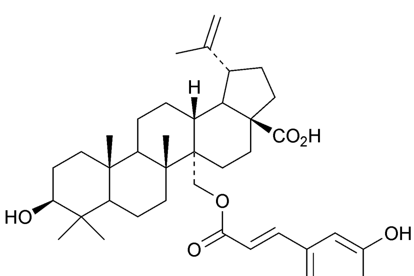

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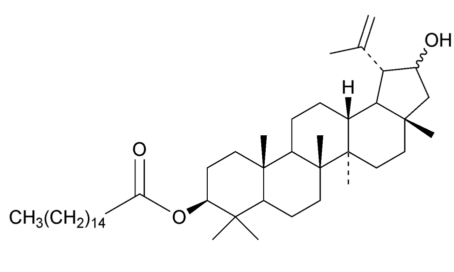
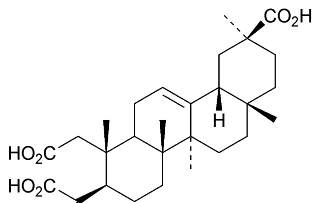


405

6 The oleanane group

Several ring-A *seco*-oleanane triterpenoids have been isolated, including the 2,3-*seco*-oleanenetrioic acid **406** from *Dillenia philippinensis*,[172] dysoxyhainic acid F **407**, G **408**, I **409** and J **410** from *Dysoxylum hainanense*,[159] the 12-ketone **411** and 13(18)-ene **412** from *Betula pendula*,[173] the 3-methyl ester **413** from *Kalopanax pictus*[174] and ivorengenin B **414** from *Terminalia ivorensis*.[175] The unusual 9,25-cycloolean-12-en-3β-yl β-D-glucofuranoside **415** has been reported to be a constituent of *Celestris australis*[176] and the same group has identified 9,25-cyclo-3β-(β-D-glucopyranosyloxy)-16α-hydroxyolean-12-en-28-oic acid **416** in *Symplocos paniculata*.[177] The 24,30-dinoroleanane **417**, 30-noroleanane **418** and 24-noroleanane **419** derivatives are present in the roots of *Paeonia rockii* ssp. *rockii*.[178] A review covering the structures and pharmacological activity of noroleanane triterpenoids has been published.[179] The antitumour activities of oleanane triterpenoids have been surveyed.[180]

Fatsicarpains A–G **420–426** are oleanane derivatives from leaves and twigs of *Fatsia polycarpa*.[181] The structures of fatsicarpain A **420** and the co-occurring known oleananes **427** and **428** were confirmed by X-ray analyses. 15α-Hydroxysoyasapogenol B **429**, 7β,15α-hydroxysoyasapogenol B **430** and 7β,29-dihydroxysoyasapogenol **431** are metabolites of the



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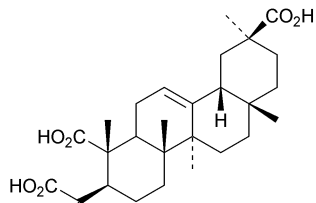

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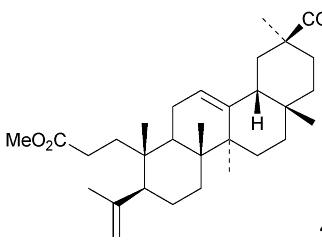

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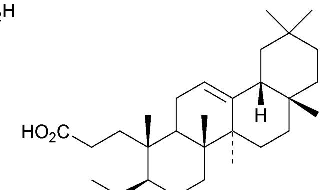
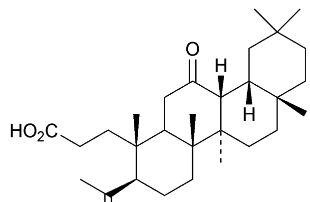


409
410 9,11-didehydro



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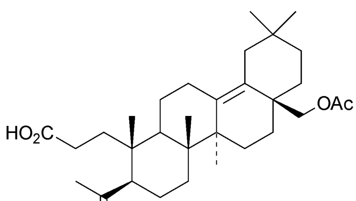

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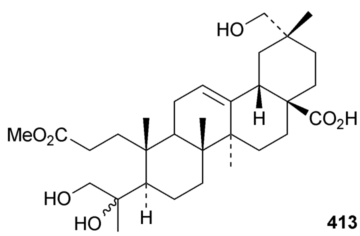

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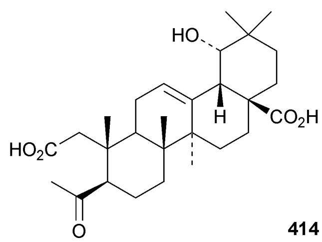

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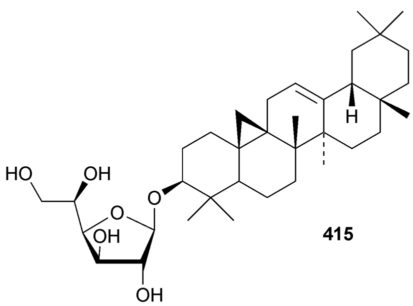

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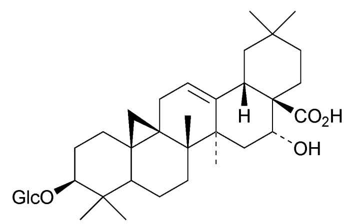

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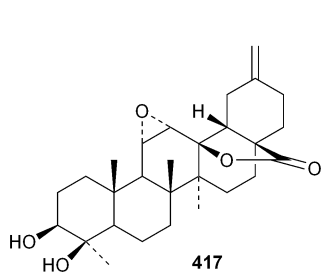

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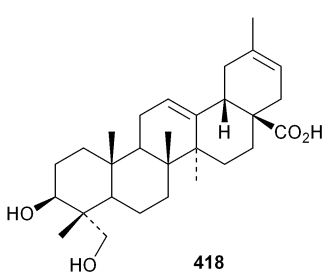

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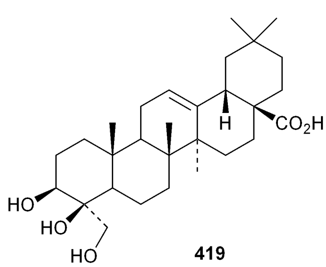

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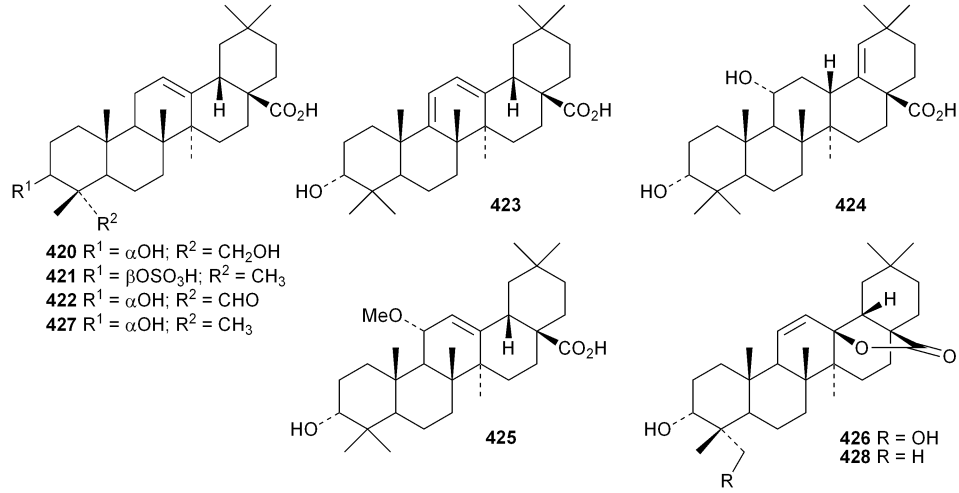
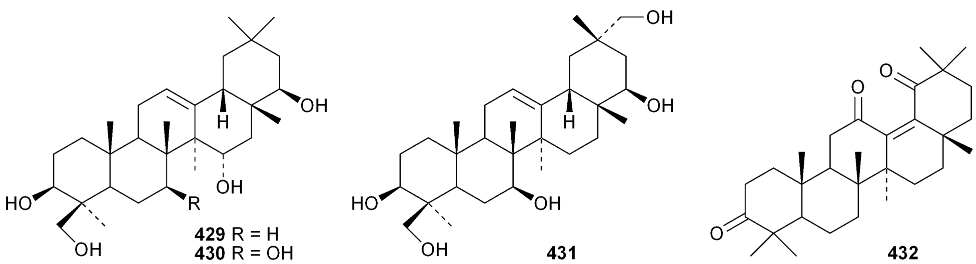


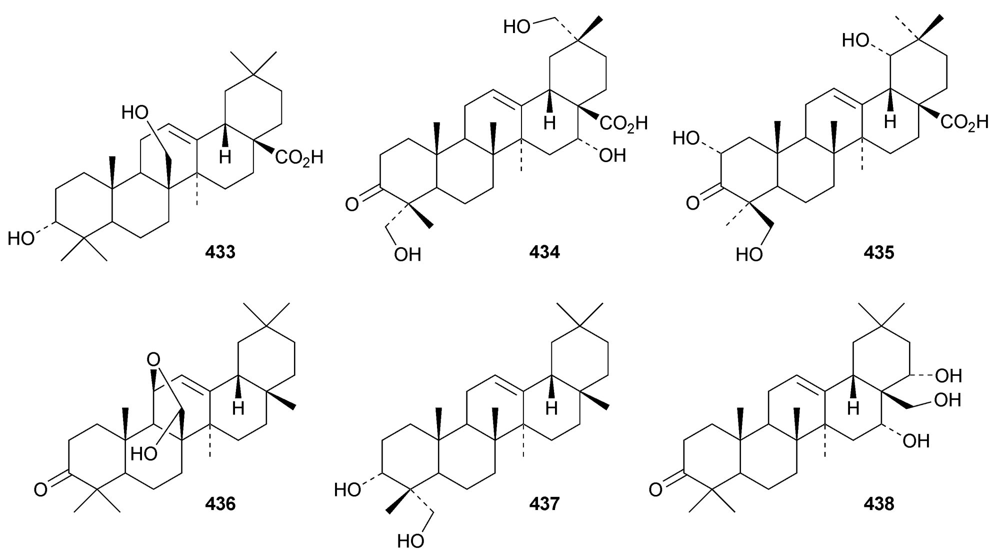
420 R^1 = αOH; R^2 = CH_2OH
421 R^1 = βOSO_3H; R^2 = CH_3
422 R^1 = αOH; R^2 = CHO
427 R^1 = αOH; R^2 = CH_3
423 **424** **425**
426 R = OH
428 R = H

endophytic fungus *Pestalotiopsis clavispora*, isolated from *Bruguiera sexangula*.[182] The structure of 15α-hydroxysoyasapogenol B **429** was confirmed by X-ray analysis. The structure of olean-13(18)-ene-3,12,19-trione **432**, from *Sedum linare*, was also established by X-ray analysis.[183]

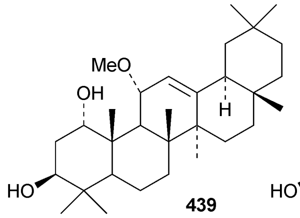
Other new simple oleanane derivatives include ambradiolic acid A **433** from *Liquidambar formosana*,[160] 16α,23,29-trihydroxy-3-oxoolean-12-en-28-oic acid **434** from *Kalopanax pictus*,[174] ivorengenin A **435** from *Terminalia ivorensis*,[175] salacetal **436** from *Salacia longipes* var. *camerunensis*,[184] olean-12-ene-3α,23-diol **437** from *Salvia miltiorrhiza*,[185] camelliagenone **438** from *Barringtonia asiatica*,[186] the 1,3-diols **439** and **440** from *Viburnum chingii*,[187] 2α,3α,19α,23-tetrahydroxyolean-12-en-28-oic acid **441** from *Rosa laevigata*,[188] 3β-hydroxyolean-18-en-1-one **442** from



429 R = H
430 R = OH
431 **432**



433 **434** **435**
436 **437** **438**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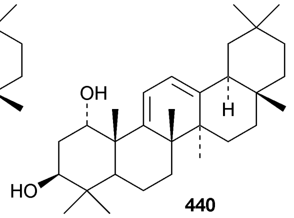
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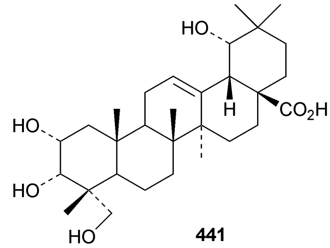
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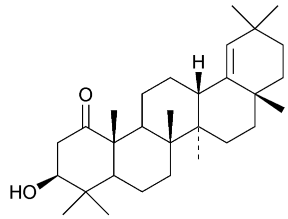
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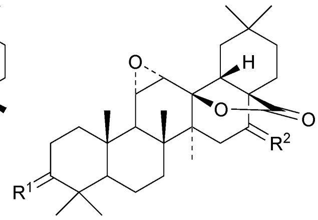
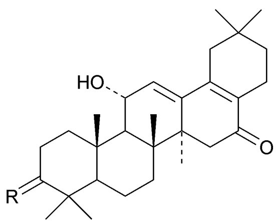
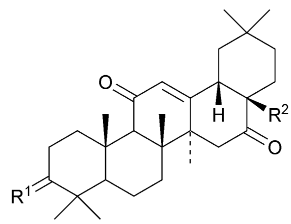
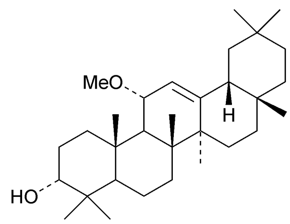
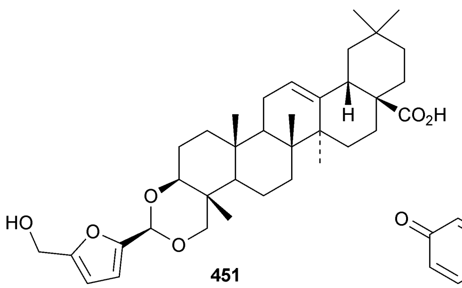

443 $R^1 = \beta OH,H$; $R^2 = \alpha OH,H$
444 $R^1 = O$; $R^2 = \alpha OH,H$
445 $R^1 = \beta OH,H$; $R^2 = O$


446 $R = \beta OH,H$
447 $R = O$

448 $R^1 = \beta OH,H$; $R^2 = OH$
449 $R^1 = O$; $R^2 = H$

450

Juglans chinensis,[189] **443–449** from *Nannoglottis carpesioides*[190] and olibanumol E **450** from olibanum, the gum resin of *Boswellia carterii*.[162]

Pulsatilla triterpenic acids B **451** and C **452**, from *Pulsatilla chinensis*, are hederagenin acetal derivatives.[167] The first glycyrrhetic acid amino acid conjugate, dendrophen **453**, has been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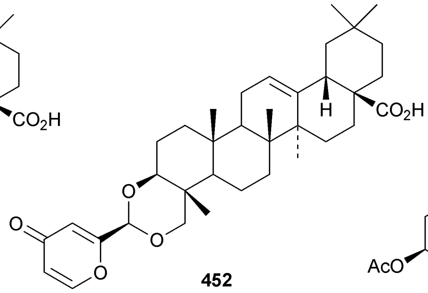
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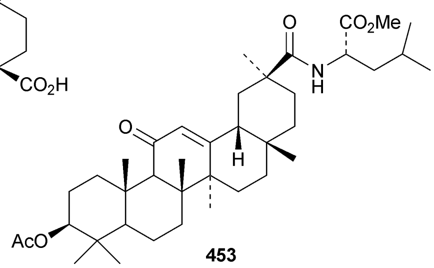
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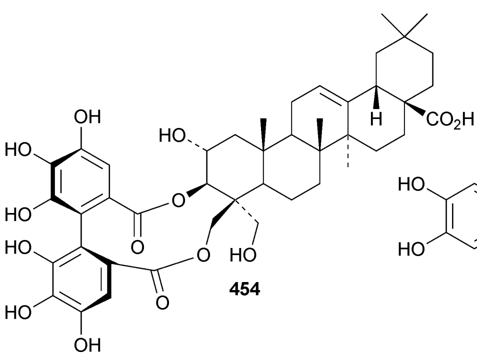
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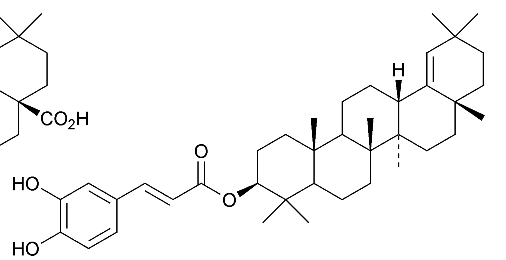
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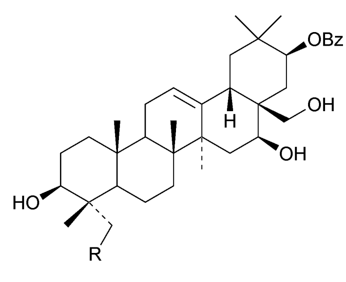
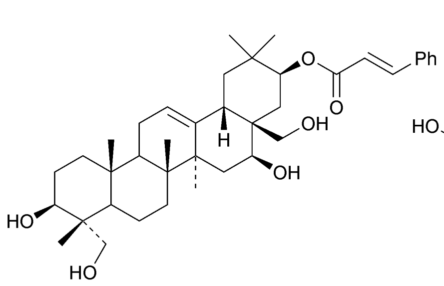
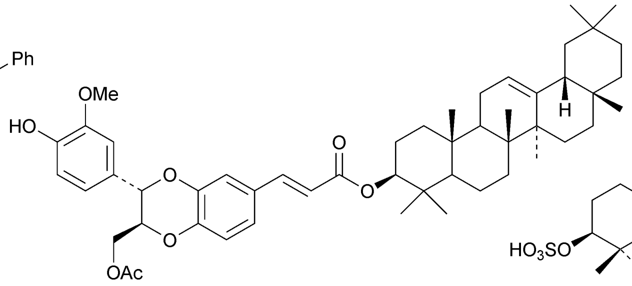

456 R = OH
457 R = H



458
459 *Z*-isomer



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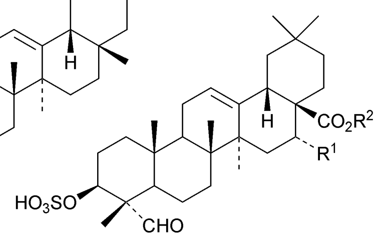
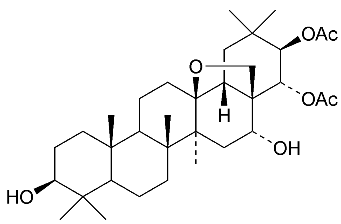


461 R^1 = H; R^2 = Glc
462 R^1 = R^2 = H
463 R^1 = OH; R^2 = H



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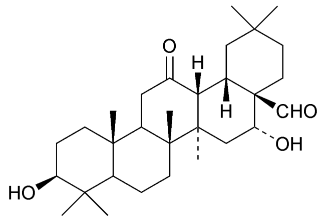

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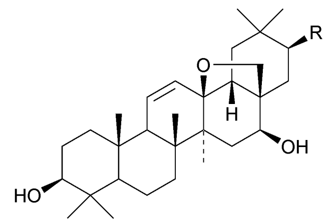
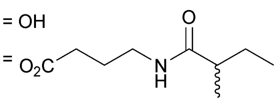
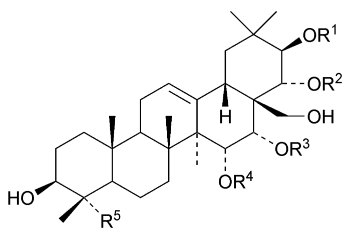
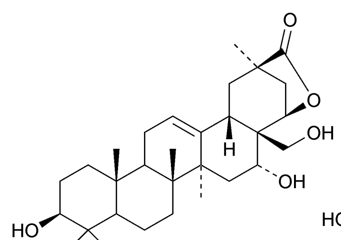


466 R = OH
467 R =





468 R^1 = R^3 = R^4 = Ac; R^2 = 2-methylbutanoyl; R^5 = CH_2OH
469 R^1 = R^3 = R^4 = Ac; R^2 = angeloyl; R^5 = CH_2OH
470 R^1 = angeloyl; R^2 = 2-methylbutanoyl; R^3 = Ac; R^4 = H; R^5 = CH_2OH
471 R^1 = angeloyl; R^2 = 2-methylbutanoyl; R^3 = R^4 = H; R^5 = CHO
472 R^1 = angeloyl; R^2 = 2-methylbutanoyl; R^3 = Ac; R^4 = H; R^5 = CHO
473 R^1 = angeloyl; R^2 = 2-methylbutanoyl; R^3 = Ac; R^4 = H; R^5 = CO_2Me



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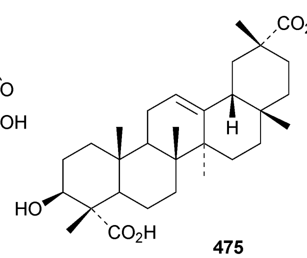
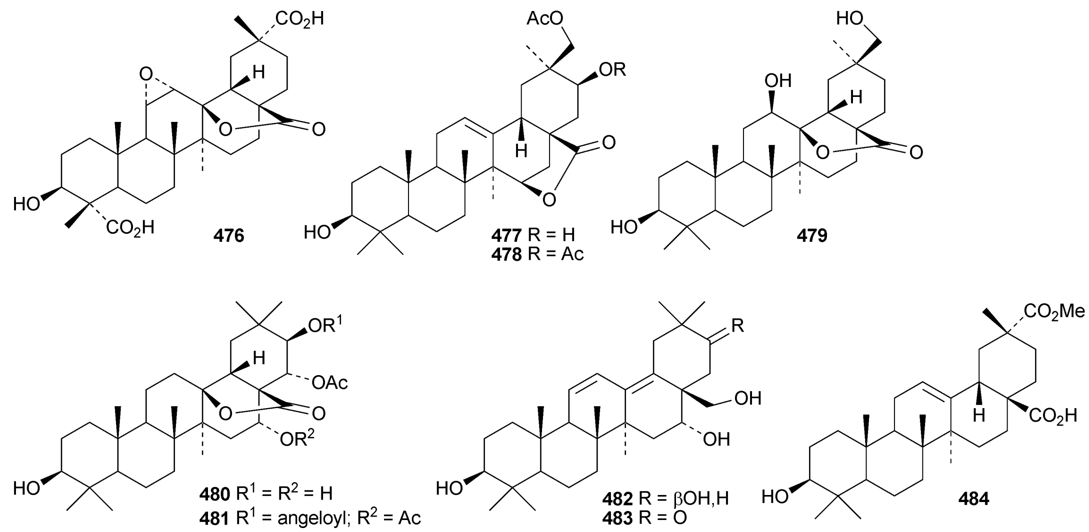


475

isolated from *Dendronephthya hemprichi*.[191] The aglycone **454** of the known castanopsinin E_a has been found in leaves of *Castanopsis fissa*.[192] Other new oleanane ester derivatives include the caffeoyl ester of germanicol **455** from *Barringtonia asiatica*,[186] esters **456–459** from *Glochidion assamicum*,[193] uragogin **460** from *Crossopetalum uragoga*,[194] and the sulfate esters **461–463** from *Gypsolphila pacifica*.[195]

Clethroidosides A–G are oleanane saponins from *Lysimachia clethroides*.[196] Clethroidosides F and G have the new genins **464** and **465**, respectively; the others have known genins. Heterogenoside F, from *Lysimachia heterogenea*, is identical to clethroidoside F and it is found with heterogenoside E that has a known genin.[197] The genins of glaucasides A and B, from *Atriplex glauca* var. *ifiniensis*, are the new compounds **466** and **467** whereas glaucaside C has the known genin saikogenin G. *Camellia sinensis* is a rich source of saponins including rogchaponins R1–R10.[198] Rogchaponins R1, R2 and R4–R7 have the new genins **468–473**, respectively. Myrseguinoside D, from *Myrsine seguinii*, has the new genin **474**.[199] It is accompanied by myrseguinoside E which is the same as the known ardisicrenoside J. Dianthosaponins A–F are found in *Dianthus japonicus*.[200] Dianthosaponins E and F have the new genins **475** and **476**, respectively. Bridgesides A1, C1, C2, D1, D2, E1 and E2, from *Echinopsis macrogona*, include the new genins **477** and



476

477 R = H
478 R = Ac

479

480 $R^1 = R^2 = H$
481 R^1 = angeloyl; R^2 = Ac

482 R = βOH,H
483 R = O

484

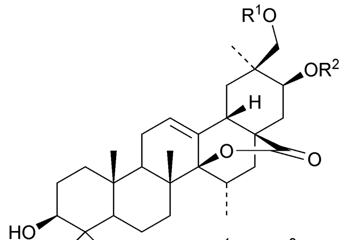
Table 1

Trivial name	Plant species	Reference
Androsacin	*Androsace integra*	206
Apodytines A–F	*Apodytes dimidiata*	207
Ardisicrenosides I, J, M	*Ardisia crenata*	208
Ardisicrenoside N	*Ardisia crenata*	209
Azafrines 1, 2	*Crocus sativus*	210
Bifinosides A–C	*Panax bipinnatifidus*	211
Blighosides A–C	*Blighia sapida*	212
Caraganosides C, D	*Caragana microphylla*	213
Caryophyllacosides A, B	*Gypsophila paniculata*	214
Catunarosides A–D	*Catunaregam spinosa*	215
Catunarosides E–H	*Catunaregam spinosa*	216
Celosins A, B	*Celosia argentea*	217
Celosins E, G	*Celosia argentea*	218
Dexyloprimulanin	*Labisia pumila*	219
Dialiumoside	*Dialium excelsum*	220
Dipsacus saponins J, K	*Dipsacus asper*	221
Elatoside L	*Aralia elata*	222
Esculentoside T	*Phytolacca acinosa*	223
Gordonosides I–P	*Gordonia chrysandra*	224
Halimodendrin I	*Halimodendron halodendron*	225
Libericosides A_1, A_2, B_1, B_2, C_2	*Atroxima liberica*	226
Lonimacranthoide I	*Lonicera macranthoides*	227
Mandshunosides A, B	*Clematis mandshurica*	228
Micranthosides A–C	*Polygala micrantha*	229
Mollusides A, B	*Albizia mollis*	230
Onjisaponin Wg	*Polygala tenuifolia*	231
Parkiosides A–C	*Butyrospermum parkii*	232
Platycoside O	*Platycodon grandiflorum*	233
Pseudoginsenoside RT1 butyl ester	*Panax japonicus* var. *major*	96
Puberosides C–E	*Glochidion puberum*	234
Rheedeiosides A–D	*Entada rheedei*	235
Scoposides F, G	*Cephalaria* spp.	236
Umbellatosides A, B	*Hydrocotyle umbellata*	237

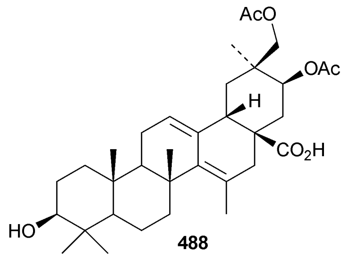
Table 2

Plant species	Reference
Albizia inundata	238
Anemone rivularis var. *flore-minore*	239
Anemone taipaiensis	240
Aralia elata	241
Arenaria montana	242
Bellis perennis	243
Catunaregam spinosa	244
Cylicodiscus gabunensis	245
Dianthus superbus	246
Erthrophleum fordii	247
Ganoderma applanatum	248
Gymnocladus chinensis	249
Gypsophila perfoliata	250
Juglans sinensiss	189
Kalopanax pictus	174
Lathyrus rattan	251
Medicago polymorpha	252
Microsechium helleri	253
Nephelium lappaceum	254,255
Panacis majoris	256
Phytolacca americana	257
Salsola imbricata	258
Sanguisorba tenuifolia var. *alba*	259
Symplocos caudata	260
Symplocos lancifolia	261

478.[201] Other oleanane saponins with new genins include 3β,12β,30-trihydroxyoleanan-28,13β-olide **479** from *Patrinia scabiosaefolia*,[202] the esters **480** and **481** from *Maesa lanceolata*,[203] oleana-11,13(18)-diene-3β,16α,21β,28-tetrol **482** and the corresponding 21 ketone **483** from *Bupleurum falcataum* and *Bupleurum rotundifolium*,[204] and coryternic acid **484** from *Corydalis ternate*.[205]



485 R^1 = H; R^2 = Ac
486 R^1 = Ac; R^2 = H
487 R^1 = R^2 = Ac



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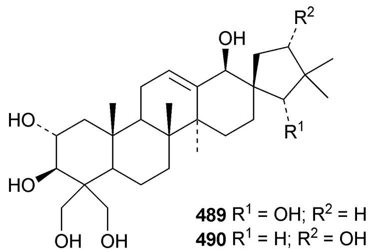
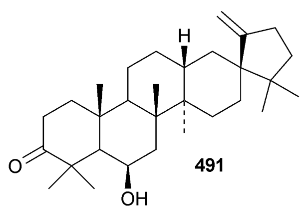


489 R^1 = OH; R^2 = H
490 R^1 = H; R^2 = OH



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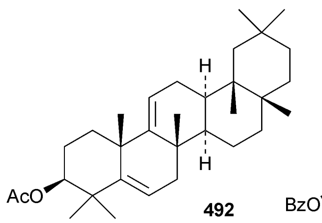

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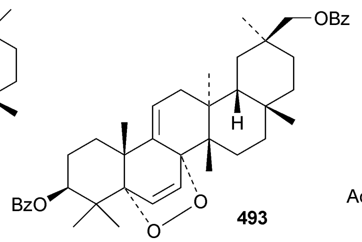

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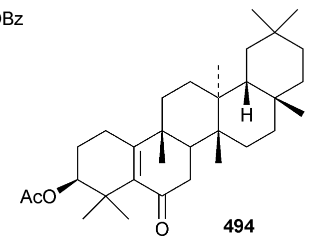


494

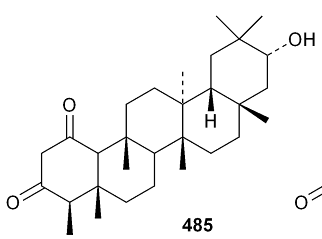
New oleanane saponins with known genins that have been assigned trivial names are listed in Table 1.

The sources of new oleanane saponins with known genins that have not been assigned trivial names are listed in Table 2.

Pachanosides C1, E1, F1 and G1 are pachanane saponins from *Echinops macrogona* with the genins **485–488**, respectively.[201] The structure of pachanol C **485** has been revised.

The rearranged oleanane derivatives phlomishexaols C **489** and D **490** have been found in the roots of *Phlomis umbrosa*.[262,263] The biosynthetic origin of the spirotriterpenoid cleistanone **491**, from *Cleistanthus indochinensis*, is not clear from its structure.[263] The rearranged oleanane derivative **492** has been claimed from *Rhododendron campanulatum*.[264] The stereochemistry of the methyl group at C-18 of **492** is unusual. The multiflorane endoperoxide dibenzoate **493** is a constituent of processed seeds of *Trichosanthes kirilowii*.[265] 3β-Acetoxyglutin-5(10)-en-6-one **494** has been found in roots of *Scorzonera austriaca*.[266]

New friedelane triterpenoids include 21α-hydroxyfriedelane-1,3-dione **495** from *Salacia verrucosa*,[267] 12α-hydroxyfriedelane-3,16-dione **496**[268] and 12α,29-dihydroxyfriedelan-3-one **497**[269] from *Maytenus gonoclada*, 3β-hydroxyfriedelane-7,12,22-trione **498** from *Drypetes laciniata*[270] and 11α-friedelan-3-one **499** from *Myrica rubra*.[271] The norfriedelane derivative 3-*O*-methyl-6-oxo-pristimerol **500** is a constituent of *Maytenus chubensis*.[272] Blepharodin **501**, from *Maytenus magellanica*, is an adduct with a phenylpropanoid derivative.[194]



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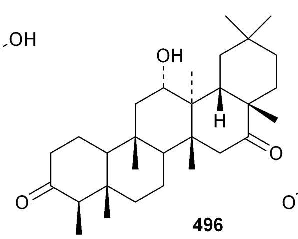

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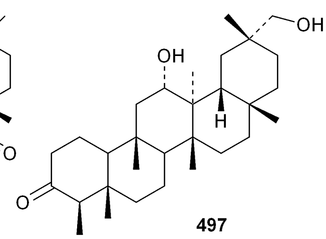

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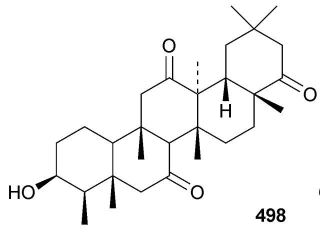

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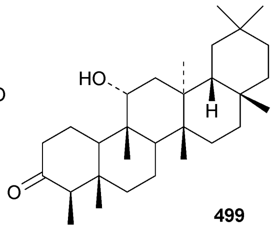

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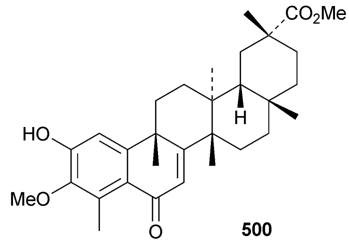

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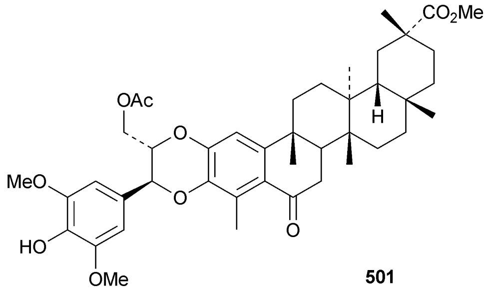
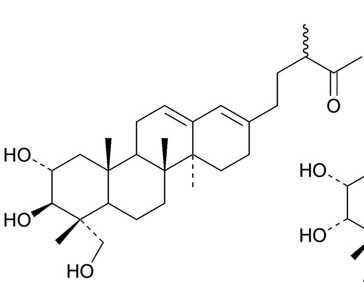


501

7 The ursane group

The 18,19-secoursane derivatives **502** and **503** have been isolated from *Rosa laevigata* together with 28-norursa-12,17-diene-2α,3β,23-triol **504** and the arabinoside **505** whose genin has an unusual 19α-stereochemistry.[188] The related 18,19-secoursane derivative **506** has been reported from leaves of *Diospyros kaki*.[273] Atriplicaide A **507** is an unusual *N*-acetyl lactam from *Zygophyllum eurypterum* where it is found with atriplicaide B **508** which is 3β,24dihydroxyursan-28,13-olide.[274] Related 28,13-olides **509** and **510** have been isolated from *Isodon coetsa*[275] and *Schefflera heptaphylla*,[276] respectively. Proceraursenolide **511**, from the roots of *Calatropis procera*, is claimed to be 18α*H*-urs-12-en-25,3β-olide.[277] Other new simple ursane derivatives include cordinoic acid **512** from *Cordia latifolia*,[278] urs-12-ene-3α,23-diol **513** from *Salvia miltiorrhiza*,[185] 18α*H*-ursene-3β,20β-diol **514** from *Boswellia carterii*,[116] 1α,2α,3β,16α,19α,20β-hexahydroxyurs-12-en-28-oic acid **515** from *Pedicularis kansuensis*,[279] glutinolic acid **516** from *Rehmannia glutinosa*,[280] and 3β,7β,24-trihydroxyurs-12-en-28-oic acid **517** from *Saurauja roxburghii*.[281] New ursane ester derivatives include conrauidienol **518** from *Ficus conraui*,[282] 3β-acetoxyursa-11,13(18)-dien-28-oic acid **519** from *Eucalyptus camaldulensis*,[283] 3-*O*-acetyluncaric acid **520** from *Radermachera boniana*,[73] sambucilate **521** from *Sambucus adnata*[284] and the palmitate esters **522** and **523** from *Viburnum betulifolium*.[285]

Clethroidoside H, from *Lysimchia clethroides*, is an ursane saponin with the new genin ursa-9(11),12-diene-2α,3β,21β,30-tetrol **524**.[196] The 18,19-secoursane derivative **525** is the genin of dunnianolactones A–C from *Ilex dunniana*.[286] A saponin given the duplicate name ilexsaponin C, from *Ilex pubescens*, has the



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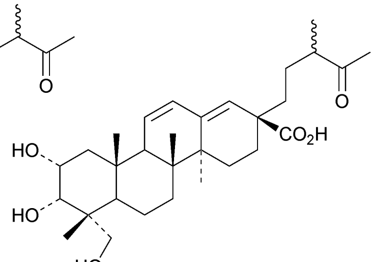

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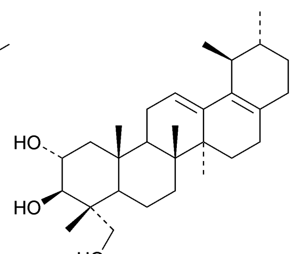

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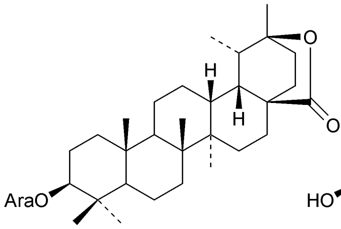

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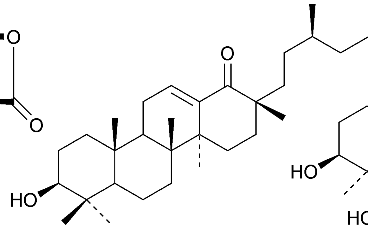

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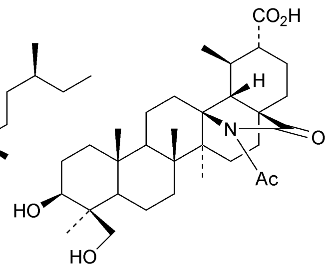

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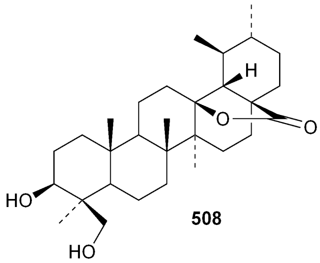
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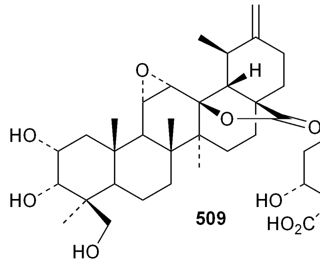
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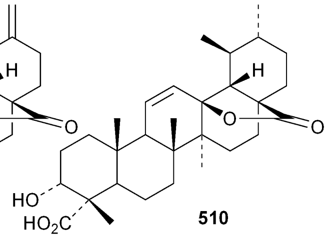
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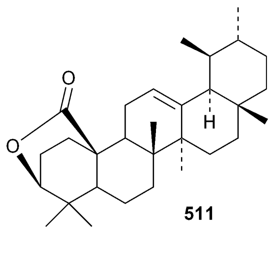
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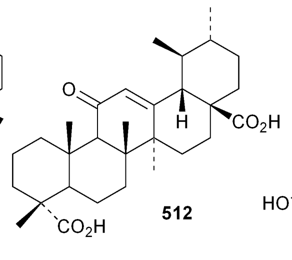
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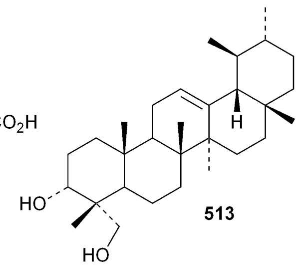
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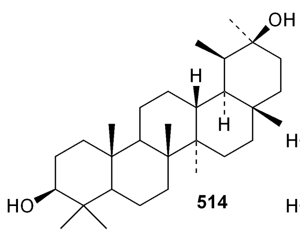
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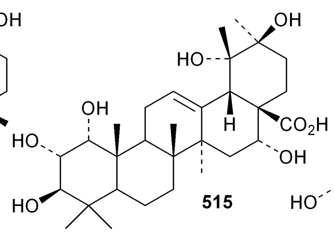
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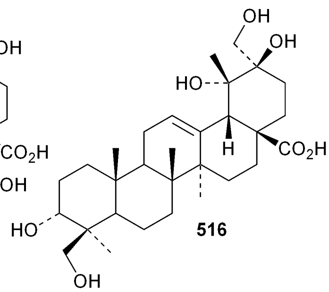
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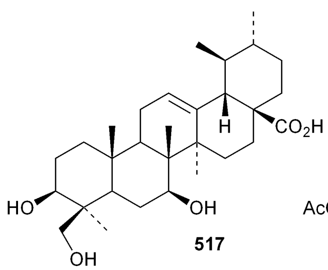
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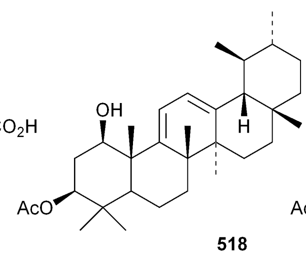
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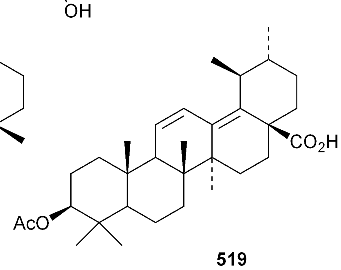
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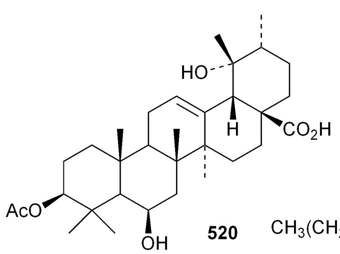
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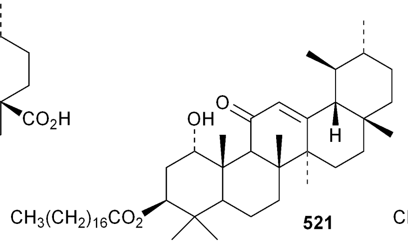
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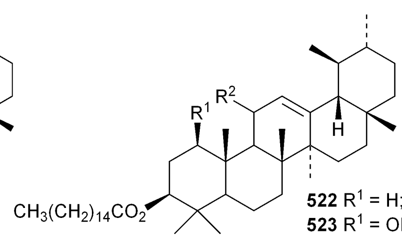
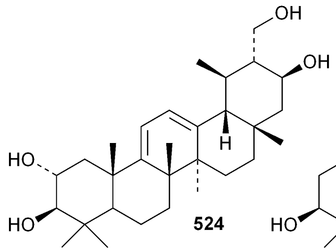

522 R^1 = H; R^2 = βOH
523 R^1 = OH; R^2 = αOH

new genin 28-norursa-12,17-dien-2β-ol **526**.[287] Other unnamed ursane saponins with the new genins include 3β,23-dihydroxy-urs-12-en-28-oic acid **527** from *Jugalans sinensis*,[189] and 2,3β,16α,23-tetrahydroxyurs-12-en-28-oic acid **528** from *Lathyrus aphaca*.[251]

Ursane saponins with known genins include asiaticoside G from *Centella asiatica*,[288] clethric acid 28-*O*-β-D-glucopyransyl ester and mussaendoside T from *Anthocephalus chinensis*,[289] ilekudinchosides A–D[290] and W[291] from *Ilex kudincha*, symplocosins A and B from *Symplocos cochinchinensis* var. *philippensis*,[292] zygophylloside S from *Zygophyllum coccineum*[293] and unnamed saponins from *Ilex chamaedryfolia*,[294] *Juglans sinensis*,[189] *Sanguisorba tenuifolia* var. *alba*[259] and *Symplocos lancifolia*.[261]

19β-Hydroxy-3,4-seco-4(23),20(30)-taraxastadien-3-oic acid **529** has been isolated from buds of *Betula pendula*.[173] The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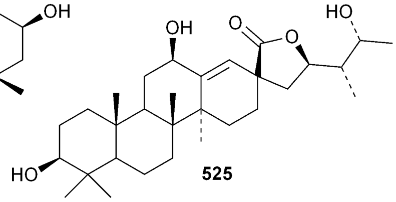
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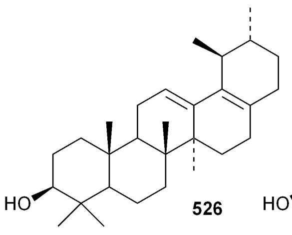
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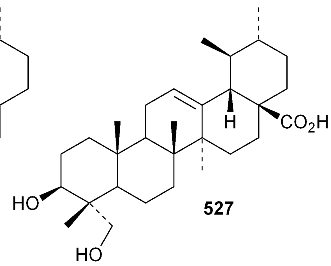
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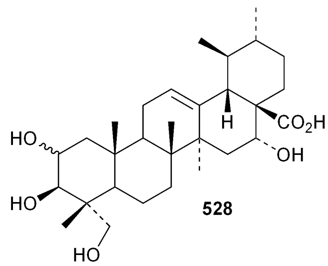
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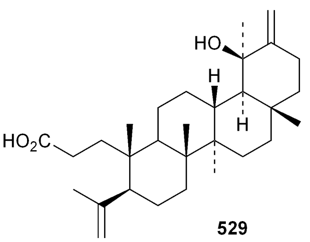
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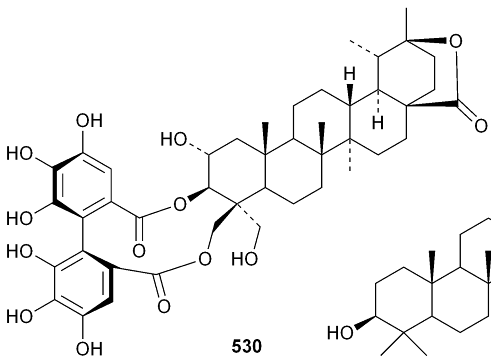
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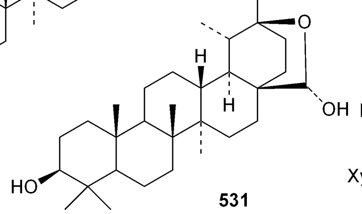
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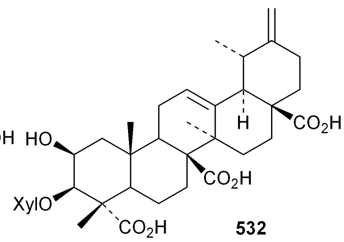
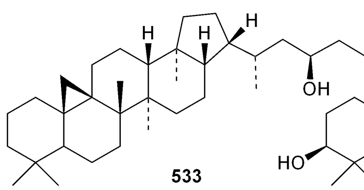

532

tannin ester **530** of 2α,3β,23,24-tetrahydroxytaraxastan-28,20β-olide is a constituent of leaves of *Castanopsis fissa*.[192] The taraxastane hemiacetal **531** has been found in *Geum japonicum*.[295] Celosin F **532** appears to be a taraxastane xyloside from *Celosia argentea*.[218]

8 The hopane group

The current knowledge of squalene-hopene cyclases has been reviewed.[296] The unusual 9,25-cyclo-29-propylhopan-31-ol **533** and 3β-hydroxy-29-propylhopan-31-one **534** have been identified in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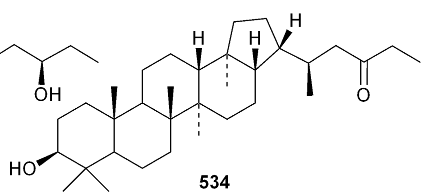
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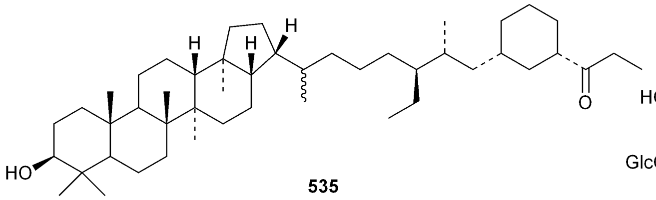
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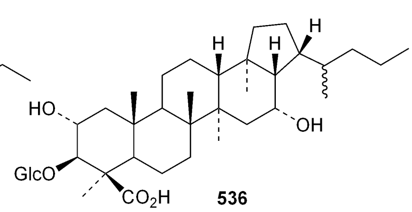
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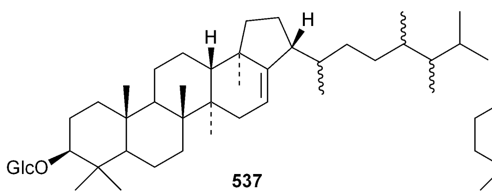
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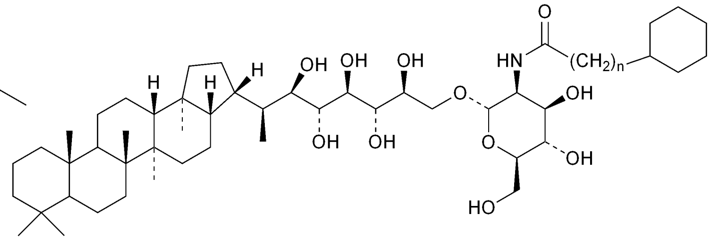
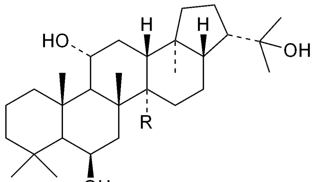
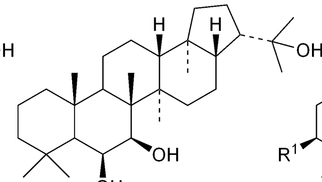

538 n = 8, 10, 12, 14, 16, 18, 20, 22


539 R = CO_2H
540 R = CH_2OH

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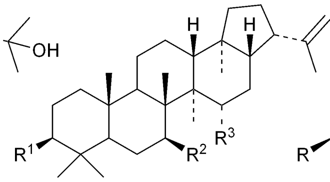
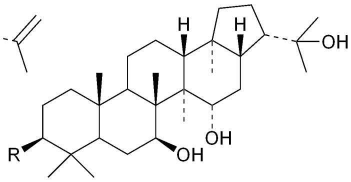
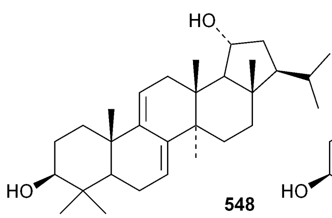

542 R^1 = H; R^2 = R^3 = OH
543 R^1 = R^2 = OH; R^3 = H
544 R^1 = OAc; R^2 = H; R^3 = OH

545 R = OH
546 R = OAc
547 R = H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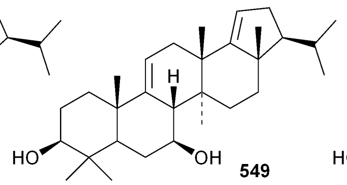
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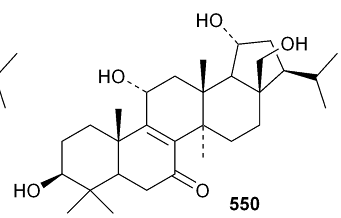
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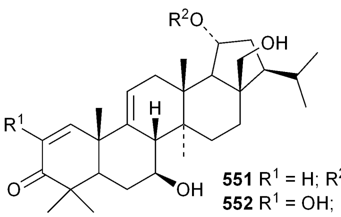
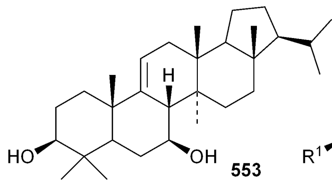

551 R^1 = H; R^2 = Ac
552 R^1 = OH; R^2 = H

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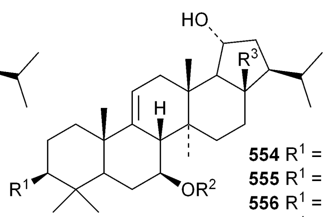
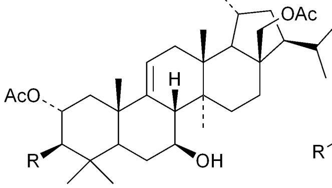
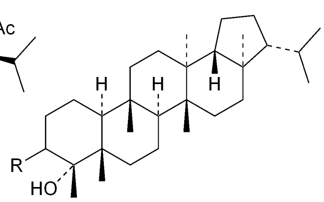
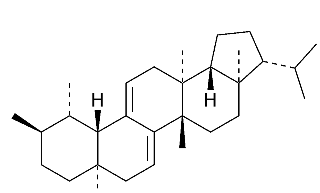

554 R^1 = OH; R^2 = Ac; R^3 = CH_2OH
555 R^1 = OGlc(1->2)Glc; R^2 = H; R^3 = CH_2OH
556 R^1 = OGlc(1->6)Glc; R^2 = H; R^3 = CH_2OAc
557 R^1 = OGlc(1->6)Glc; R^2 = H; R^3 = CHO

Celestris australis.[176] The same group claim that the cyclohexylhopane derivative **535** is also found in *Celestris australis*[297] and that the 29-ethylhopane derivative **536** and 32,33,34-trimethylbacteriohopan-3β-yl β-D-glucopyranoside **537** are constituents of *Symplocos paniculata*.[177] Several *N*-acylated bacteriohopanehexol mannosamine derivatives **538** have been identified in the thermophilic bacterium *Alicyclobacillus acidoterrestris*.[298] The simple hopane derivatives **539–541**[299] and **542–547**[38] are metabolites of the entomopathogenic fungi *Conoideocrella tenuis* and *Hypocrella* sp. BCC 14524, respectively.

Twelve arborinane triterpenoids have been isolated from *Rubia yunnanensis* including rubiyunnanols A–C **548–550,** rubiarbonone E 19-acetate **551,** 2-hydroxyrubiarbonone E **552,** 19,28-didehydroxyrubiarbonol A **553,** rubiarbonol A 7-acetate **554,** the

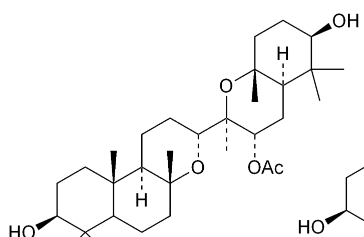

558 R = O(6-*O*-Ac)Glc
559 R = OGlc(1->6)Glc

560 R = βOH
561 R = αOMe

562

rubiarbonol A glycoside **555**, rubiarboside G 28-acetate **556**, rubiarboside G 28-aldehyde **557**, 2α-acetoxyrubiarboside 28-acetate **558** and the rubianol E glycoside **559**.[300] *Adiantum capillus-veneris* is the source of filicane-3β,4α-diol **560** and the corresponding 3α-methyl ether **561**.[301] Canarene **562** is an unusual rearranged filicane derivative from *Canarium schweinfurthii*.[302] The structure of canarene **562** was confirmed by X-ray analysis and a biosynthetic scheme for its formation has been proposed.

9 Miscellaneous compounds

Phyteumosides A and B, from *Phyteuma orbiculare*, have as aglycones the partially cyclised onocerane triterpenoid **563** and the polypodane derivative **564**, respectively.[303] The structures of the aglycones **563** and **564** were established by X-ray analysis. *Lansium domesticum* is the source of the onocerane derivatives lamesticumin A **565** and the corresponding ethyl ester **566**, lamesticumins B–E **567–570**, the 3-ethyl ester of lansic acid **571** and ethyl lansiolate **572** together the polypodane derivative lamesticumin F **573**.[304] Other onocerane derivatives include cupacinoxepin **574**, from *Cupania cinerea*[305] and kokosanolide B **575** and onocera-7,14-diene-3,21-dione **576** from *Lansium domesticum* cv. Kokossan.[126]

The isomalabaricane triterpenoids stelliferins J–N **577–581** are constituents of the sponge *Rhabdastrella cf. globostellata*.[306] Stelliferins L–N **579–581** have a cyclised side-chain similar to rhabdastins D–G. A sponge of the genus *Lipastrotethya* is the source of pouosides F–I **582–585** and pouogenins A–E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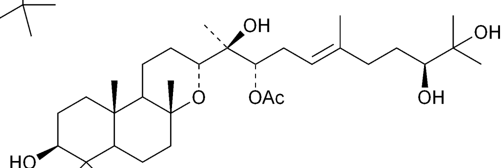
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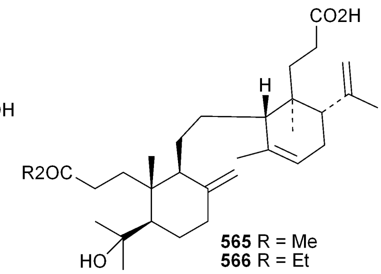
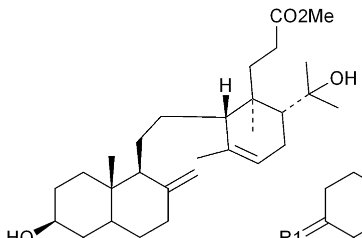

565 R = Me
566 R = Et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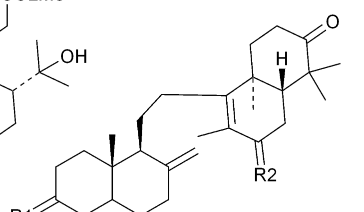
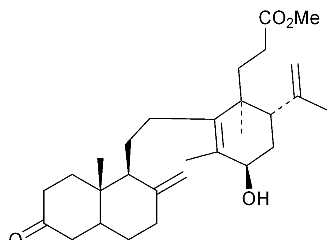

568 R1 = βOH; R2 = O
569 R1 = O; R2 = βOH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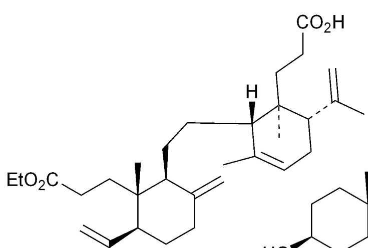
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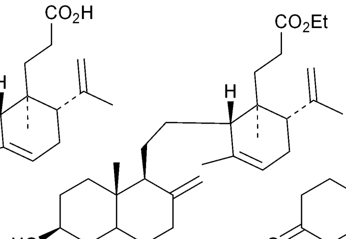
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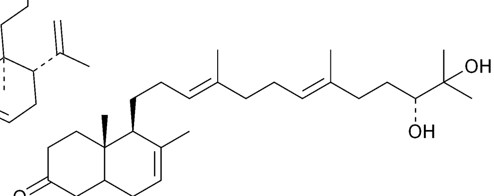
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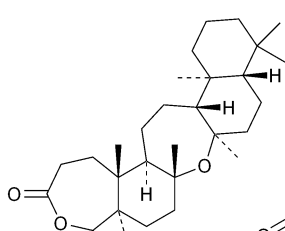
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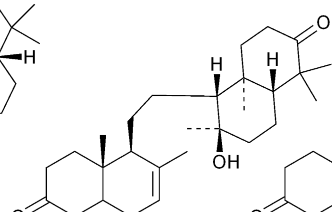
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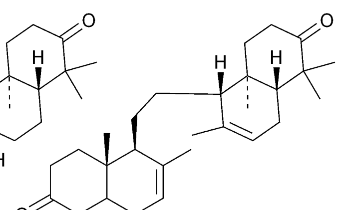
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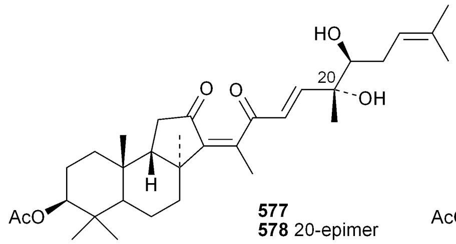
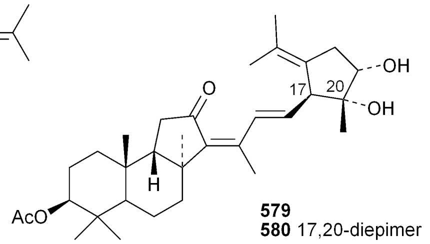
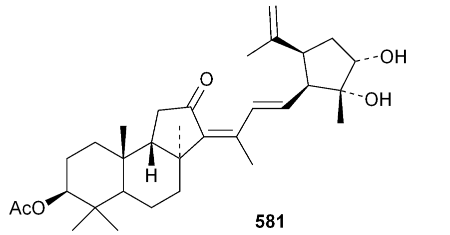


577
578 20-epimer



579
580 17,20-diepimer



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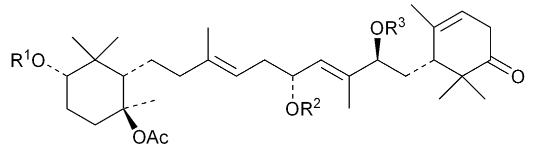
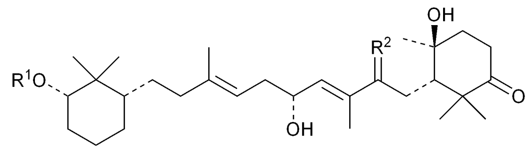
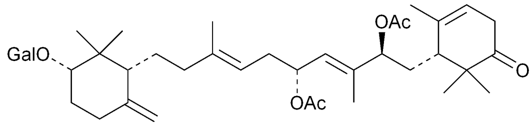


582 R^1 = Gal; R^2 = R^3 = H
586 R^1 = R^2 = R^3 = H
587 R^1 = H; R^2 = R^3 = Ac
588 R^1 = R^3 = H; R^2 = Ac



583 R^1 = Gal; R^2 = βOAc,H
584 R^1 = Gal; R^2 = O
589 R^1 = H; R^2 = βOAc,H
590 R^1 = H; R^2 = O



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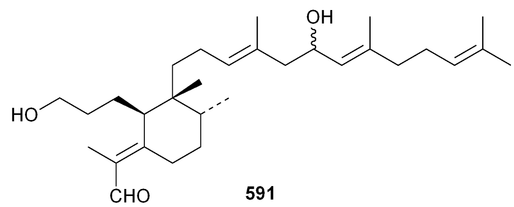

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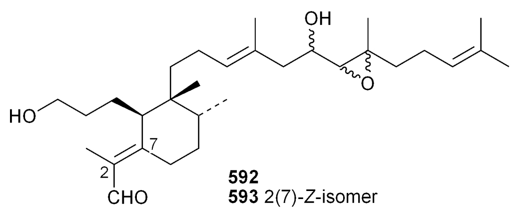

592
593 2(7)-*Z*-isomer

586–590.[307] Three iridal triterpenoids **591–593** have been isolated from *Iris delavayi*.[308]

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