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Triterpenoids

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Covering 2015. Previous review: *Nat. Prod. Rep.*, 2018, **35**, 1294–1329

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This review covers the isolation and structure determination of triterpenoids reported during 2015 including squalene derivatives, lanostanes, holostanes, cycloartanes, cucurbitanes, dammaranes, euphanes, tirucallanes, tetranortriterpenoids, quassinoids, lupanes, oleananes, friedelanes, ursanes, hopanes, serratanes, isomalabaricanes and saponins; 320 references are cited.

1. Introduction

Reviews have been published on the biological properties of triterpenoids including hypoglycaemic,[1] antiparasitic[2] and immunomodulatory[3] activities and neutrophil elastase inhibition.[4] Triterpenoid saponins have been highlighted for a range of bioactivities[5] and for their neuroprotection.[6] Reviews have also appeared covering triterpenoids found in *Albizia* species,[7] *Alstonia scholaris*,[8] plants of the Amaranthaceae,[9] *Codonopsis* species,[10] *Medicago sativa*,[11] *Olea europaea*[12] and *Terminalia* species.[13] Triterpenoids with a five-membered A-ring have also been covered.[14]

2. The squalene group

Structure **1** has been proposed for auxarthonoside, a squalene glycoside from the sponge-derived fungus *Auxarthron reticulatum*.[15] Four derivatives, silphasqualols A **2**–D **5**, have been found in the compass plant *Silphium laciniatum*.[16] A compound from cultures of the basidiomycete *Antrodiella albocinnamomea* apparently has the non-standard structure **6**.[17] Saponaceolides Q **7**, R **8** and S **9** are further constituents of the European mushroom *Tricholoma terreum*.[18] *Laurencia viridis* is a rich source of squalene derivatives.[19] New compounds include 28-hydroxysaiyacenol B **10**, saiyacenol C **11** and epoxythyrsiferol A **12** and its 15*R*,16*S*-isomer epoxythyrsiferol B. A new pathway for the synthesis of squalene in bacteria has been discovered and the responsible genes identified.[20]

3. The lanostane group

A range of protostane derivatives from the rhizomes of *Alisma orientale*, that show inhibitory effects on human carboxylesterase 2, includes alismanols A **13**–G **19**, 20-hydroxyalisol C **20**, 25-*O*-ethylalisol A **21** and compounds **22**–**24**.[21] The helvolic acid-related compound **25**, from the endophytic fungus *Aspergillus fumigatus*, has an unusual secofusidane skeleton.[22]

The Tibetan medicinal mushroom *Ganoderma leucocontextum* is full of lanostanes including ganoleucoins A **26**–L **37** and the meroterpenoid esters ganoleucoins M **38**–P **41**.[23] Many of these compounds inhibit HMG-CoA reductase and α-glucosidase. Ganoboninones A **42**–F **47** are secolanostanes from the medicinal mushroom *Ganoderma boninense* that show antiplasmodial activity.[24] Constituents of *Ganoderma tropicum* include[25] compounds **48**, **49**, and **50** while *Ganoderma hainanense* contains[26] ganohainanic acids A **51**, its acetate **52**, B **53**, C **54**, D **55**, its acetate **56** and E **57**. The structure of ganohainanic acid A **51** was confirmed by X-ray crystallographic analysis. Other constituents of this mushroom include hainanic acids A **58** and B **59**, the keto alcohols **60** and **61**, hainanaldehyde A **62** and compounds **63** and **64**.

Reviews have appeared highlighting the importance and variety of lanostanes from *Ganoderma lucidum*.[27,28] Newly isolated compounds include ganoderic acid X1 **65**,[29] ganoderlactones A **66**–E **70** and ganodernoids A **71**–G **77**,[30]

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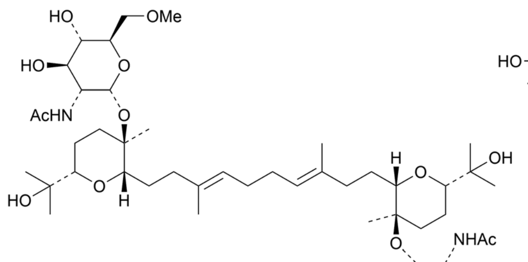

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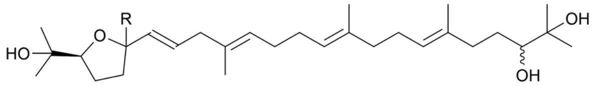
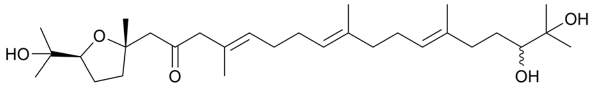


2 R = βCH_3
3 R = αCH_3



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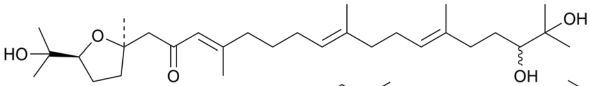

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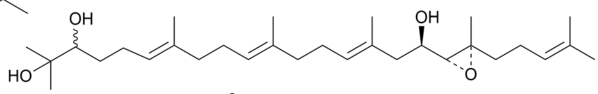

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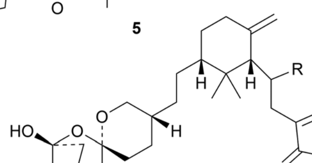
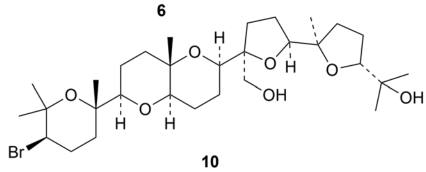


7 R = H
8 R = βOMe
9 R = αOMe



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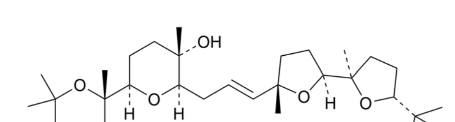

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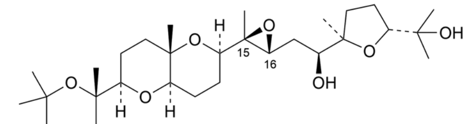

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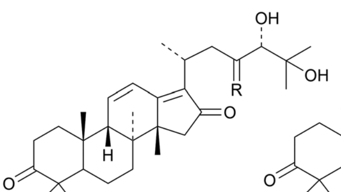
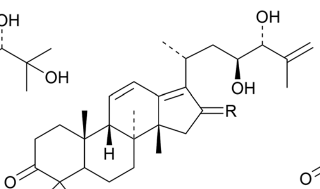
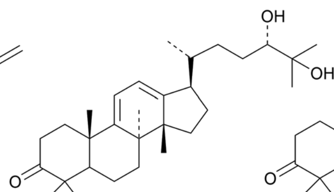


13 R = O
15 R = βOAc, H



14 R = O
24 R = H_2; 11,12-dihydro



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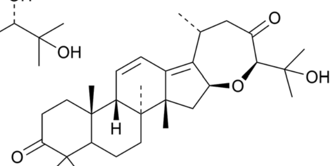

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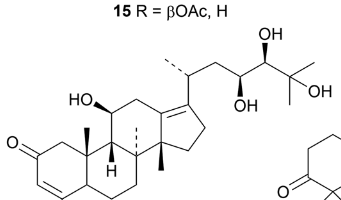

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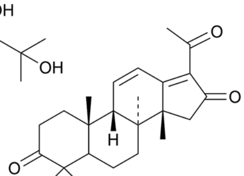

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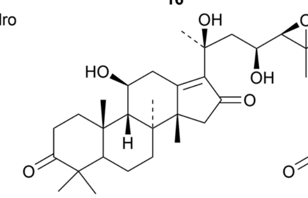

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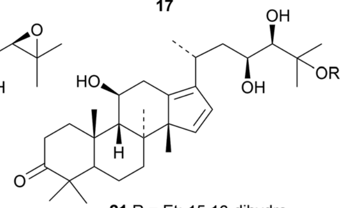
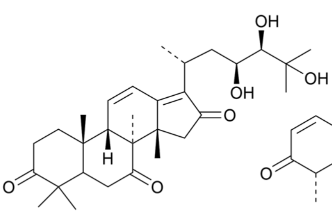


21 R = Et; 15,16-dihydro
22 R = H



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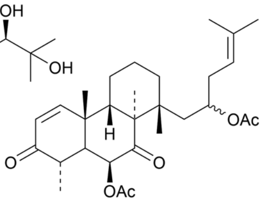

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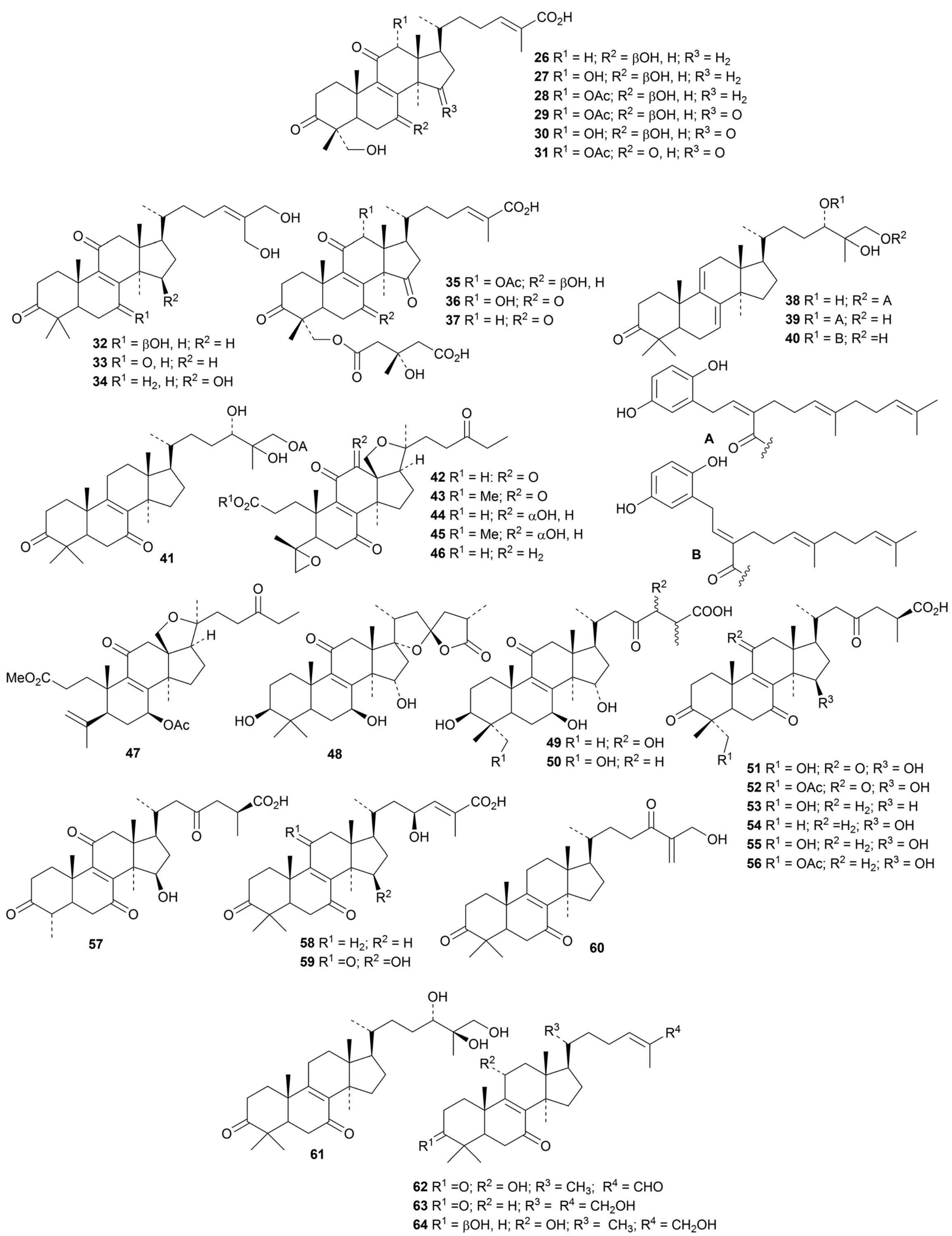
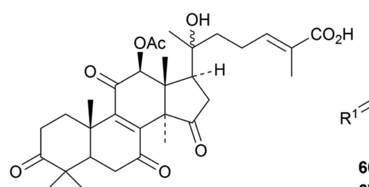


compounds **78** and **79** from the fruiting bodies[31] and the triacetate **80**.[32] Ganocochlearic acid A **81** is an interesting rearranged hexanorlanostane from the fruiting bodies of *Ganoderma cochlear* where it occurs with cochlate C **82**, cochlearic acids A **83** and B **84** and ganodercochlearins D **85**–K **92**.[33] The structures of **83** and **85** were confirmed by X-ray crystallographic analyses.

Other fungal products include fomefficinin **93** from *Fomes officinalis*,[34] hexagonins A **94**–E **98** from the fruiting bodies of *Hexagonia apiaria*,[35] the 21-oic acid **99**, the 3,4-seco 3,21-dioic



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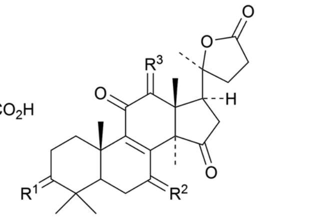
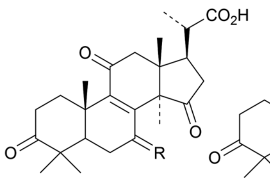
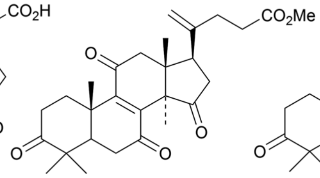


66 R^1 =O; R^2 = βOH, H; R^3 = αOH, H
67 R^1 = R^2 = O; R^3 = H_2
68 R^1 = R^2 = O; R^3 = βOAc, H
69 R^1 = R^2 = R^3 = βOH, H
70 R^1 = R^2 = βOH, H; R^3 = O



71 R = O
72 R = βOH, H



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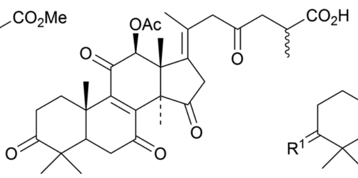

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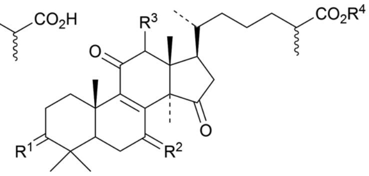
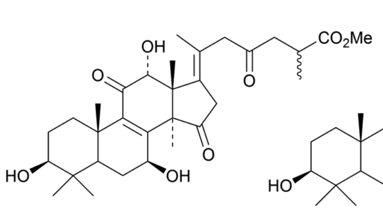


75 R^1 = R^2 = βOH H; R^3 = αOH; R^4 = Me
77 R^1 = βOAc, H; R^2 = O; R^3 = βOH; R^4 = H



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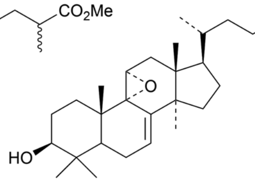

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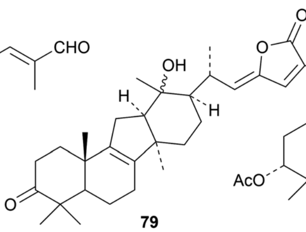

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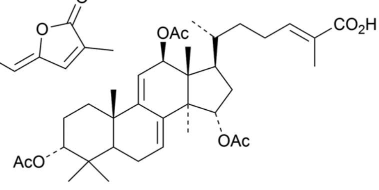

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acid **100** and its 3-methyl ester from the fruiting bodies of *Laetiporus sulphureus* var. *miniatus*[36] and astrasiate **101** and astrasiaone **102** from the edible mushroom *Astraeus asiaticus*.[37] The metabolites **103–111** of *Haddowia longipes* ressemble those of *Ganoderma* species.[38] Compound **110** is lucidone H, which is a duplicate name, and **111** is the 3-acetate of ganodermatriol. *Diaporthe* sp. LG23, an endophytic fungus from *Mahonia fortunei*, produces the ring B aromatic lanostane **112**.[39]

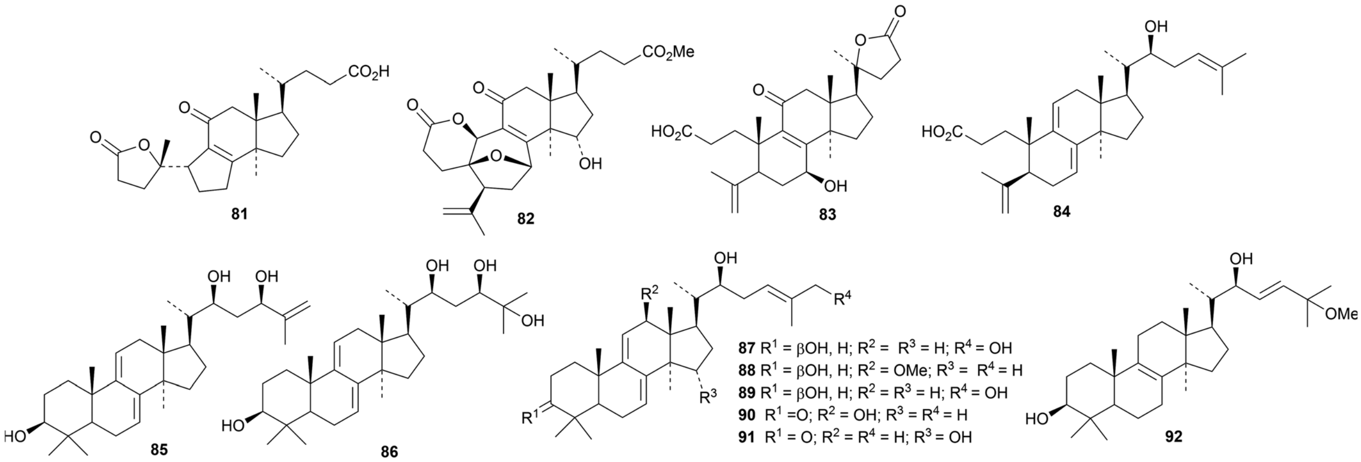
Ascosteroside C **113** is a mitochondrial respiration inhibitor isolated from an *Aspergillus* species.[40] Gloeophyllins A **114**–J **123** form an interesting group of normal and rearranged cytotoxic lanostanes from the Tibetan fungus *Gloeophyllum abietinum*.[41] The structures of compounds **114**, **115** and **122** were confirmed by X-ray analyses. Gloeophyllin B **115** has also been isolated from *Gloeophyllum odoratum*, together with the related compound **124**.[42]

The 21,24-cyclised lanostanes inonotusanes A **125** and B **126** and the trinorderivatives inonotusane C **127** and obliquic acid **128** are constituents of *Inonotus obliquus*.[43] Scillascillol **129** and scillascillone **130** have been isolated from *Scilla scilloides*.[44] The aglycone **131** of bellevalioside D has been found in *Eucomis vandermerwei*.[45]

Spirochensilides A **132** and B **133** are rearranged lanostanes from *Abies chensiensis*.[46] The structure of spirochensilide A **132** was confirmed by X-ray analysis. Two groups of compounds, neoabieslactones G **134**–K **138** and abiestrines K **139**–M **142**, have been reported from *Abies faxoniana*.[47] Neoabieslactone I **136** shows interesting topoisomerase II inhibitory activity.

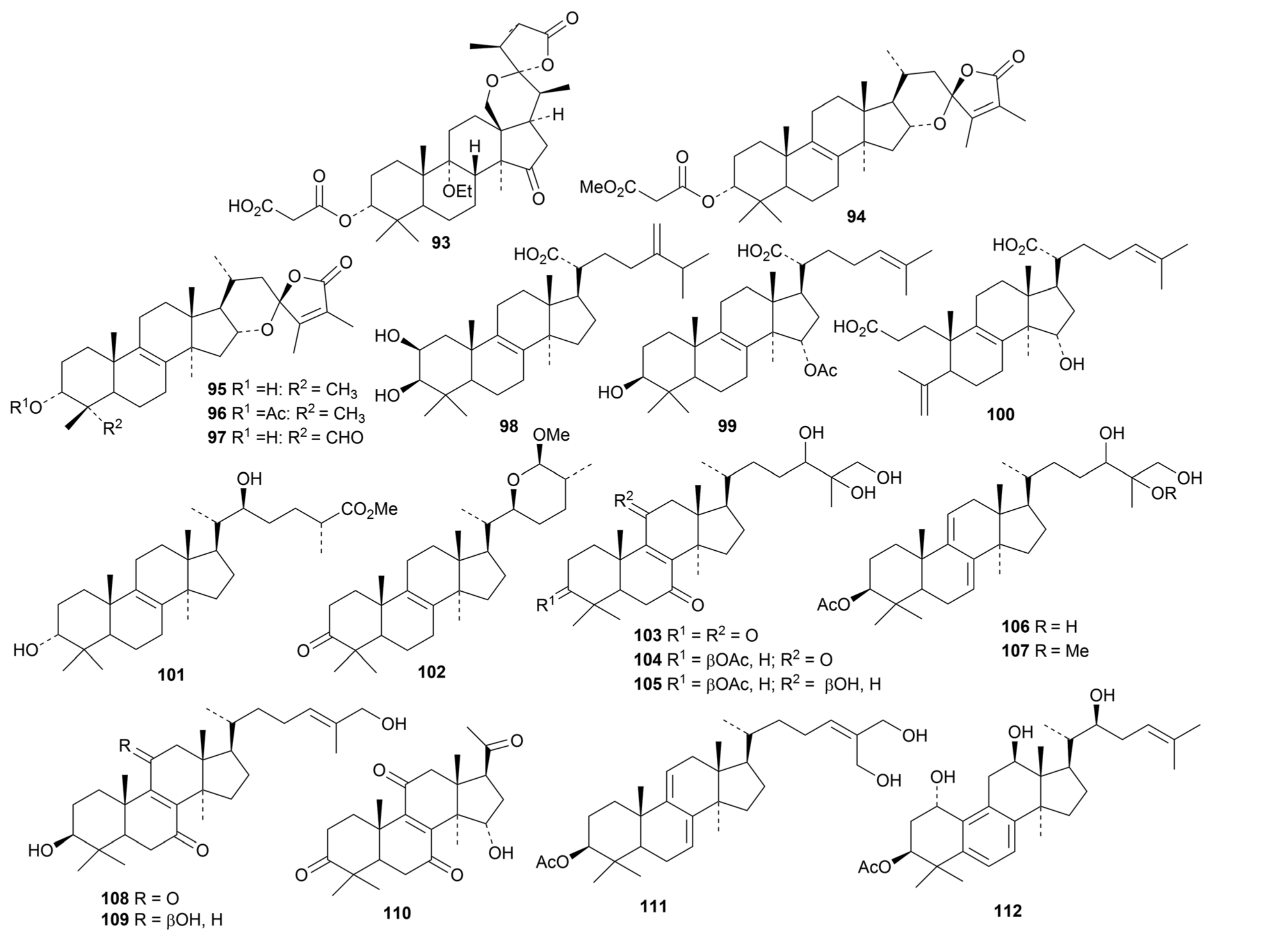
DFT calculations and ROESY data have been used in the stereochemical assignment of abibalsamins C **143**–I **150** from the oleoresin of *Abies balsamea*.[48] The abibalsamins are Diels–Alder adducts of lanostane and rearranged lanostane triterpenoids with the monoterpenoid myrcene. *Kadsura coccinea* is the source of two interesting groups of lanostane derivatives, kadcoccinic acids A **151**–J **160** (ref. 49) and kadcoccinones A **161**–F **176**.[50] The structures of **153**, **161**, **164**, **165** and **166** were all confirmed by X-ray crystallographic analyses. Ethyl manwuweizate **167** and methyl manwuweizate **168** are 3,4-secolanostane derivatives from *Kadsura heteroclita*.[51]

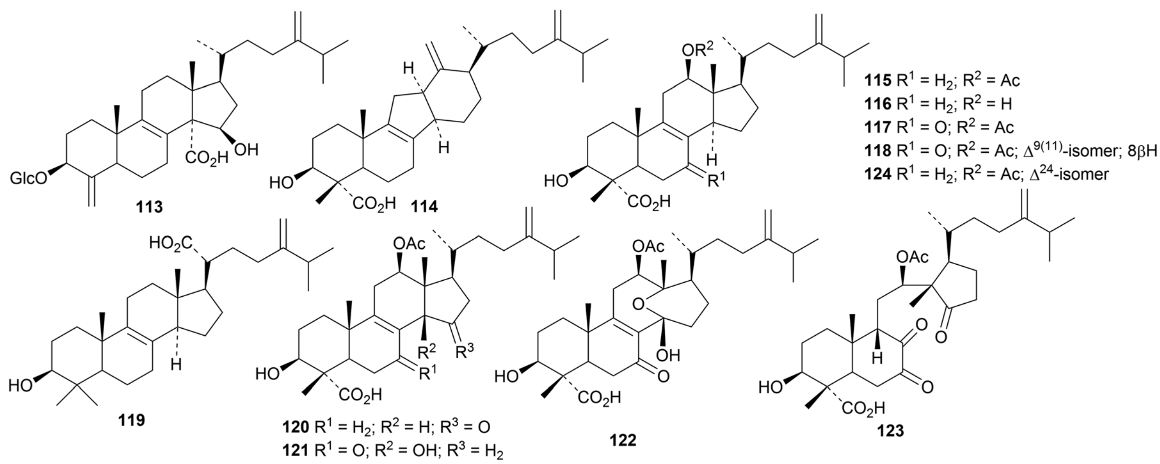
Compounds **169–176** are minor constituents of a Vietnamese *Penares* species.[52] The saponin **177**, with a new hexanorlanostane genin, has been reported from the sponge *Clathria gombawuiensis*.[53] Lanostane saponins with known genins include eryloside W from *Dictyonella marsilii*,[54]

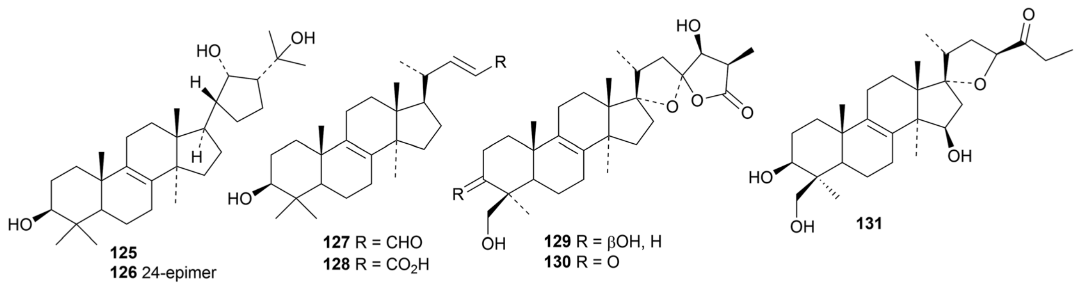


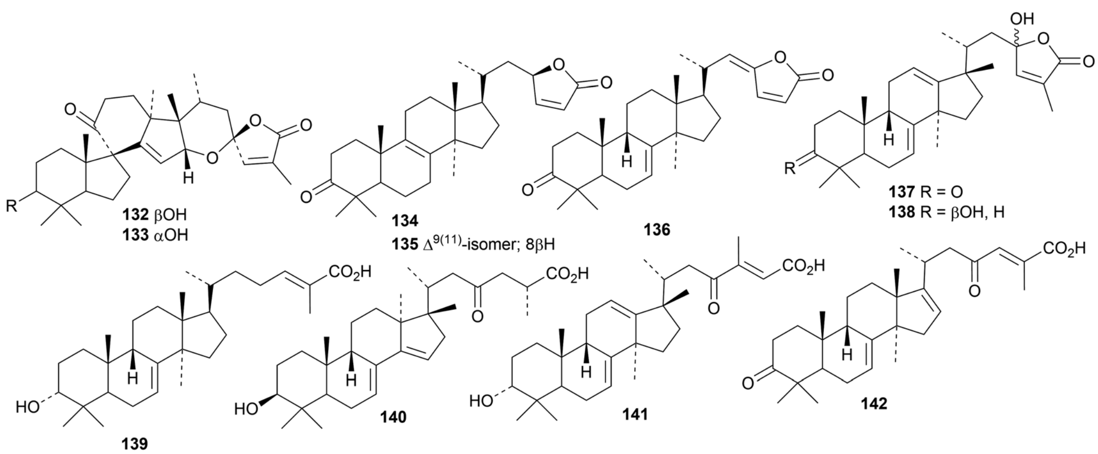
scillascilloside B1 from *Scilla scilloides*[44] and saponins from *Mussaenda luteola*.[55]

The holostane saponins cladolosides C_3, E_1, E_2, F_1, F_2, G, H_1 and H_2, from the sea cucumber *Cladolabes schmeltzii*, have the new genins **178** (C_3), **179** (E_2, F_2, G, H_2) and **180** (E_1, F_1, H_1).[56] The saponins lessoniosides A, B and D, with the new genin **181**, C and E, with the new genin **182**, and F and G, with the new genin **183**, have been reported from the viscera of the sea cucumber *Holothuria lessoni*.[57] Among the saponins of the sea cucumber *Colochirus robusta*, colochirosides B_1 and B_3 have the new genins **184** and **185** respectively whereas colochirosides B_2 and C have known genins.[58] The C-22 configuration of the



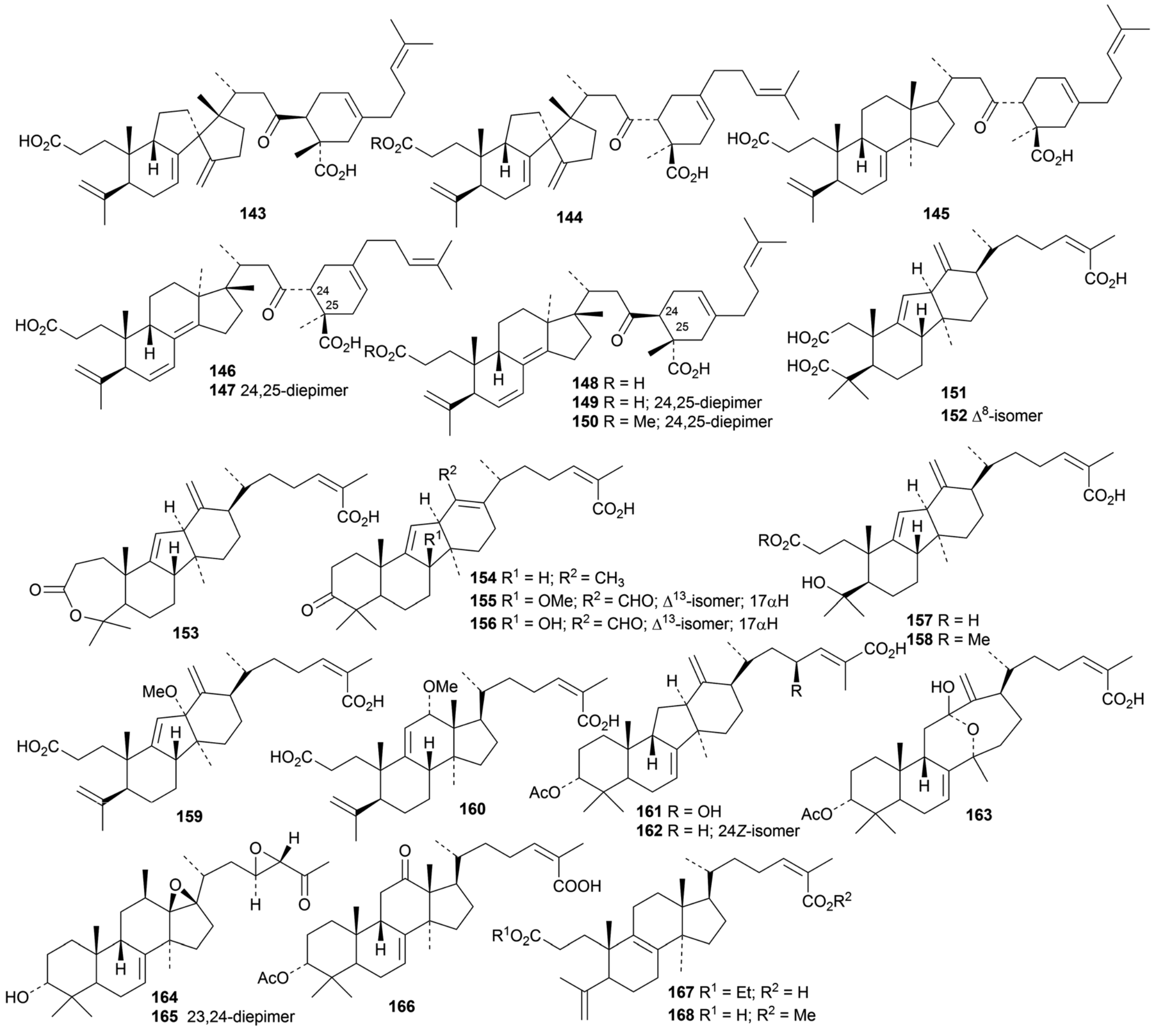






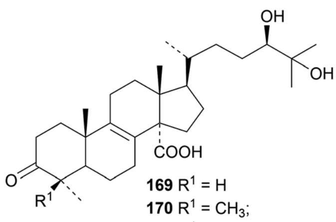
saponins of the sea cucumber *Cladolabes schmeltzii* has been assigned as *R*.[59] Other holostane saponins with known genins include cercodemasoides A–E from *Cercodemas anceps*,[60] cucumarioside E from *Cucumaria japonica*[61] and moebioside A from *Holothuria moebii*.[62] Reviews covering biological and taxonomic significance of sea cucumber holostane saponins[63] and their antitumour, anti-inflammatory and immunostimulatory properties[64] have been published.

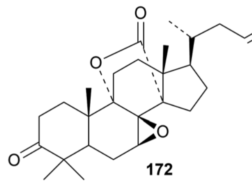
Cimyunnins A **186**–D **189** are cycloartane derivatives with interesting side-chains, from the fruit of *Cimicifuga yunnanensis*.[65] A mixture of **187** and **188** was used to confirm the structures by X-ray crystallographic analysis. Cimyunnin A **186** is a potent angiogenesis inhibitor. Ananosins A **190**–E **194**, cycloartanes from *Kadsura ananosma*, have some unusual structures.[66]



Abies faxoniana is the source of an impressive group of pairs of lanostane and cycloartane derivatives A_1/A_2 **195**/**196**–H_1/H_2 **209**/**210**, with epimeric spiro-side chains.[67] Fourteen new cycloartane derivatives, **211–216** (ref. 68) and **217–224**,[69] have been isolated from *Beesia calthifolia*. Other cycloartanes include **225**, **226** and **227** from the leaves and twigs of *Dysoxylum gotadhora*,[70] huangqiyegenins V **228** and VI **229** together with the saponins huangqiyenins K and L with the new genins **230** and **231**, respectively, from the leaves of *Astragalus membranaceus*,[71] the 21-epimer **232** of the known argenteanone A from the leaves of *Lansium domesticum*,[72] the 3,4-seco derivative **233** from the leaves of *Hopea odorata*,[73] and mangiferenes A **234** and B **235** from *Mangifera foetida*.[74] The structures of **225** and **232** were confirmed by X-ray crystallographic analyses. The 3,4-seco-cycloartanes macrocoussaric acids D **236**, E **237** and F **238** have been isolated from *Coussarea macrophylla*.[75]

Gambosides A–F are cycloartane glycosides from *Astragalus gombo*.[76] Gambosides A, B and F have the new genins **239**, **240** and **241**, respectively. Interest in the cycloartane saponins from *Cimicifuga simplex* continues.[77] Glycosides from the aerial parts of *Cimicifuga simplex* include the new genins **242–245**.[78] The structure of the 3-*O*-β-D-xylopyranoside of **244** was confirmed by X-ray crystallographic analysis. Compounds reported from *Cimicifuga heracleifolia* include cimiheracleins A **246**–D **249**, 12β-hydroxyacerinol **250**, 11-dehydroxy-15α-hydroxycimicidanol **251**, cimigenol-3,12-dione **252**, the related enones **253** and **254**, compound **255** and 1β-hydroxycimigenol **256** and its 24-epimer **257**.[79] Two new 18-norschiartane derivatives, wuwezidilactones A **258** and B **259**, have been reported from *Schisandra lancifolia*.[80] Two reviews of triterpenoids from *Schizandra* species have been published.[81,82] Cycloartane saponins with known genins include amphipaniculosides C and D from *Amphilophium paniculatum*[83] and saponins from *Cimicifuga foetida*[84] and *Mussaenda luteola*.[55]


169 R^1 = H
170 R^1 = CH_3;
171 R^1 = CH_3; 24-epimer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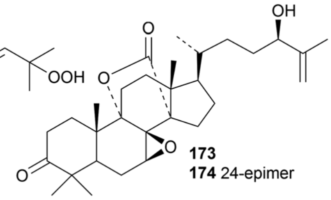
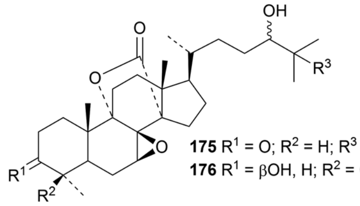
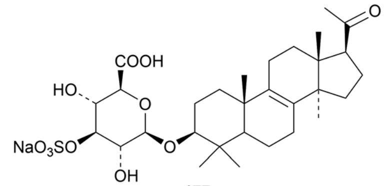

173
174 24-epimer


175 R^1 = O; R^2 = H; R^3 = Cl
176 R^1 = βOH, H; R^2 = CH_3; R^3 = OEt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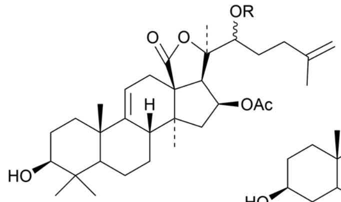
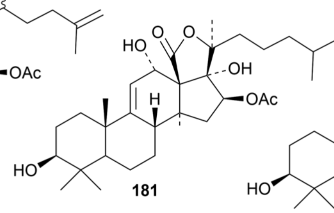

178 R = H
179 R = Ac
180 R = Ac; 25,26-dihydro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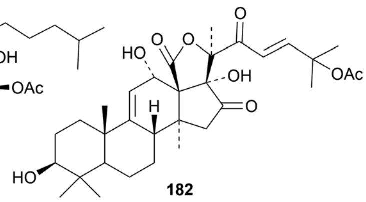
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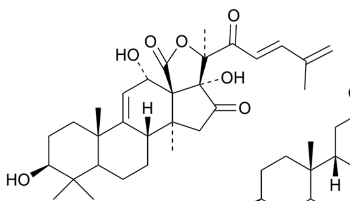
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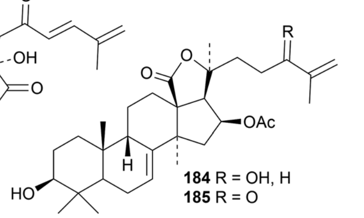
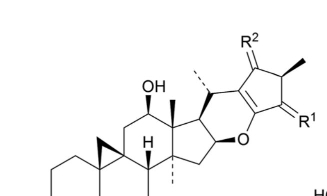
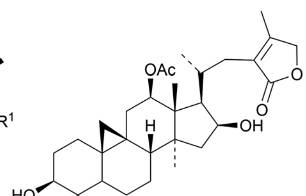

184 R = OH, H
185 R = O


186 R^1 = O; R^2 = H_2
187 R^1 = H_2; R^2 = O
188 R^1 = H_2; R^2 = O; 24-epimer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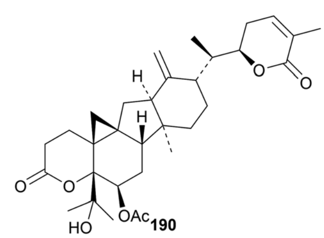
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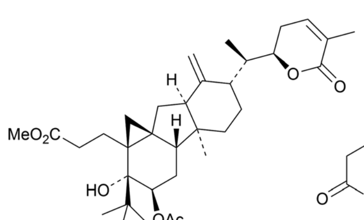
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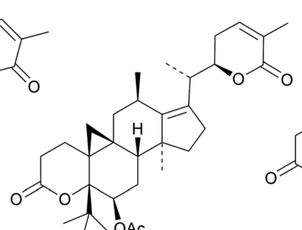
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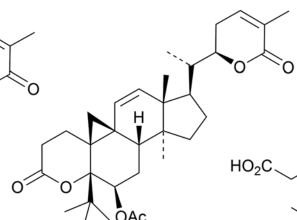
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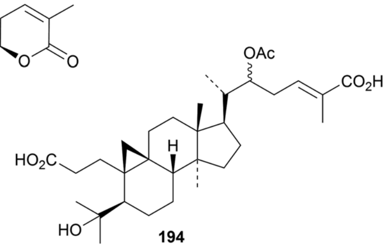
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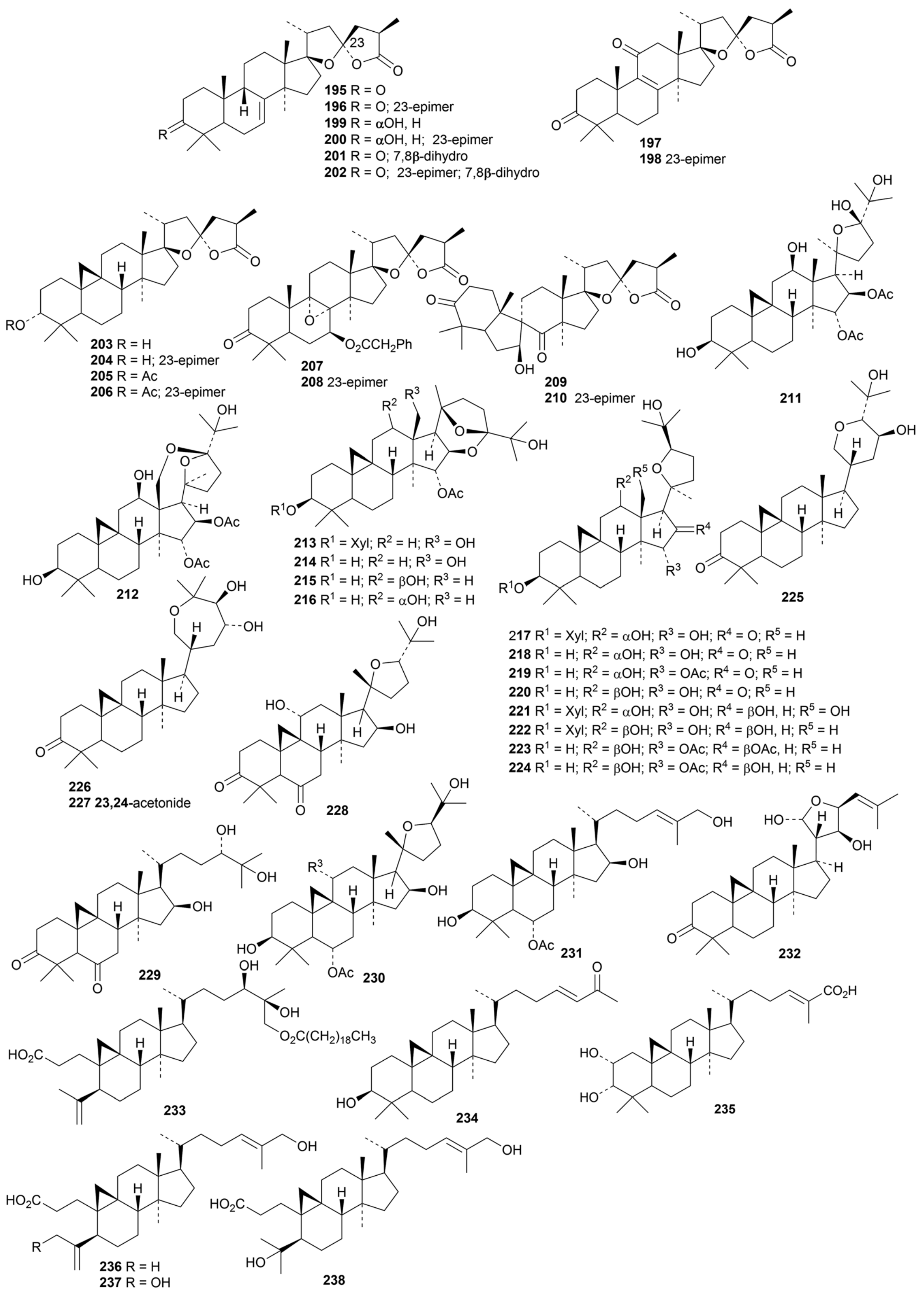
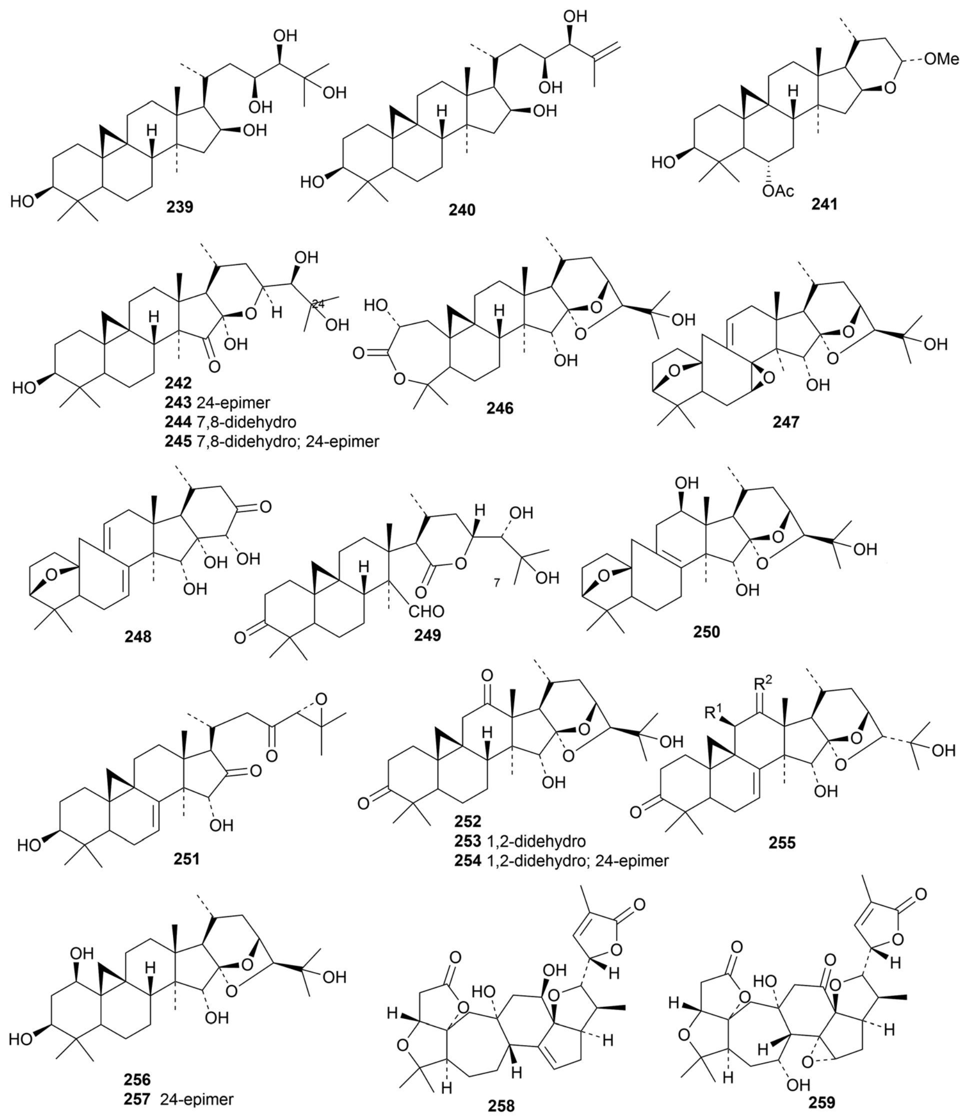
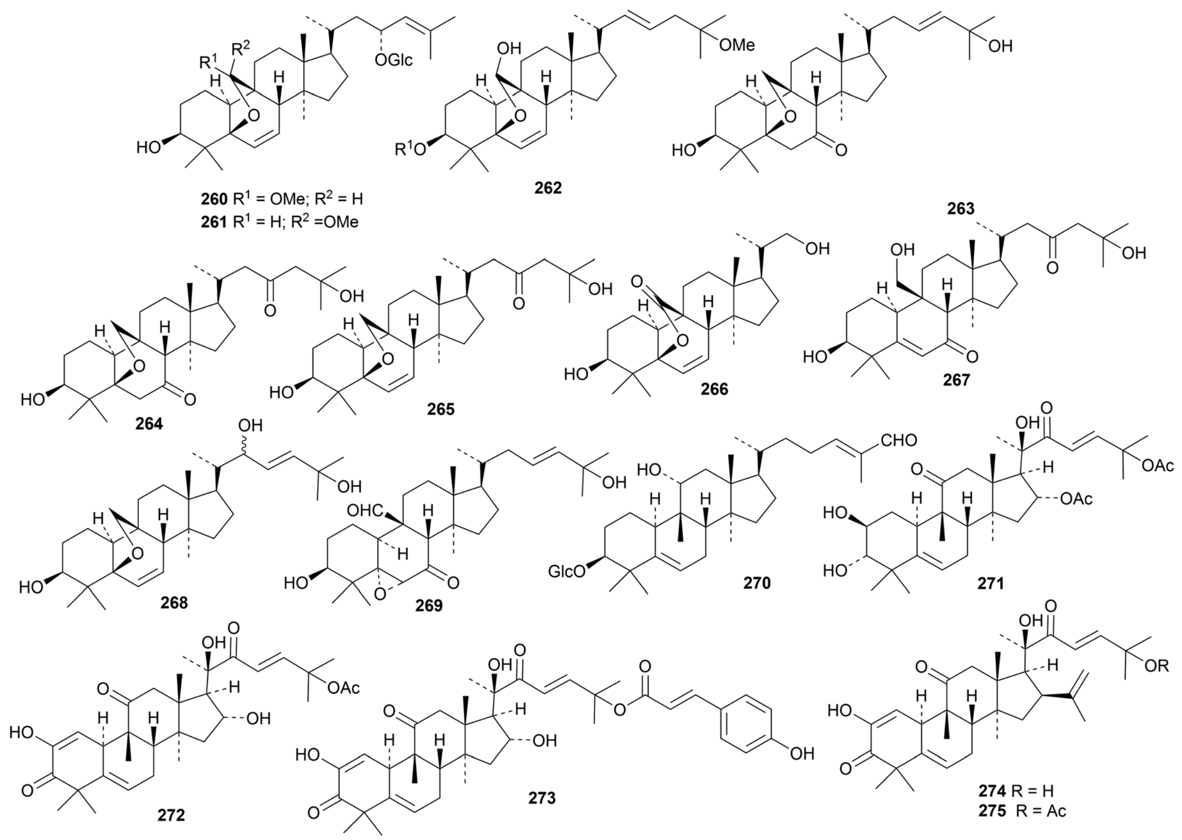

195 R = O
196 R = O; 23-epimer
199 R = αOH, H
200 R = αOH, H; 23-epimer
201 R = O; 7,8β-dihydro
202 R = O; 23-epimer; 7,8β-dihydro
197
198 23-epimer
203 R = H
204 R = H; 23-epimer
205 R = Ac
206 R = Ac; 23-epimer
207
208 23-epimer
209
210 23-epimer
211
212
213 R1 = Xyl; R2 = H; R3 = OH
214 R1 = H; R2 = H; R3 = OH
215 R1 = H; R2 = βOH; R3 = H
216 R1 = H; R2 = αOH; R3 = H
217 R1 = Xyl; R2 = αOH; R3 = OH; R4 = O; R5 = H
218 R1 = H; R2 = αOH; R3 = OH; R4 = O; R5 = H
219 R1 = H; R2 = αOH; R3 = OAc; R4 = O; R5 = H
220 R1 = H; R2 = βOH; R3 = OH; R4 = O; R5 = H
221 R1 = Xyl; R2 = αOH; R3 = OH; R4 = βOH, H; R5 = OH
222 R1 = Xyl; R2 = βOH; R3 = OH; R4 = βOH, H; R5 = H
223 R1 = H; R2 = βOH; R3 = OAc; R4 = βOAc, H; R5 = H
224 R1 = H; R2 = βOH; R3 = OAc; R4 = βOH, H; R5 = H
225
226
227 23,24-acetonide
228
229
230
231
232
233
234
235
236 R = H
237 R = OH
238



The cucurbitacins have interesting pharmaceutical potential.[85,86] Cucurbitacin E has been investigated for a wide range of activities.[87] The biosynthesis of the bioactive mogrosides from *Siraitia grosvenorii* has been studied.[88] Three papers describe further cucurbitacin constituents of *Momordica charantia*, including taikugausins C **260**, D **261** and E **262**,[89] kuguacins II **263**–VI **267** (ref. 90) and kaguacin X **268**.[91] The structure of kuguacin II **263** was confirmed by X-ray crystallographic analysis. Citriodora A **269** has been obtained from *Eucalyptus citriodora*.[92] Hemsleypenside B **270** and the 16,25-diacetate **271** of cucurbitacin F have been isolated from *Hemsleya jinfushanensis*.[93] Hemsleypenside B **270** has a new genin. Other cucurbitacin saponins with the new genins **272** and **273** (ref. 94) and **274** and **275** (ref. 95) have been isolated from the leaves and fruit of *Citrullus colocynthis*. Genins **274** and **275** have an unusual three carbon unit at C16. Cucurbitacin saponins with known genins include mogroside VA_1 from *Siraitia grosvenorii*,[96] kaguaglycoside I[91] and taikugausins A and B[89] from *Momordica charantia* and hemsleypensides C, D and E from *Hemsleya jinfushanensis*.[93]

4. The dammarane group

The pharmaceutical use of dammarane triterpenoids has been reviewed.[97] Reviews have also appeared on the saponins from *Panax ginseng*[98] and *Panax notoginseng*.[99,100] Four new ginsenosides, with melanogenesis inhibitory activity, have been isolated from *Panax ginseng* but only one of them, 23-*O*-methylginsenoside Rg_{11}, has a new genin **276**.[101] Six new dammaranes **277–282** have been obtained from the acidic hydrolysate of the stems and leaves of *Panax ginseng*.[102] The steamed roots of



Panax notoginseng yielded notoginsenosides SP1–SP4 with the new genins **283–286** (ref. 103) and notoginsenosides ST7–ST10, 13 and 14 with the genins **287–292**.[104]

Other dammarane derivatives include gypensapogenins H **293**–L **297** from the hydrolysate of the total saponins of *Gynostemma pentaphyllun*,[105] cyclocariosides I **298** (duplicate name) and J **299** from the leaves of *Cyclocarya paliurus*,[106] glylongiposides I and II, with the new genins **300** and **301**, from *Gynostemma longipes*,[107] compound **302** from the green walnut husks of *Juglans mandshurica*[108] and compounds **303–306** from *Cissus quadrangularis*.[109]

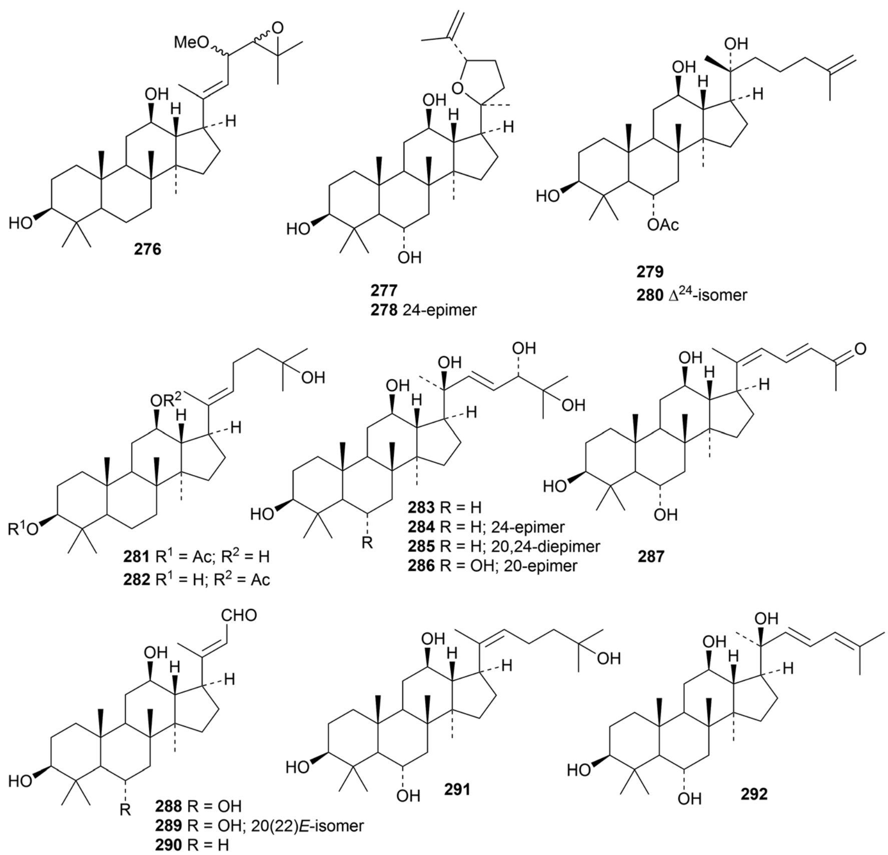
Two groups of nordammarannes, compounds **307**, **308** and **309** from *Sanguisorba officinalis*[110] and hupehenols A **310**–E **314** from *Viburnum hupehensis*,[111] have been reported. Macrocoussaric acids A **315**, B **316** and C **317** are 3,4-secodammaranes from the Ecuadorian plant *Coussarea macrophylla*.[75]

Epoxynotoginsenoside A is a saponin from *Panax notoginseng* that is identical to the previously isolated quinquefoloside L_b.[112] Dammarane saponins with known genins include actinostemmosides I and J, from *Actinostemma lobatum*,[113] cyclocarioside K from *Cyclocarya paliurus*,[106] 20*S*-ginsenoside RF_2 from *Panax ginseng*,[114] notoginsenosides SP5–SP18 (ref. 103) and notoginsenosides ST6, ST11 and ST12 from *Panax notoginseng*[104] and saponins from *Gynostemma pentaphyllum*[115] and *Panax ginseng*.[116–118] The current knowledge of the key enzymes involved in the biosynthesis of saponins from *Panax notoginseng* has been surveyed.[119]

Ricinidols A **318** and B **319** have a new rearranged euphane skeleton.[120] They occur in *Ricinodendron heudelotii* together with the euphane derivatives ricinodols C **320**–G **324**. The structure of 16-epikulinone **325**, from *Melia azedarach*, was established by X-ray crystallographic analysis.[121] Other euphanes include the antibacterial toosendanin A **326** from *Melia toosendan*[122] and 25-methoxy-8,23-euphadien-3β-ol **327** from *Euphorbia pekinensis*.[123]

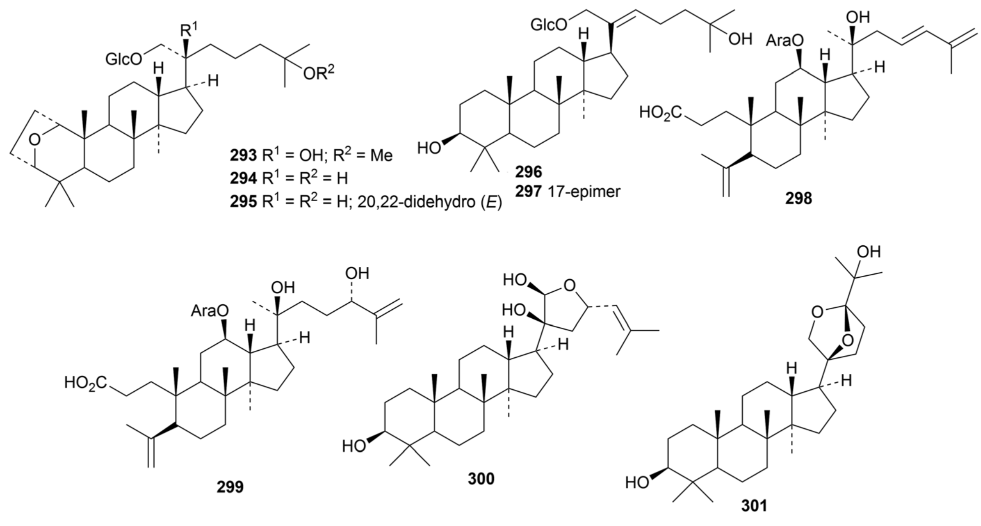
New tirucallane derivatives include 3β-*O*-tigloylmelianol **328** from *Guarea kunthiana*,[124] congoensins A **329** and B **330** from the bark of *Entandrophragma congoënse*,[125] compounds **331**, **332** and **333** from *Anopyxis klaineana*,[126] ficutirucins A **334**–I **342** from the fruit of *Ficus carica*,[127] 24,25-dihydrolimocinol **343** from *Melia azadirachta*[128] and secotiaminic acid **344** from *Entandrophragma congoense*.[129] Paramigniosides A–E are tirucallane saponins from *Paramignya scandens*, all with the same genin **345**.[130]

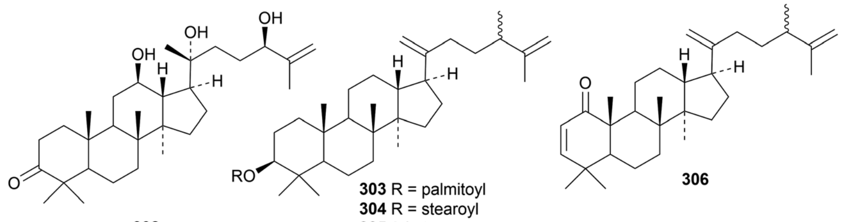
Polygonifoliol **346**, from the latex of the seaside sandmat *Euphorbia polygonifolia*, is an apotirucallane with an 18(17→14)-abeo rearrangement.[131] Piscidinols H **347**–L **351** are apotirucallane derivatives from the leaves of *Walsura trifoliata* that



show moderate insecticidal activities.[132] The apotirucallol derivative **352** has been isolated from the seeds of *Xylocarpus granatum*.[133]

The apotirucallane and glabretal derivatives prototiamins A **353**–G **359** are constituents of the bark of *Entandrophragma congoënse*.[129] The structure of prototiamin C **355** was confirmed

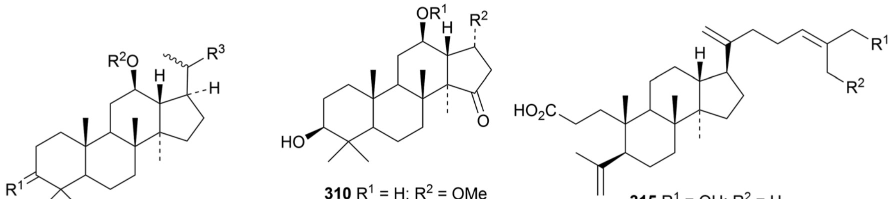




302

303 R = palmitoyl
304 R = stearoyl
305 3-ketone

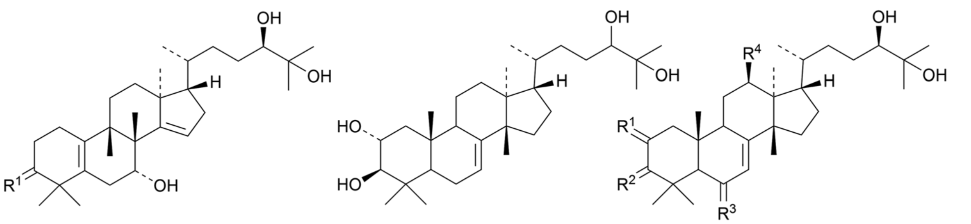
306



307 R¹ = βOH, H; R² = Ac; R³ = CH₂OH
308 R¹ = O; R² = H; R³ = CH₂OH
309 R¹ = βOH, H; R² = H; R³ = CHO

310 R¹ = H; R² = OMe
311 R¹ = Ac; R² = OMe
312 R¹ = Ac; R² = OH
313 R¹ = H; R² = H; 16,17-didehydro
314 R¹ = Ac; R² = H; 16,17-didehydro

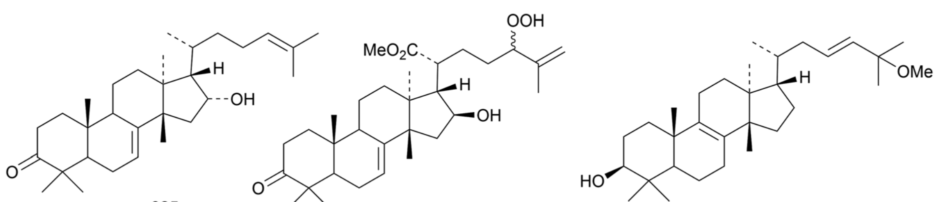
315 R¹ = OH; R² = H
316 R¹ = R² = OH
317 R¹ = OAc; R²= OH



318 R = βOH, H
319 R = O

320

321 R¹ = R³ = H₂; R² = O; R⁴ = OH
322 R¹ = H₂; R² = R³ = O; R⁴ = H
323 R¹ = αOH, H; R² = O; R³ = H₂; R⁴ = H
324 R¹ = O; R² = βOH, H; R³ = H₂; R⁴ = H



325 **326** **327**

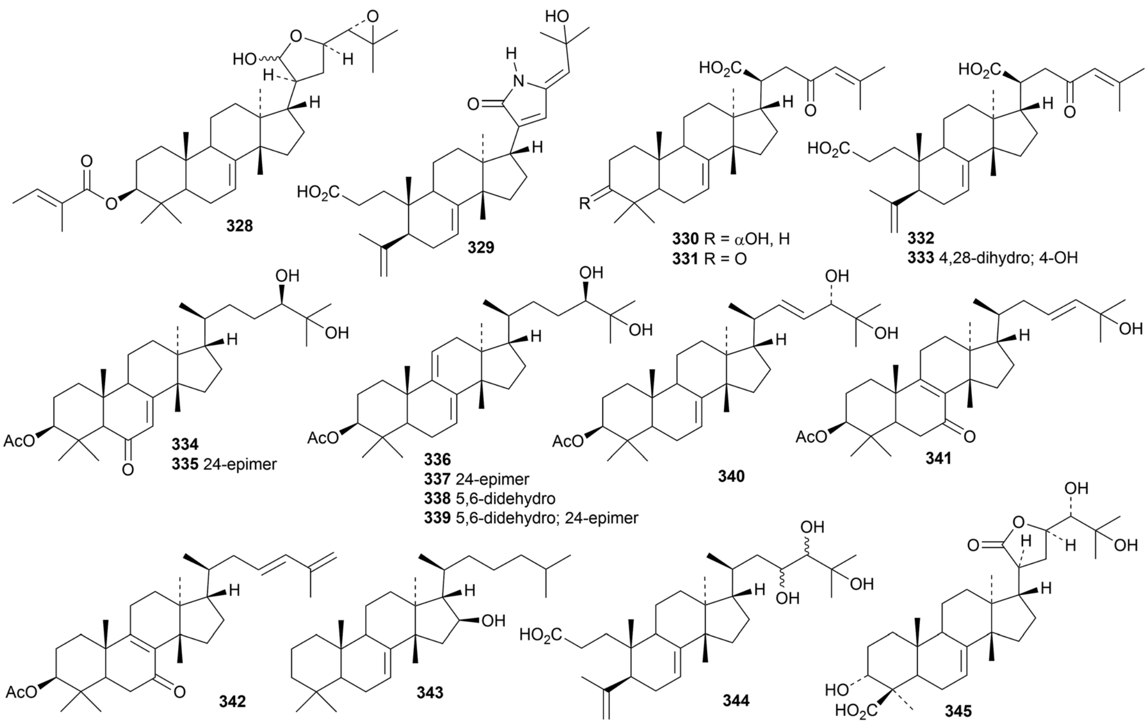
by X-ray analysis. Other glabretal derivatives include dictabretals A **360**–D **363** from the root bark of *Dictamnus dasycarpus*,[134] pancastatins A **364** and B **365** from the immature fruit of *Poncirus trifoliata*,[135] compound **366** from *Atalantia buxifolia*[136] and dysomollins A **367** and B **368** from *Dysoxylum mollissimum* var. *glaberrimum*.[137]

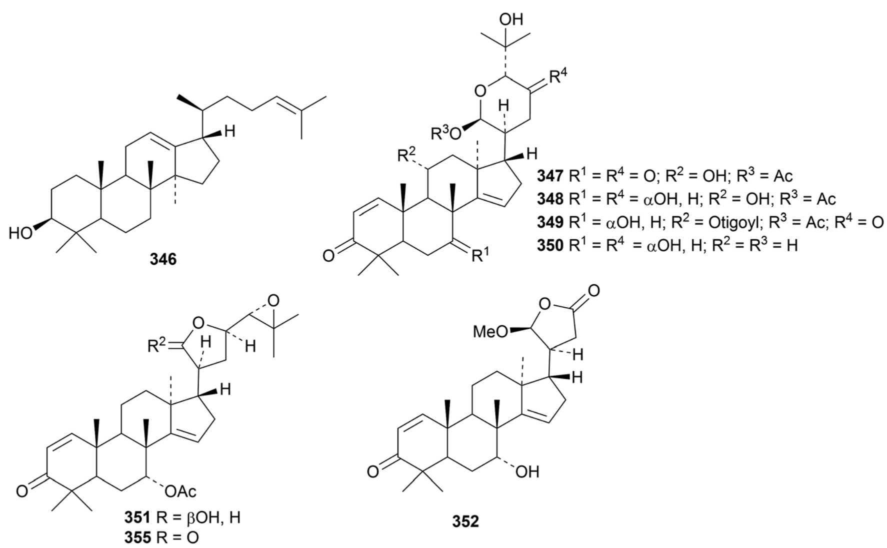
Phainanoids A **369**–F **374**, from *Phyllanthus hainanensis*, have an interesting new carbon skeleton.[138] The structures of A and B were confirmed by X-ray crystallographic analyses. Phainanoids A **369**–F **374** exhibited potent immunosuppressive activities. Songbodichapetalin **375** is a new constituent of *Phyllanthus songboiensis* with cytotoxic activity.[139]

4.1. Tetranortriterpenoids

Many new limonoids have been reported this year. Dysomollides A **376**–G **382** are constituents of *Dysoxylum mollissimum* var. *glaberrimum*.[137] *Dysoxylum mollissimum* is also the source of dysoxylumosins A **383**–M **395**.[140]

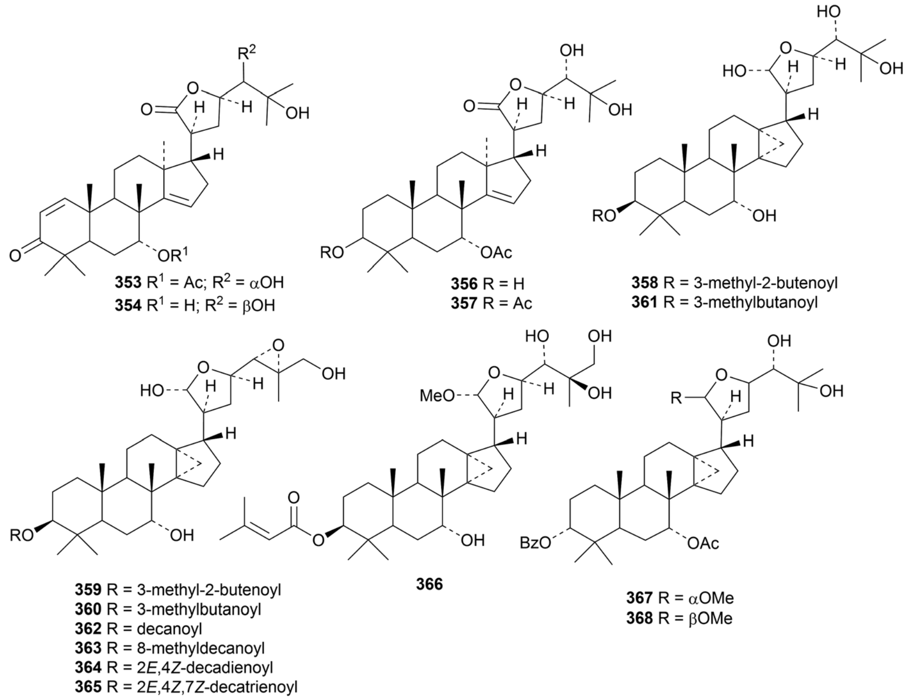
The leaves of *Trichilia americana* are rich in cedrelone derivatives, including americanolides A **396**–D **399** and compounds **400**–**405**.[141] The structure of americanolide A **396** was confirmed by X-ray crystallographic analysis.





Munronins A **406**–N **419** (ref. 142) and O **420**, P **421** and Q **422** (ref. 143) are constituents of *Munronia henryi*. Unfortunately, the names munronins A–G have been used before and munronin L **415** is the known 23-*O*-methylvolkensin. The structure of munronin H **412** was confirmed by X-ray crystallographic analysis. Many of the munronins show strong anti-tobacco mosaic virus activity.

Several 29-nor and related limonoids, toonaciliatones A **423**–H **430**, have been found in the stem bark of *Toona ciliata* var. *yunnanensis*.[144] Toonaciliatones A–F are names that have already been used. New compounds from *Azadirachta* species include azadiraindins A **431**–D **434**,[145] E **435**, F **436** and G **437** (ref. 146) and nimbolicidin **438** and nimbocin **439** (ref. 147) from *Azadirachta indica* and mehaneemin **440** from *Azadirachta excelsa*.[148]



Ciparasins A **441**–P **456** constitute an impressive array of rearranged limonoids from *Cipadessa cinerascens*.[149] Ciparasins A **441** and P **456** show strong anti-HIV activities.

The Thai mangrove *Xylocarpus moluccensis* is the source of thaixylomolins G **457**–N **464**, the xyloccensin U derivatives **465** and **466** and the mexicanolide derivatives **467**and **468**,[150] while the seeds of Indian *Xylocarpus moluccensis* yielded procer-anolide propanoate **469** and deacetylangustidienolide **470**.[151] 2,3-Dideacetylxyloccensin S **471** and 30-deacetylxyloccensin W **472** have been isolated from the seeds of *Xylocarpus granatum*.[133] The seeds of *Swietenia macrophylla*[152] and *Swietenia humilis*[153] are the respective sources of swietemacrophin **473** and humilinolides G **474** and H **475**. Swietemacrophin **473** is the same as the previously isolated 2-acetylruageanin B and 2-acetoxyswietemahonolide. The structure of humilinolide G **474** was confirmed by X-ray crystallographic analysis.

Khaysenelides A **476**–F **481** are modified furan derivatives from the stem bark of *Khaya senegalensis*.[154] The structures of khaysenelides A **476** and C **478** were confirmed by X-ray crystallographic analyses. Khaysenelide F **481** shows neuroprotective activity. An impressive group of mexicanolide derivatives, khasenegasins A **482**–N **495**, has been reported from the seeds of *Khaya senegalensis*.[155]

New compounds from *Carapa guianensis* (andiroba) include andirolides W **496**, X **497** and Y **498** from the flower oil[156] and carapanolides T **499**–X **503** (ref. 157) and M **504**–S **510** (ref. 158) from the seeds. The structures of khasenegasin A **482** and carapanolide N **505** were confirmed by X-ray crystallographic analyses. Carapanolide V **501** is the same as andirolide F, isolated in 2011.

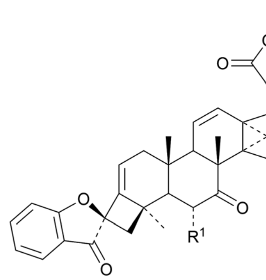
Tabulalins K **511**, L **512** and **513** (ref. 159) and velutabularins K **514**, L **515** and M **516** (ref. 160) are new phragmalin derivatives from *Chukrasia tabularis* var. *velutina*. The structure of velutabularin K **514** was confirmed by X-ray crystallographic analysis. Further phragmalin derivatives, chukvelutilides I **517**–X **532**, have been isolated from *Chukrasia tabularis*.[161] This paper adds to the confusion in the literature by using duplicate names (chukvelutilides I–O). In addition, chukvelutilides U and V are the same as the previously published chukvelutilides I and L.

4.2. Quassinoids

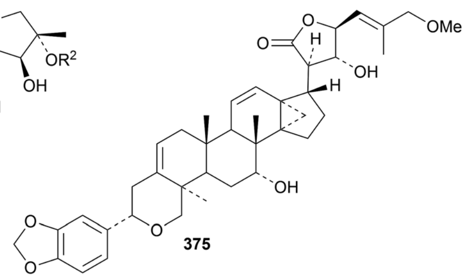
Perforalactones A **533**, B **534** and C **535** are interesting new quassinoids from *Harrisonia perforata*.[162] Perforalactones A **533** and B **534** have been shown to have insecticidal activity but no cytotoxic activity. *Brucea javanica* yielded the new derivative bruceene A **536**.[163] The structures of perforalactone A **533** and bruceene A **536** were confirmed by X-ray analyses. Several new quassinoids, picrajavanicins A **537**–G **543**, have been reported from *Picrasma javanica*, collected in Myanmar.[164]

5. The lupane group

24-Norbetulin **544** has been identified in *Dracaena cinnabari*.[165] The highly oxygenated lupane derivatives **545** and **546** are constituents of cashew nuts (*Anacardium occidentale*).[166] The



369 $R^1 = R^2 = H$
370 $R^1 = OH$; $R^2 = H$
371 $R^1 = OH$; $R^2 = Me$
372 $R^1 = OH$; R^2 = 6-hydroxyhexanoyl
373 $R^1 = OH$; R^2 = 4-hydroxy-3*R*-methoxybutanoyl
374 $R^1 = OH$; R^2 = 3*R*,4-dimethoxybutanoyl



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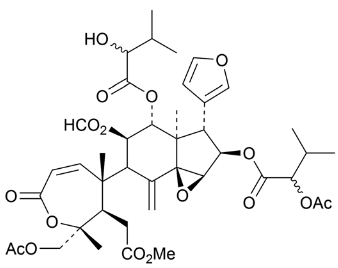
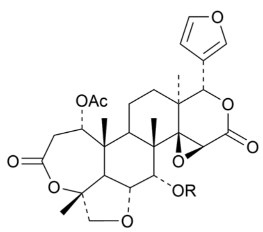
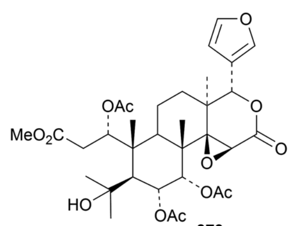


376



377 R = H
378 R = 2-hydroxy-3-methylbutanoyl



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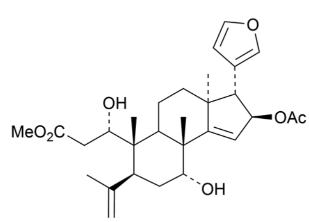

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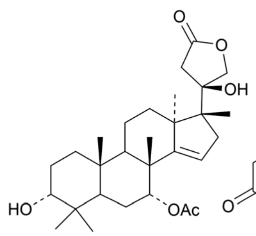

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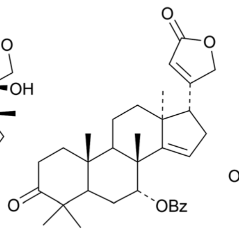

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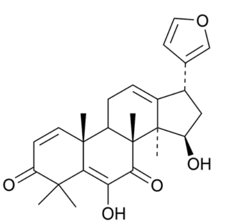

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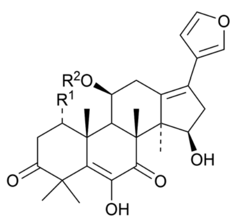
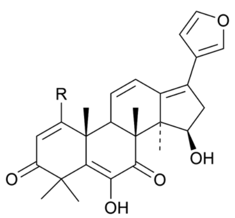
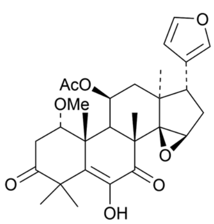


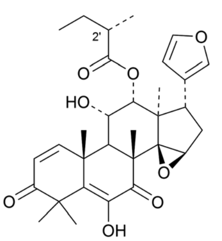
384 $R^1 = OMe$; $R^2 = H$
385 $R^1 = OMe$; $R^2 = Ac$
386 $R^1 = H$; $R^2 = Ac$



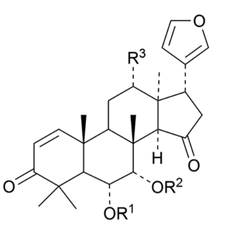
387 R = H
388 1,2-dihydro; R = αOMe



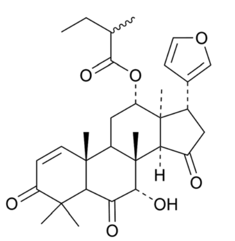
389



390
391 2'-epimer



392 $R^1 = Ac$; $R^2 = H$
393 $R^1 = H$; $R^2 = Ac$



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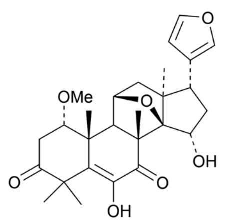
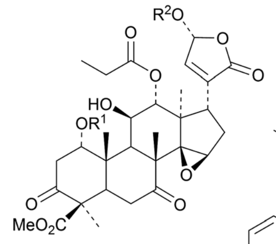
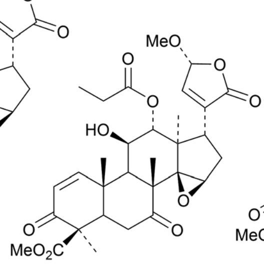


395

related compounds **547** and **548** have been found in Egyptian apple peel (*Malus domestica*).[167,168] *Cassine xylocarpa* is the source of four new lupane derivatives **549–552** and a further two, **553** and **554**, are from *Maytenus cuzcoina*.[169] Other new lupane derivatives include the antibacterial 3β-hydroxy-9(11),12-lupadien-28-oic acid **555** from *Sonneratia alba*[170] and



396 R^1 = H; R^2 = Me
397 R^1 = R^2 = Me
399 R^1 = R^2 = H



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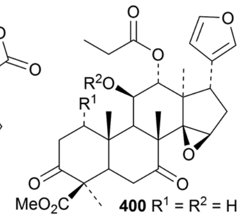
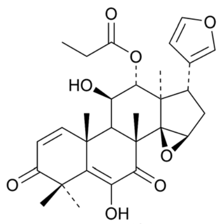


400 R^1 = R^2 = H
401 R^1 =OH; R^2 = H
402 R^1 =OH; R^2 = Ac
403 R^1 =OMe; R^2 = H



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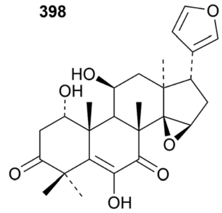

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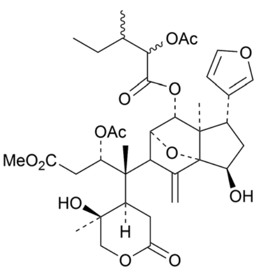

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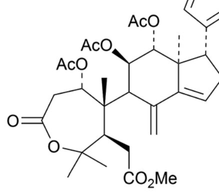

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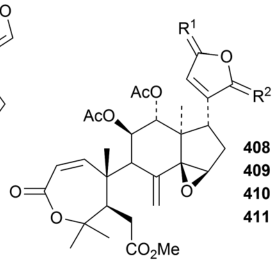
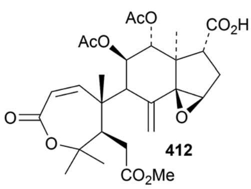


408 R^1 = OH, H; R^2 = O
409 R^1 = OMe, H; R^2 = O
410 R^1 = OMe, H; R^2 = H_2
411 R^1 = O; R^2 = OH. H



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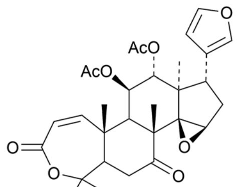

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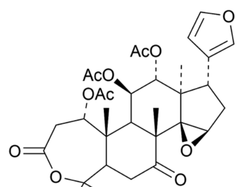

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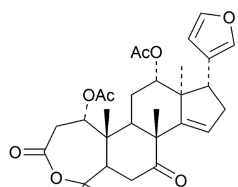
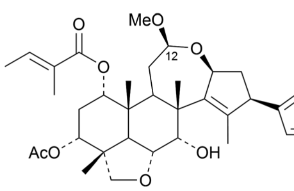
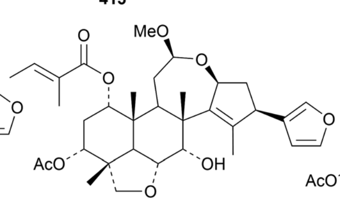


415



416
417 12-epimer



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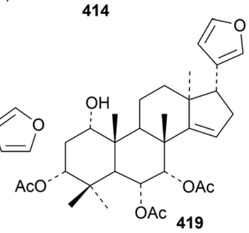

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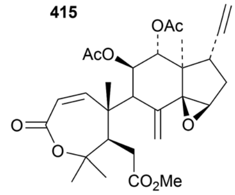

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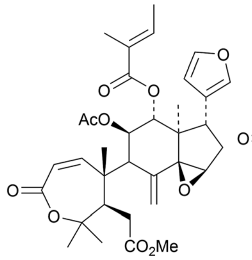

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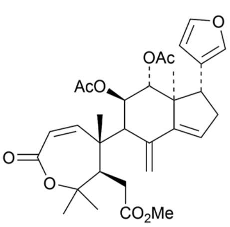

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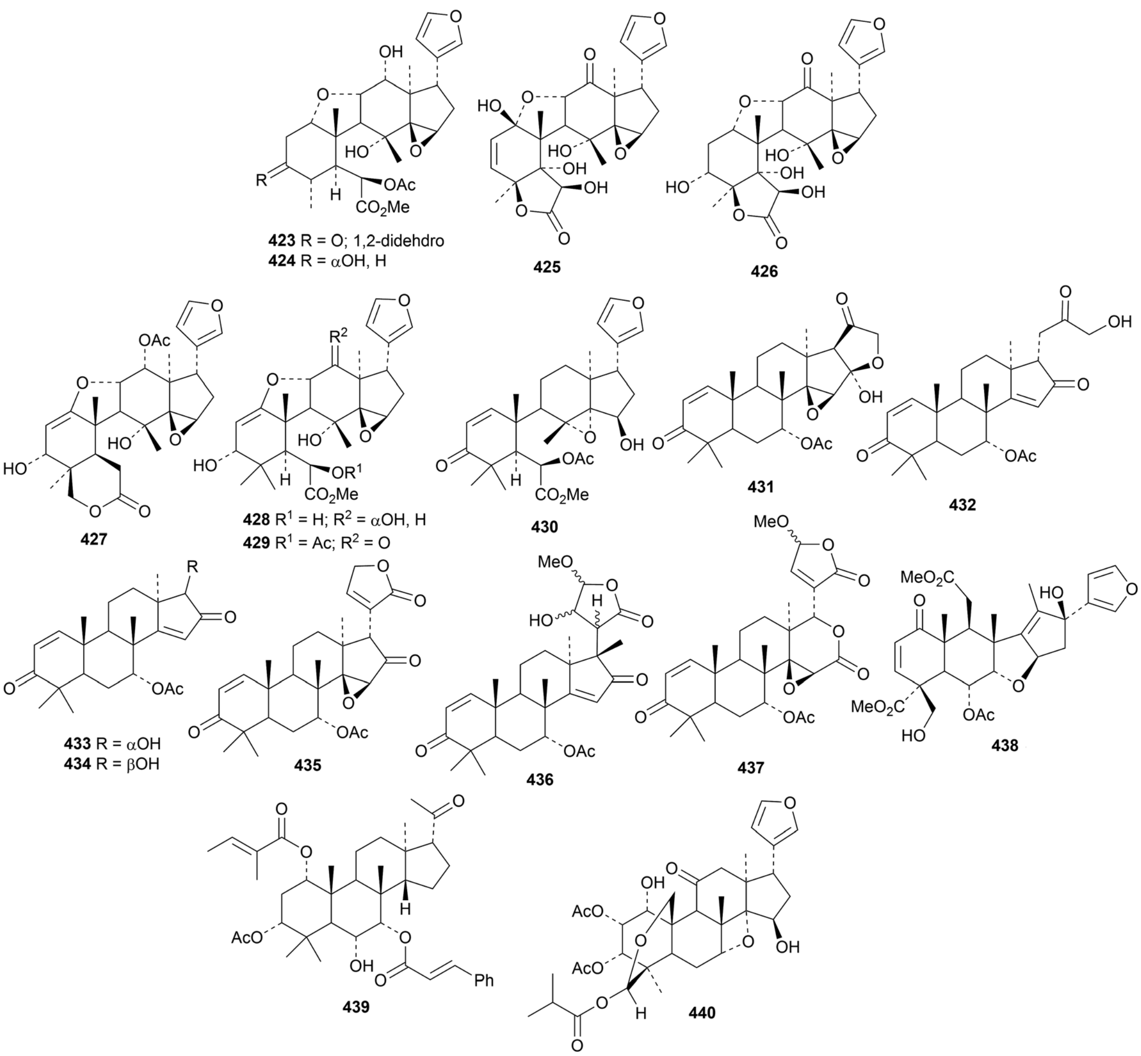
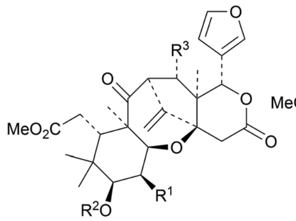


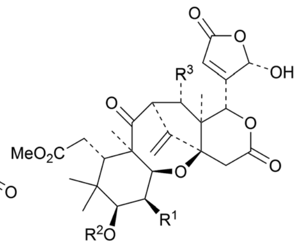
3β-hydroxy-7-oxo-20(29)-lupen-28-oic acid **556** from *Manilkara zapota*.[171] Novel lupane esters include the 3-hexadecanoyl ester **557** of 20(29)-lupene-3β,7β-diol from *Scurrula parasitica* parasitic on *Nerium indicum*,[172] the 4-hydroxy-3-methoxybenzoyl ester **558** from *Paullinia pinnata*,[173] the cafeoyl ester **559** from *Celastrus stylosus*[174] and the 2-benzoyl ester of alphitolic acid from *Rubus innominatus*[175] Hancokinoside, from *Allophylus africanus*, is the 2-*O*-β-D-glucopyranoside of the known hancokinol although the diagram in the reference is inaccurate.[176] Other lupane saponins with known genins include royleanumioside from *Teucrium royleanum*[177] and a saponin from *Cyperus rotundus*.[178]

6. The oleanane group

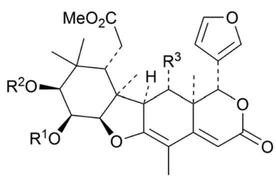
Three 24-noroleananes, **560**, **561** and **562**, have been isolated from biogas slurry.[179] The structure of 24-nor-12-oleanene-3,22-dione **562** was confirmed by X-ray crystallographic analysis. The related dione **563** has also been found in biogas slurry.[180] The 3,4-seco-oleanane derivative **564**, from *Hypericum ascyron*, contains an unusual enedione.[181] Four oleananes **565–568** with unusual hydroxylation at C18 have been isolated from hawthorn berries (*Crataegus pinnatifida*).[182] Oleananes **566**, **567** and **568** exhibited strong antiproliferative activity. Brachyanthera acid A **569**, from *Stautonia brachyanthera*, is 2α,3β,21β,23-tetrahydroxy-12-oleanene-28,29-dioic acid[183] and



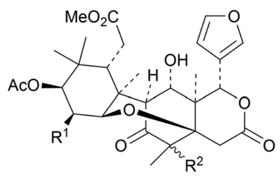
441 R^1 = OAc; R^2 = Ac; R^3 = OH
442 R^1 = OH; R^2 = Ac; R^3 = OH
443 R^1 = OH; R^2 = Ac; R^3 = OAc
444 R^1 = R^2 = R^3 = H



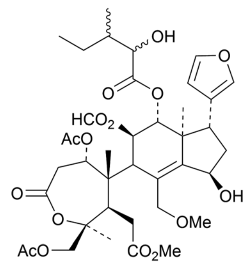
445 R^1 = R^3 = H; R^2 = Ac
446 R^1 = R^3 = OAc; R^2 = Ac
447 R^1 = H; R^2 = Ac; R^3 = OAc



448 R^1 = H; R^2 = Ac; R^3 = OH
449 R^1 = R^2 = H; R^3 = OH
450 R^1 = R^2 = R^3= H



451 R^1 =H; R^2 = αH
452 R^1 =OAc; R^2 = αH
453 R^1 =OH; R^2 = αH
454 R^1 =OAc; R^2 = βOH
455 R^1 =OAc; R^2 = αOH



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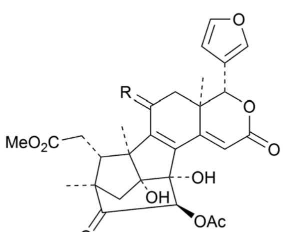
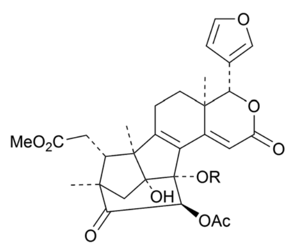
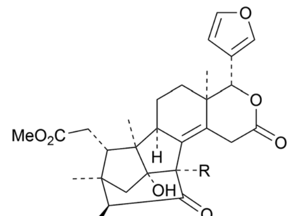


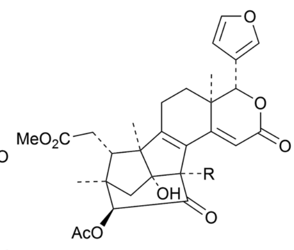
457 R = O
458 R = H_2



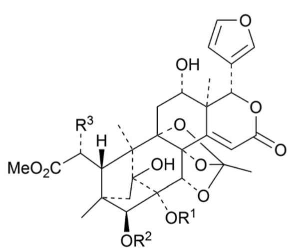
459 R = H
460 R = Et



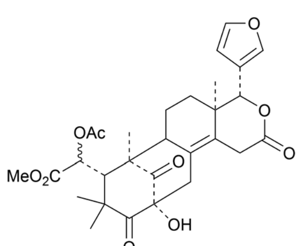
461 R = H
462 R = OEt



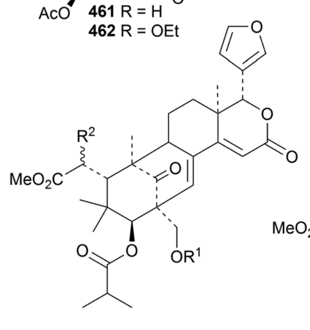
463 R = H
464 R = Otigloyl



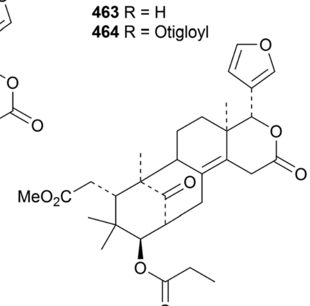
465 R^1 = R^3 = H;R^2 = Ac
466 R^1 = R^2 = Ac; R^3 = H
471 R^1 = R^2 = H; R^3 = OH



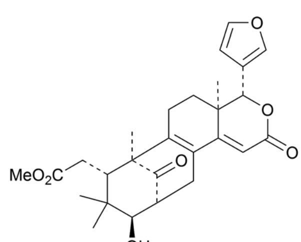
467



468 R^1 = H; R^2 = OAc
474 R^1 = Ac; R^2 = H; 14α,15-dihydro



469



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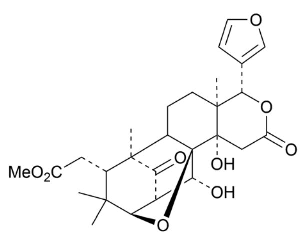
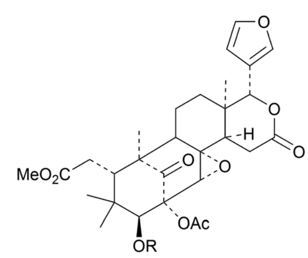
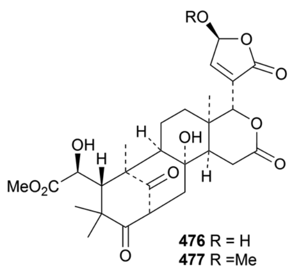


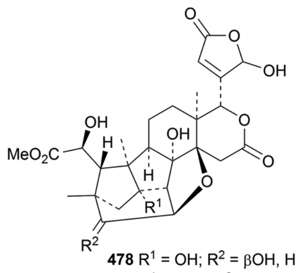
472



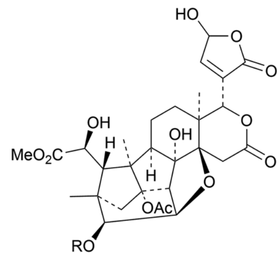
473 R = tigloyl
475 R = 2-methylpropanoyl



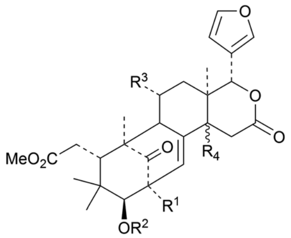
476 R = H
477 R =Me



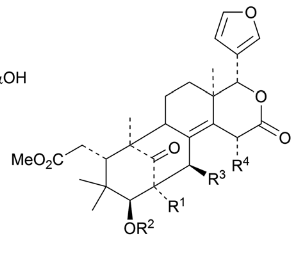
478 R¹ = OH; R² = βOH, H
479 R¹ = OAc; R² = O



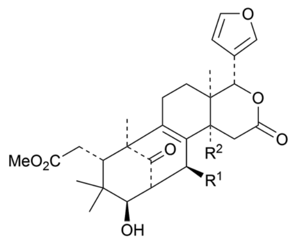
480 R = Me
481 R = H



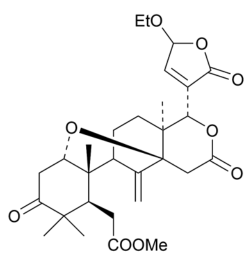
482 R^1 = H; R^2 = Ac; R^3 = OAc ; R^4 = αOH
483 R^1 = R^2 = H; R^3 = OAc; R^4 = αOH
484 R^1 = R^3 = H; R^2 = Ac; R^4 = αOH
485 R^1 = R^2 = R^3 = H; R^4 = αOH
486 R^1 = R^2 = R^3 = H; R^4 = βOH
487 R^1 = OH; R^2 = R^3 = R^4 = H
488 R^1 = OH; R^2 = R^4 = H; R^3 = OAc
489 R^1 = R^2 = R^4 = H; R^3 = OH
490 R^1 = R^2 = R^3 = R^4 = H; 3-epimer



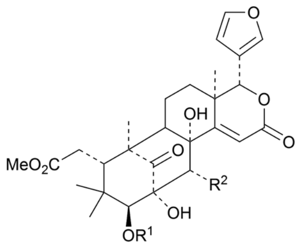
491 R^1 = R^4 = OH; R^2 = R^3 = H
492 R^1 = R^2 = R^3 = H; R^4 = OH
493 R^1 = R^4 = H; R^2 = Ac; R^3 = OH



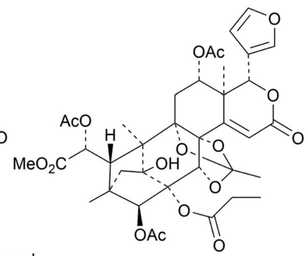
494 R^1 = H; R^2 = OH
495 R^1 = OH; R^2 = H



496



497 R^1 = Ac; R^2 = 2-methylpropanoyl
499 R^1 = 2-methylpropanoyl; R^2 = H
500 R^1 = tigloyl; R^2 = H



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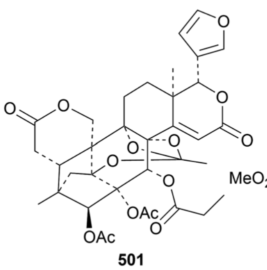

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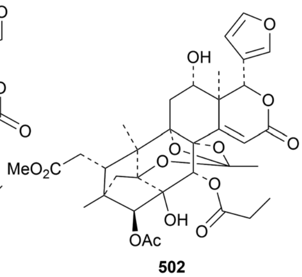

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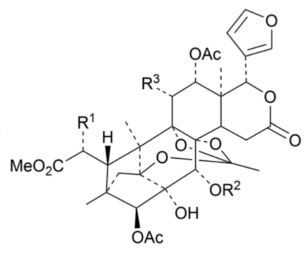
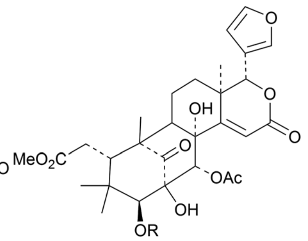


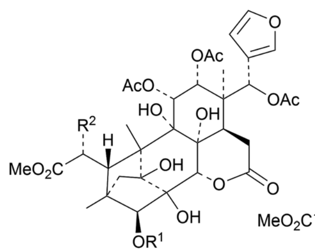
503 R^1 = OH; R^2 = propanoyl; R^3= OAc
504 R^1 = H; R^2 = propanoyl; R^3= OH
505 R^1 = R^3 = OAc; R^2 = 2-methylpropanoyl
506 R^1 = OAc; R^2 = 2-methylpropanoyl; R^3= OH
507 R^1 = OAc; R^2 = propanoyl; R^3= OH
508 R^1 = OAc; R^2 = propanoyl; R^3= H



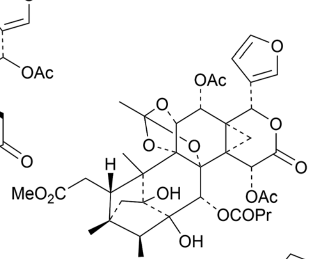
509 R = 2-methylpropanoyl
510 R = tigloyl

pashia acid **570**, from *Pyrus pashia*, is 2α,3β,27-trihydroxy-12-oleanen-28-oic acid.[184]

Other new oleanane derivatives include cyrillin A **571** from *Cyrilla racemiflora*,[185] lancamarolide **572** from *Lantana camara*,[186] silphanolic acid C **573** from *Silphium laciniatum*,[16] termichebulolide **574** from *Terminalia chebula*,[187] ulubelenolide **575** from *Tanacetum chiliophyllum* var. *monocephalum*,[188] the 28,19-olides **576** and **577** from *Styrax tonkinensis*,[189] the pentahydroxyoleanenone **578** and the corresponding 3-ketone **579** from *Gueldenstaedtia verna*,[190] the 11-hydroperoxide **580** from *Holarrhena curtisii*,[191] 3β,6β,29-trihydroxy-12-oleanen-28-oic acid **581** from *Spermacoce latifolia*,[192] 2α,3β,29-trihydroxy-12-



511 $R^1 = R^2 = H$
512 $R^1 = H$; $R^2 = OAc$
513 $R^1 = Ac$; $R^2 = OAc$



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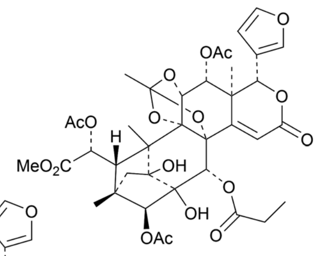

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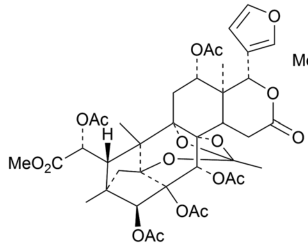

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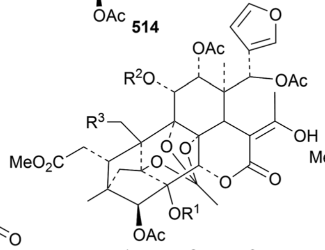
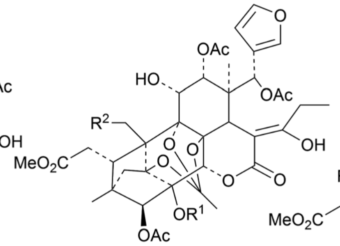
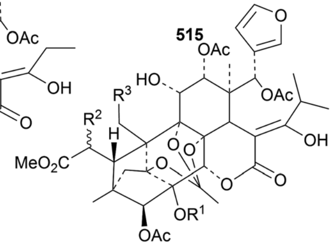


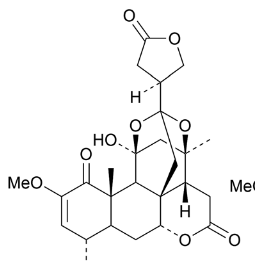
517 $R^1 = Ac$; $R^2 = H$; $R^3 = OAc$
518 $R^1 = R^2 = H$; $R^3 = OAc$
519 $R^1 = R^2 = Ac$; $R^3 = OAc$
520 $R^1 = H$; $R^2 = Ac$; $R^3 = OAc$
521 $R^1 = Ac$; $R^2 = R^3 = H$
522 $R^1 = R^2 = R^3 = H$
523 $R^1 = R^2 = Ac$; $R^3 = H$
524 $R^1 = R^3 = H$; $R^2 = Ac$



525 $R^1 = Ac$; $R^2 = OAc$
526 $R^1 = H$; $R^2 = OAc$
527 $R^1 = Ac$; $R^2 = H$
528 $R^1 = R^2 = H$



529 $R^1 = Ac$; $R^2 = H$; $R^3 = OAc$
530 $R^1 = H$; $R^2 = H$; $R^3 = OAc$
531 $R^1 = Ac$; $R^2 = OAc$; $R^3 = H$
532 $R^1 = R^3 = H$; $R^2 = OAc$



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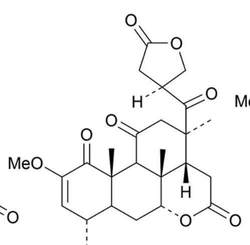

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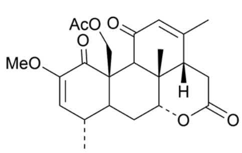

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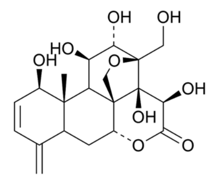

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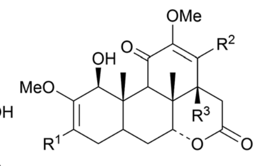
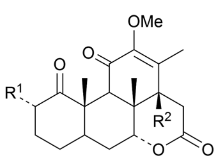
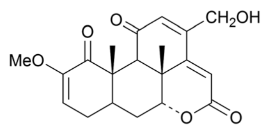


537 $R^1 = R^3 = H$; $R^2 = CHO$
538 $R^1 = OMe$; $R^2 = CH_3$; $R^3 = H$
539 $R^1 = OMe$; $R^2 = CH_3$; $R^3 = OH$



540 $R^1 = OH$; $R^2 = H$
541 $R^1 = OMe$; $R^2 = H$
542 $R^1 = R^2 = OH$



543

oleanen-28-oic acid **582** and related compounds **583** and **584** from *Akebia trifoliata*,[193] the 12(18)-enes **585** and **586** from *Schnabelia oligophylla*[194] and 1-oxosiaresinolic acid **587** and 2α,3α-dihydroxy-11,13(18)-oleanadien-28,19β-olide **588** from *Rubus innominatus*.[175]

Termichebuloside A **589**, a dimeric oleanane diglucosyl ester from *Terminalia chebula*, is the 4,4′-diepimer of the known ivorenoside A.[187] The rhamnoside **590**, from *Gueldenstaedtia verna* has a new genin.[190] Pachystelanoside B is a saponin from *Pachystela msolo* with the new genin 7α-hydroxyprotobassic acid **591**.[195] Silenorubicosides E–I are saponins from *Silene rubicunda* with the new genins **592** (E, F and G), **593** (H) and **594** (I).[196]

Licoricesaponins P2 and Q2 are saponins from *Glycyrrhiza inflata* with the new genins **595** and **596**, respectively.[197] Genin **596** has an unusual 18α*H*. Other oleanane saponins with new genins include 22-acetyluralsaponin C from *Glycyrrhiza uralensis* with genin **597**,[198] atrioleanoside from *Atriplex* *lasiantha* with genin **598**,[199] indicacin from *Fagonia indica* with genin **599** (ref. 200) and schisusaponins G and H from *Schima superba* with genins **600** and **601**, respectively,[201] and saponins from *Anemone amurensis* with genin **602**,[202] *Bupleurum chinense* with genin **603** (ref. 203) and *Ilex cornuta* with genin **604**.[204]

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.

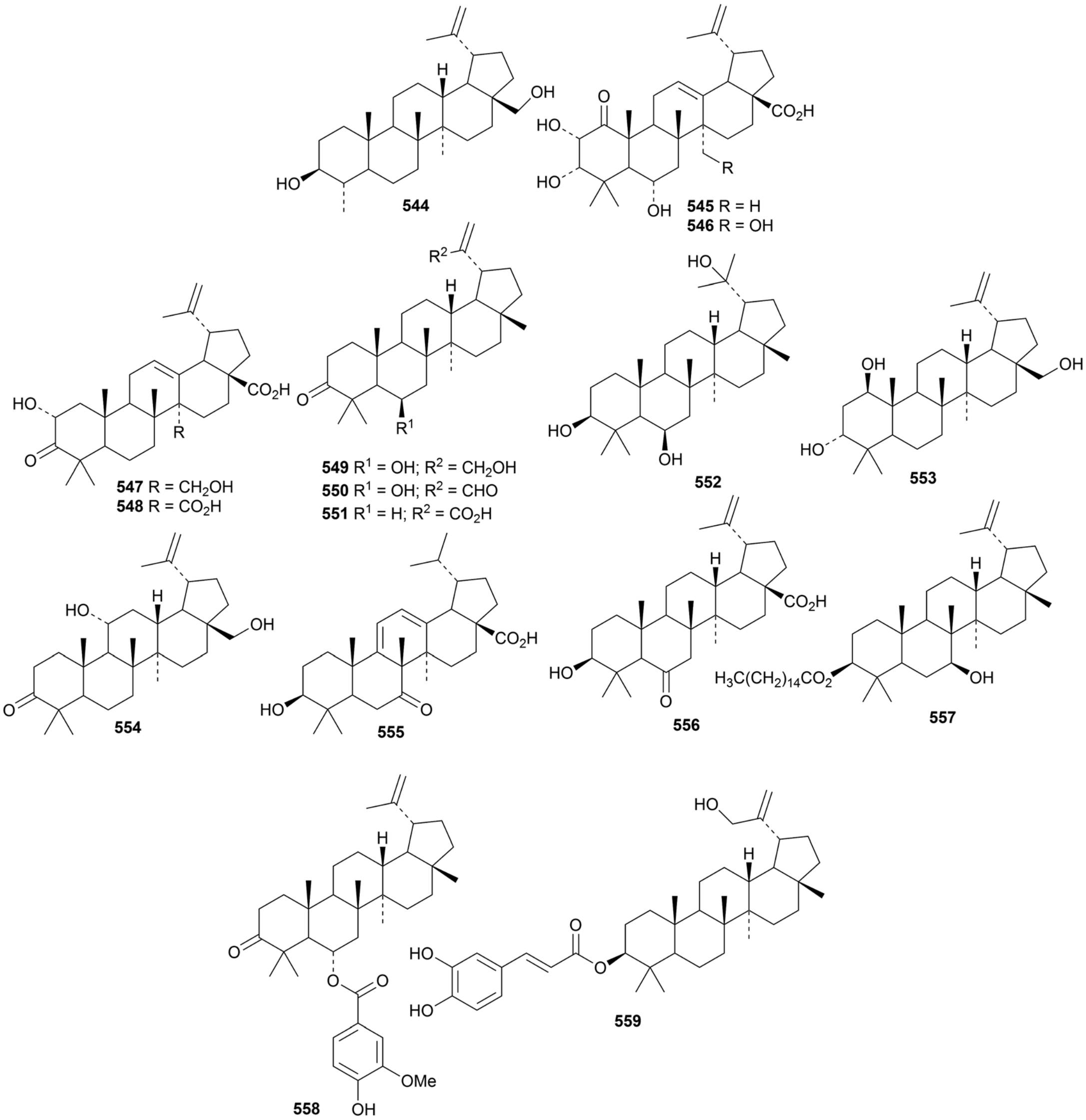
New oleanane esters from *Barringtonia racemosa* include racemosol B **605** and isoracemosol B **606** (ref. 259) and racemosols C **607** and D **608**.[260] Other new oleanane esters include the formyl ester of β-amyrin from *Dichrocephala benthamii*,[261] the caffeoyl esters **609** and **610** from *Waltheria indica*[262] and the coumaroyl ester **611** from *Astilbe rivularis*.[263]

There have been many reports of the biological activities of oleanane triterpenoids and their saponins including the antitumour activity[264] and stem cell differentiation activity[265] of oleanolic acid and the antitumour activity of ardipusilloside,[266] boswellic acids,[267] β-escin[268] and raddeanin A.[269] The biological properties of glycyrrhizic acid[270] and other triterpenoids[271] from *Glycyrrhiza glabra* have been reviewed.

Genicunolides A **612** and B **613** are taraxerane 11,12-epoxides from *Euphorbia geniculata*.[272] The octacosanoyl ester of taraxerol

Table 1 Trivial names and sources of new oleanane saponins with known genins

Trivial name	Plant species	Reference
Abyssaponins A, B	*Erythrina abyssinica*	205
Aesculiosides S1, S2	*Aesculus sylvatica*	206
Akeqintoside E	*Akebia quinata*	207
Amphipaniculosides A	*Amphilophium paniculatum*	83
Aquaticasaponins A, B	*Gleditsia aquatica*	208
Ardinuloside	*Ardisia insularis*	209
Bigelovii C	*Salicornia bigelovii*	210
Bigelovii D	*Salicornia bigelovii*	211
Boromoenosides A–D	*Albizia boromoensis*	212
Brachyantheraosides A1–A5, B6, B9	*Stauntonia brachanthera*	183
Catunarosides I, J	*Catunaregam spinosa*	213
Centellasaponin H	*Centella asiatica*	214
Clematograveolenoside A	*Clematis graveolens*	215
Comastomasaponin I	*Comastoma pedunculatum*	216
Coriacea saponin A	*Holboellia coriacea*	217
Crotalariosides C, (*E*/*Z*)-D, (*E*/*Z*)-E, (*E*/*Z*)-F	*Polygala crotalarioides*	218
Cyrillin B	*Cyrilla racemiflora*	185
Enterolacaciamine	*Enterolobium cyclocarpum*	219
Floraassamsaponins I–VIII	*Camellia sinensis* var. *assamica*	220
Ginsenoside Ro sulfate	*Silphium laciniatum*	16
Glomerulosides A–H	*Glochidion glomerulatum*	221
Glomerulosides I, II	*Glochidion glomerulatum*	222
Hemslosides Ma4, Ma5	*Hemsleya chinensis*	223
Hippophosides E, F	*Hippophae rhamnoides*	224
Lebbeckosides A, B	*Albizia lebbeck*	225
Leptocarposides B, C, D	*Ludwigia leptocarpa*	226
Lobatoside O	*Actinostemma lobatum*	113
Lonicerosides K, L, M	*Weigela subsessilis*	227
Macedonoside E	*Glycyrrhiza uralensis*	198
Meliomosides A–G	*Meliosma henryi*	228
Oleiferasaponins C1, C2, C3	*Camellia oleifera*	229
Oleiferosides I–M	*Camellia oleifera*	230
Oleiferosides N, O	*Camellia oleifera*	231
Oleiferosides P–T	*Camellia oleifera*	232
Pachystelanoside A	*Pachystela msolo*	195
Perennisosides XIII–XIX	*Bellis perennis*	233
Poliusaposides A, B, C	*Teucrium polium*	234
Rotundinoside A	*Ilex rotunda*	235
Serjanioside D	*Serjania marginata*	236
Schefflerasides A, B	*Schefflera sessiliflora*	237
Schekwangsiensides Ia, Ib, IIa, IIb, III–VI, VIIa, VIIb, VIII	*Schefflera kwangsiensis*	238
Schisusaponins A–F	*Schima superba*	201
Securiosides C, D, E	*Securidaca inappendiculata*	239
Stauntosides G, H	*Stauntonia obovatifoliola*	240
Vulgaside I	*Prunella vulgaris*	241
Zanhasaponins D–H	*Zanha golungensis*	242



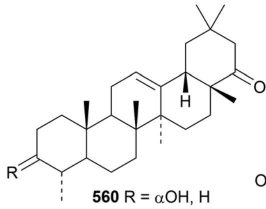
has been found in *Clerodendrum philippinum* var. *simplex*.[273] 3β-Acetoxy-14-taraxeren-12-one **614** is a constituent of *Manilkara zapota*.[171] The coumaroyl esters maesculentins A **615** and B **616** have been isolated from *Manihot esculenta*.[274] The taraxastane **617** has been reported from *Neoboutonia macrocalyx* with unusual stereochemistry at C13 and C18.[275] The 27(13→18)-abeotaraxerane derivative **618**, from *Pittosporum illicioides*, is related to isoaleuritolic acid.[276] Two taraxerane saponins with known genins have been reported from *Euphorbia dracunculoides*.[277] 9β,26-Epoxy-7-multiforen-3β-ol **619** has been isolated from *Trichosanthes baviensis*.[278] Hainanenone A **620**, from *Drypetes hainanensis*, is 23-nor-3-friedelanone[279] and the 24-norfriedelane **621** has been found in *Celastrus stylosus*.[174] *Drypetes congestiflora* is the source of 3α,16β-friedelanediol **622**.[280]

7. The ursane group

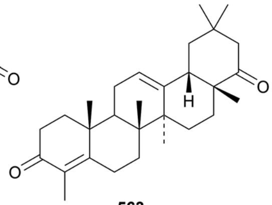
The antitumour properties of ursolic acid have been well studied.[281–283] Urmiensolide B **623** and urmiensic acid **624**, from *Salvia urmiensis*, are 17,22-secoursane derivatives that showed significant antiproliferative activity.[284] Further 17,22-

Table 2 Sources of new oleanane saponins with known genins not assigned trivial names

Plant species	Reference
Acanthophyllum laxiusculum	243
Anemone amurensis	202
Anemone taipaiensis	244
Bupleurum chinense	203
Calendula officinalis	245
Callicarpa kwangtungensis	246
Eclipta prostrata	247
Entada phaseoloides	248
Eryngium kotschyi	249
Gueldenstaedtia verna	190
Lecythis pisonis	250
Phryna ortegioides	251
Phyllanthus myrtifolius	252
Pittosporum tobira	253
Polygala crotalarioides	254
Planchonella obovata	255
Sanguisorba officinalis	256
Saponaria officinalis	257
Trifolium argutum	258



560 R = αOH, H
561 R = βOH, H
562 R = O



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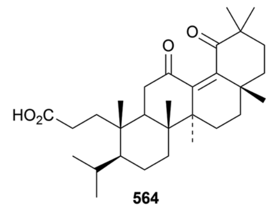

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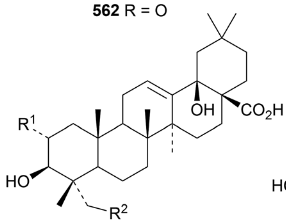
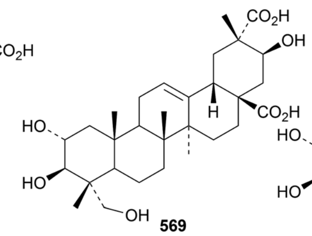


565 $R^1 = R^2 = H$
566 $R^1 = H$; $R^2 = OH$
567 $R^1 = OH$; $R^2 = H$
568 $R^1 = R^2 = OH$



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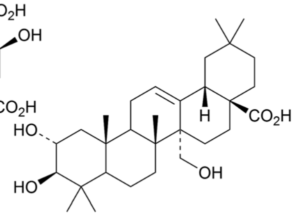

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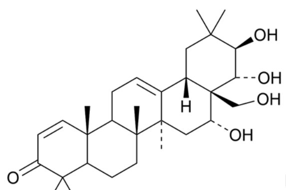

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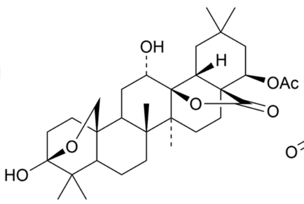

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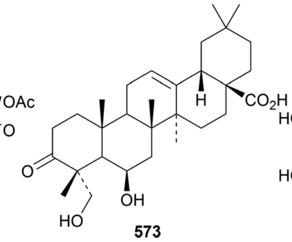

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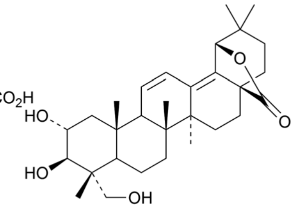

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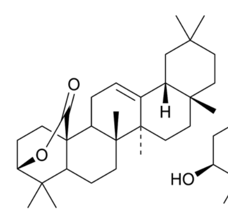

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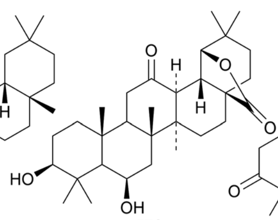

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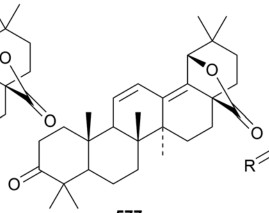

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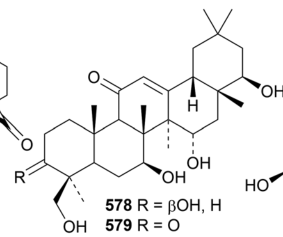
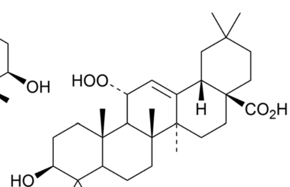


578 R = βOH, H
579 R = O



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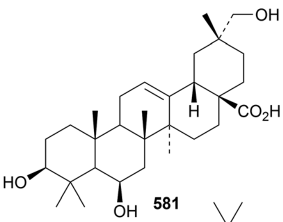

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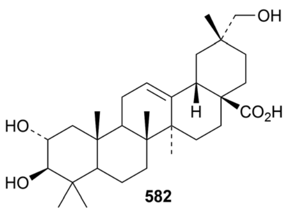

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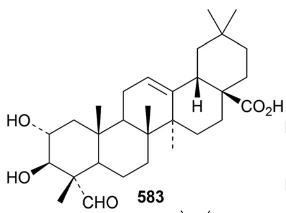

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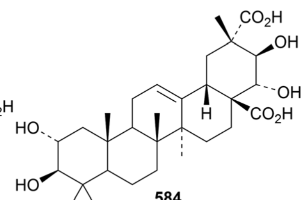

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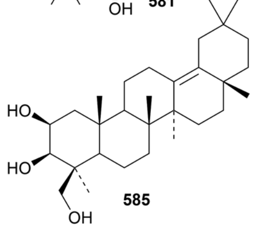

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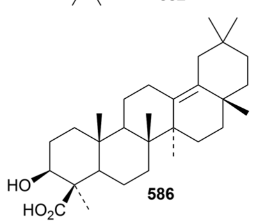

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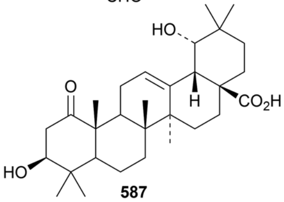

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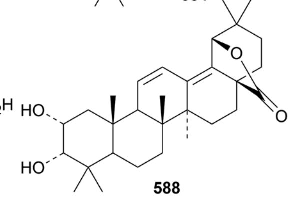

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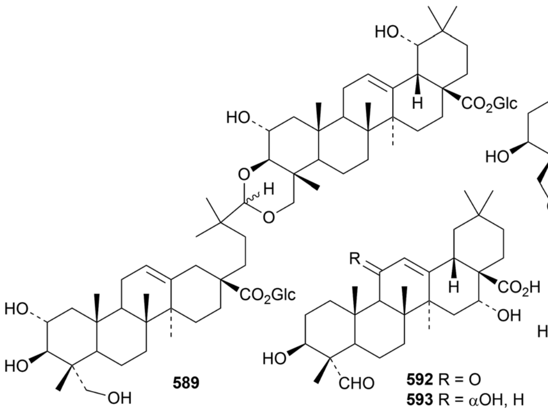
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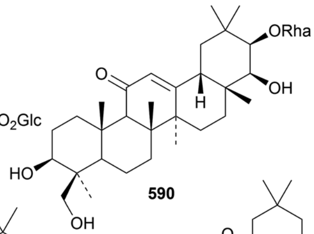
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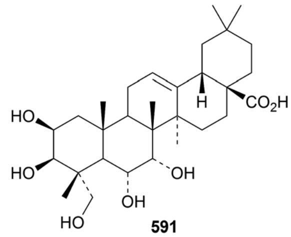
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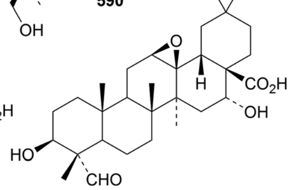
592 R = O
593 R = αOH, H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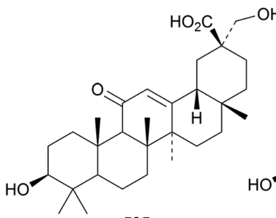
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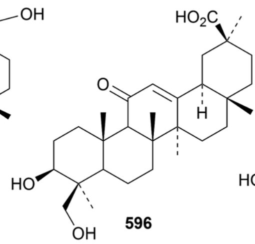
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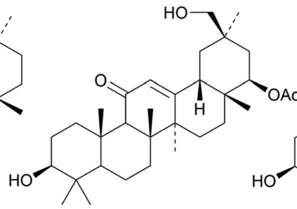
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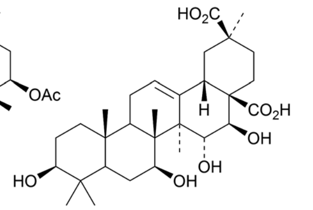
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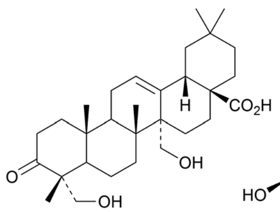
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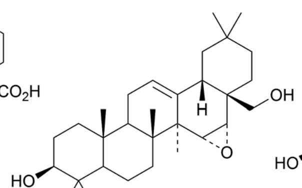
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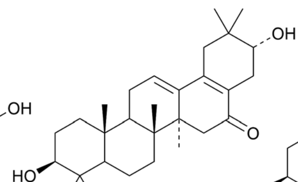
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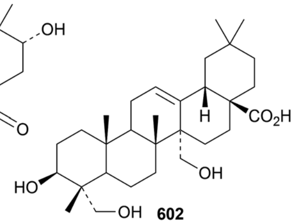
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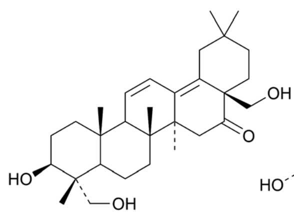
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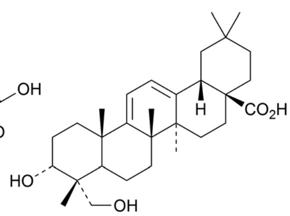
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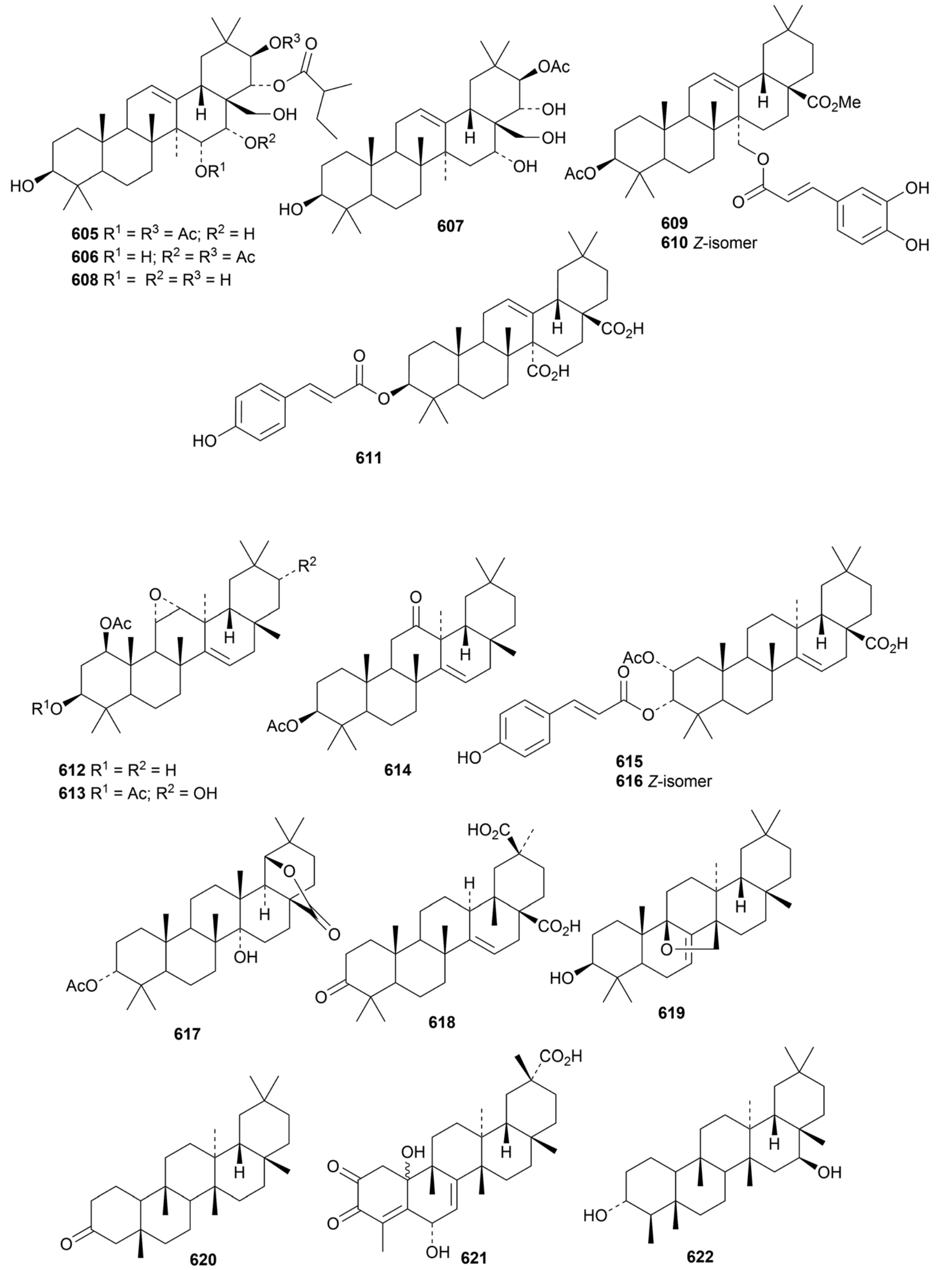
secoursanes include the apoptosis-inducing **625** from *Salvia urmiensis*[285] and **626** and **627** from *Salvia syriaca*.[286] *Rubus lambertianus* is the source of the 18,19-secoursanes **628** and **629** together with the glucopyranosyl esters **630**, **631** and **632**.[287] The related 18,19-secoursane **633** has been isolated from *Rubus innominatus* together with the ring-A contracted ursanes rubuminatus A **634** and B **635** and the ursanes **636** and **637**.[175]

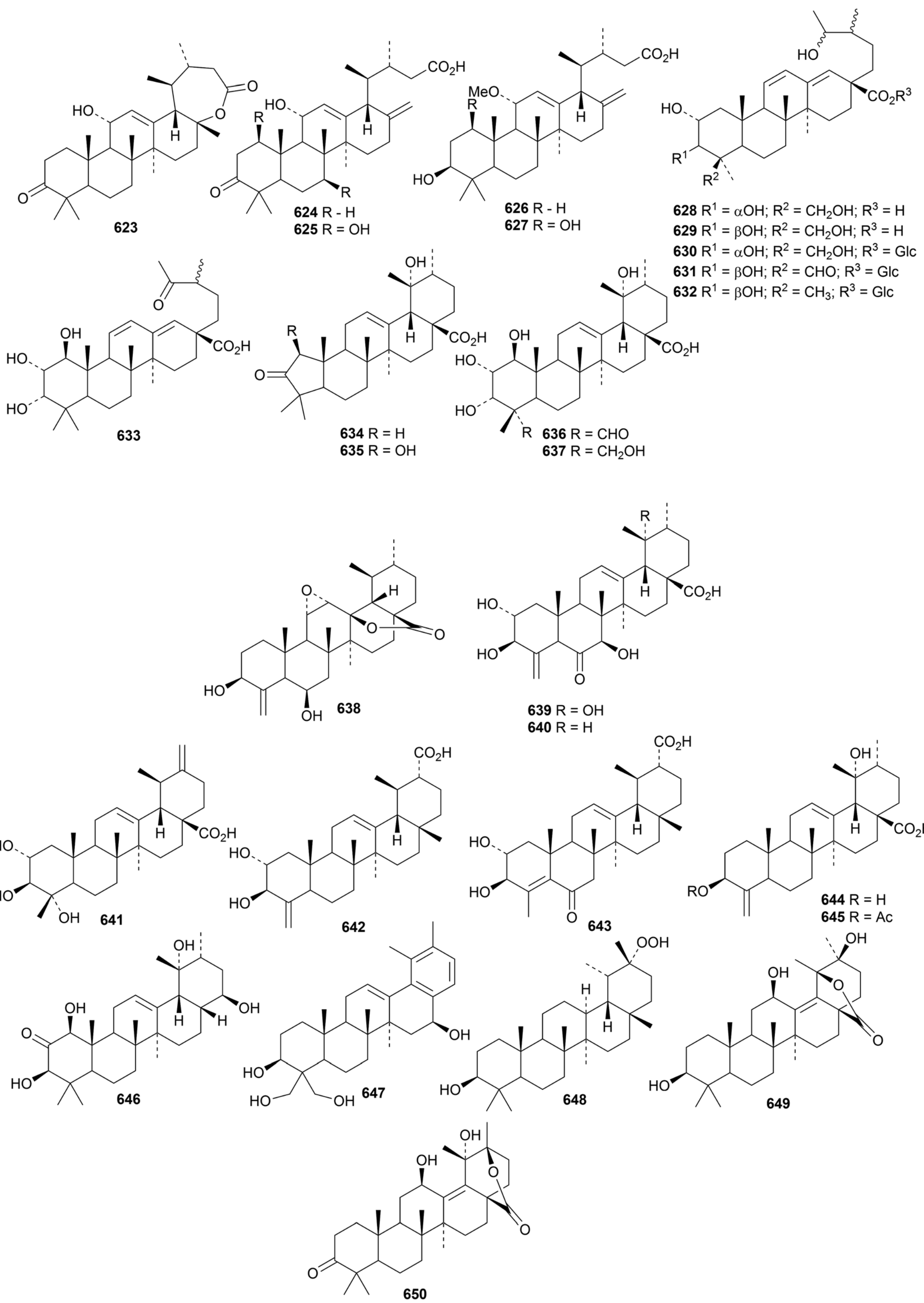
Hookerinoid C **638** from *Pterocephalus hookeri*[288] and gelsenorursanes A **639**–E **643** from *Gelsemium elegans*[289] are 24-norursanes. Further 24-norursanes **644** and **645** have been obtained from *Mostuea hirsuta*.[290] The 28-norursane **646** is a constituent of *Agrimonia pilosa*[291] and the 28-norursane **647**,



with an aromatic ring E, is present in *Gardenia jasminoides* var. *radicans*.[292] Ixeritriterpenol **648** has been reported from *Ixeris chinensis* with unusual stereochemistry at C13 and C19.[293] The structure of 3β,12β,20β-trihydroxy-13(18)-ursen-28,19β-olide **649**, from *Ilex latifolia*, was confirmed by X-ray crystallographic analysis.[294] The related lactone **650** also occurs in *Ilex latifolia*.

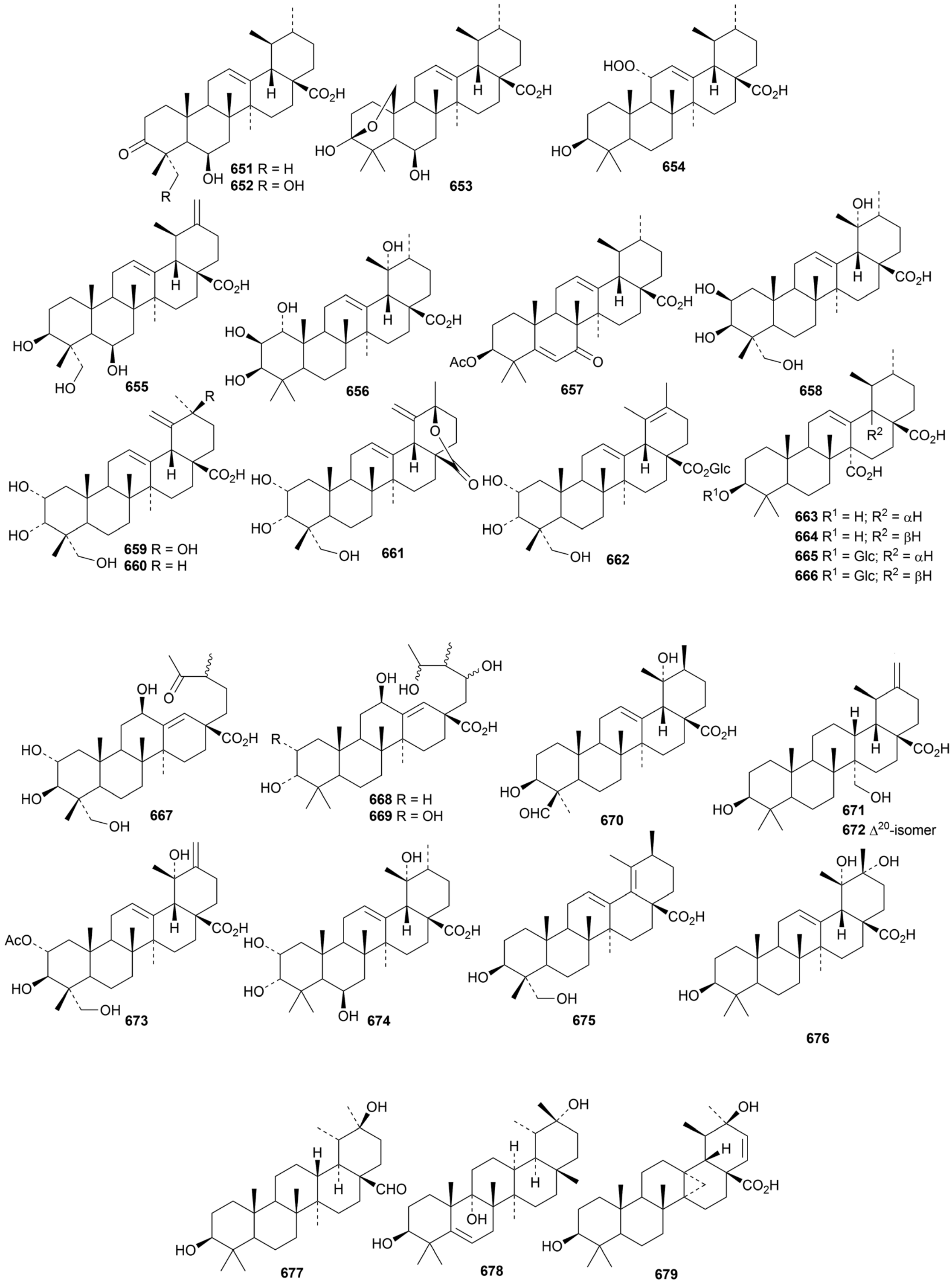
Further simple ursane derivatives include silphanolic acids A **651**, B **652** and D **653** from *Silphium laciniatum*,[16] the 11-hydroperoxide **654** from *Holarrhena curtisii*,[191] 3β,6β,23-trihydroxy-12,20(30)-ursadien-28-oic acid **655** from *Spermacoce latifolia*,[192] 1α,2β,3β,19α-tetrahydroxy-12-ursen-28-oic acid **656** from *Vitellaria paradoxa*,[295] the enone **657** from *Codium dwarkense*,[296] 2β,3β,19α,23-tetrahydroxy-12-ursen-28-oic acid **658** and its glycosyl ester from *Nauclea officinalis*,[297] the related compounds **659**, **660** and **661** and the glucosyl ester **662** from *Oenothera maritima*[298] and the 27,28-dioic acids **663** and **664** and their 3-glucosides **665** and **666** from *Crossopteryx febrifuga*.[299]

New ursane saponins with new genins include bodiniosides E, F and G with the genins **667**, **668** and **669**, respectively, from *Elsholtzia bodinieri*,[300] ilexpublesnin S with genin **670**, with an unusual 20β configuration, from *Ilex pubescens*,[301] pittangretosides C_1 and L with the genins **671** and **672**, respectively, from

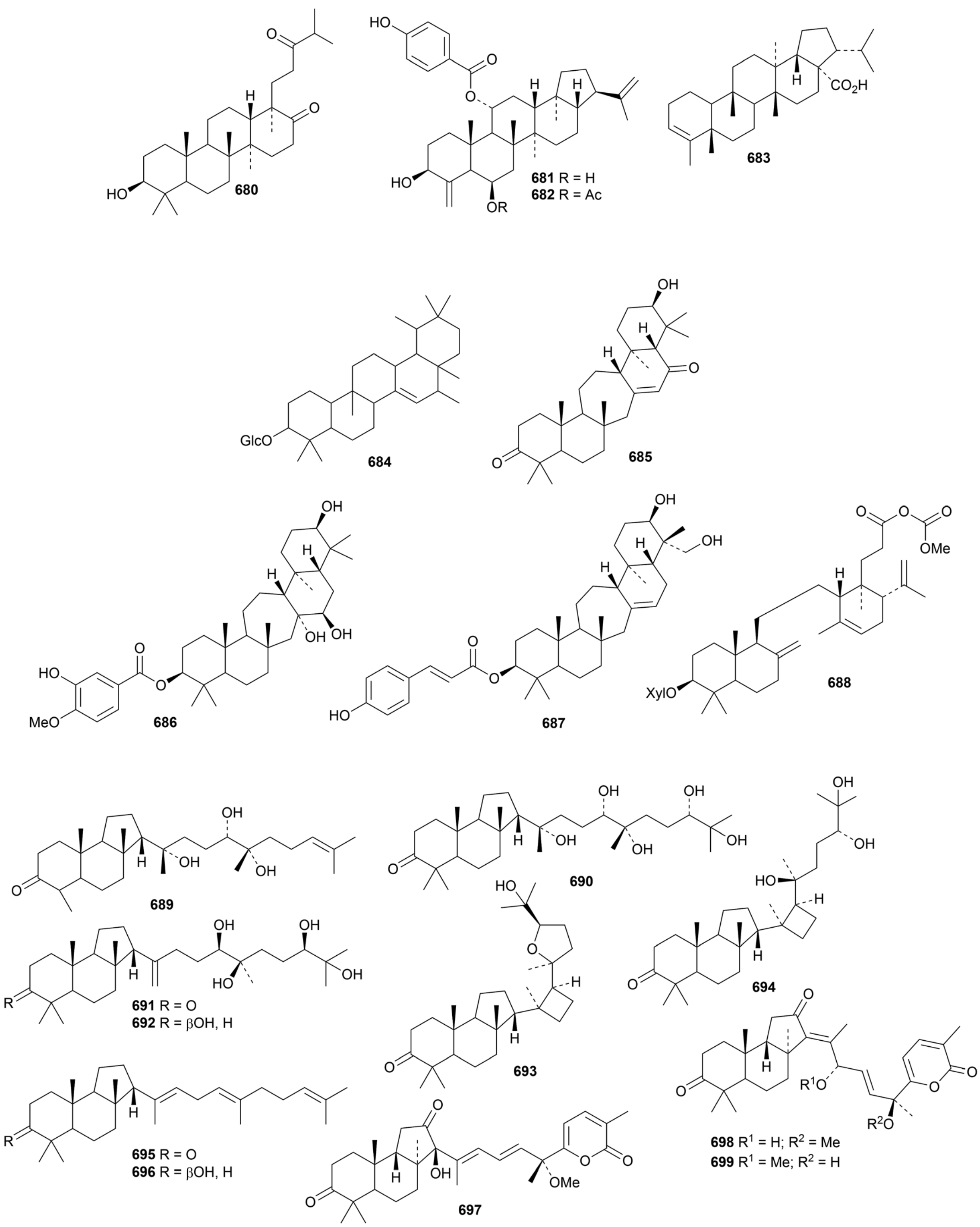


Pittosporum angustifolium[302] and vulgaside II with genin **673** from *Prunella vulgaris*[241] and saponins from *Callicarpa kwangtungensis* with genin **674**,[246] *Ilex cornuta* with genin **675** (ref. 303) and *Ilex kudingcha* with genin **676**.[304]

Named ursane saponins with known genins include amphipaniculoside B from *Amphilophium paniculatum*,[83] catunarosides K and L from *Catunaregam spinosa*,[213] centellasaponins F and G from *Centella asiatica*,[214] comastomasaponins J and K from *Comastoma pedunculatum*[216] and rotundinosides B, C and D from *Ilex rotunda*.[235] Unnamed saponins with known genins have been isolated from *Cassia siamea*,[305] *Clematoclethra scandens* ssp. *actinidioides*,[306] *Firmiana simplex*,[307] *Ilex cornuta*,[204,303,308] *Ilex kudingcha*,[304] *Ilex latifolia*[294] and *Sanguisorba officinalis*.[256]



Fagonicin **677**, from *Fagonia indica*, is 3β,20β-dihydroxytaraxastan-28-al with an unusual stereochemistry at C13 (ref. 200) and genicunolide C **678**, from *Euphorbia geniculata*, is 5-taraxastene-3β,9α,20α-triol.[272] Ilexpublenin T, from *Ilex pubescens* is a taraxastane saponin with a known genin[301] and a saponin from *Clematis uncinata* also has a known taraxastane saponin.[309] The 13,27-cyclo ursane **679** has been identified in *Ochradenus arabicus*.[310]

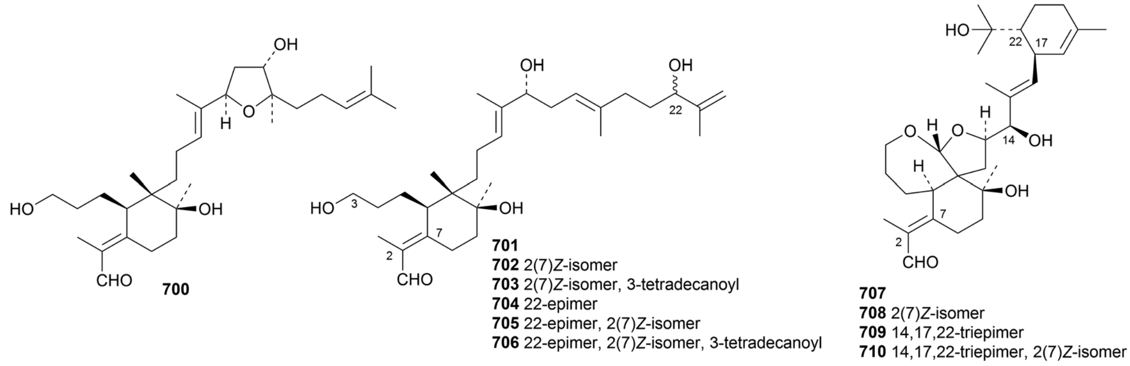


8. The hopane group

The 17,21-secohopane derivative, scabanol **680**, has been isolated from *Gentiana scabra*.[311] Exotheols A **681** and **682**, from *Exothea paniculata*, are 24-norhopane esters.[312] 3-Filicen-28-oic acid **683** is a constituent of the Chinese fern *Lepidogrammitis drymoglossoides*.[313]

9. Miscellaneous compounds

The unlikely structure **684** has been proposed for allotaraxerolide from *Allophylus africanus*.[176] 21β-Hydroxy-14-serratene-3,16-dione **685** has been isolated from *Lycopodiella cernua* together with the serratane esters **686** and **687**.[314] Lansioside D **688**, from *Lansium domesticum*, is a derivative of the 21,22-seco-



onocerane lansiolic acid.[315] Lansioside D **688** showed potent activity against Gram-positive bacteria.

Six malabaricane derivatives **689–694** have been obtained from *Ailanthus malabarica*, including two containing cyclobutane rings.[316] Further malabaricanes **695** and **696** have been found in *Bursera microphylla*.[317] The isomalabaricane derivatives stellettins N **697**, O **698** and P **699** have been identified in extracts of the marine sponge *Stelletta tenuis*.[318] All three stelletins showed significant cytotoxic activities. Stelletin N is a duplicate name.

Iris tectorum is the source of several iridal triterpenoids including iritectols C **700**–F **703** and the 22-epimers **704**, **705** and **706** (ref. 319) and polycycloiridals A **707**–D **710**.[320]

10. Conflicts of interest

There are no conflicts of interest.

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