

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.

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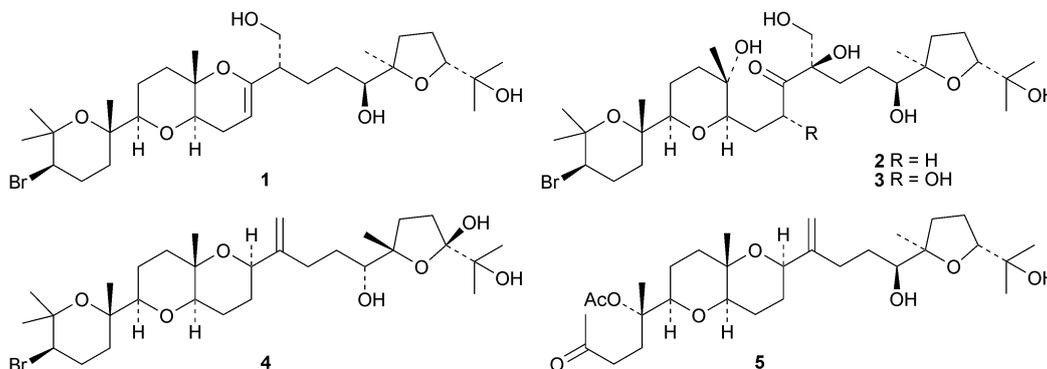
1 Introduction

Interest in the biological activities of triterpenoids continues with reviews on their anti-inflammatory,^{1,2} antiviral,³ anti-tumour,^{4–6} anti-HIV⁷ and insecticidal⁸ 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 Pinaceae¹⁴ and Meliaceae¹⁵ families. Triterpenoid saponins show a range of biological activities¹⁶ and this has generated interest in their biosynthesis¹⁷ and improvement of yields from natural sources.¹⁸ Reviews covering triterpenoid saponins from *Camellia*¹⁹ and *Polygala*²⁰ species and the Theaceae²¹ and Caryophyllaceae and Illecebraceae²² families have appeared.

2 The squalene group

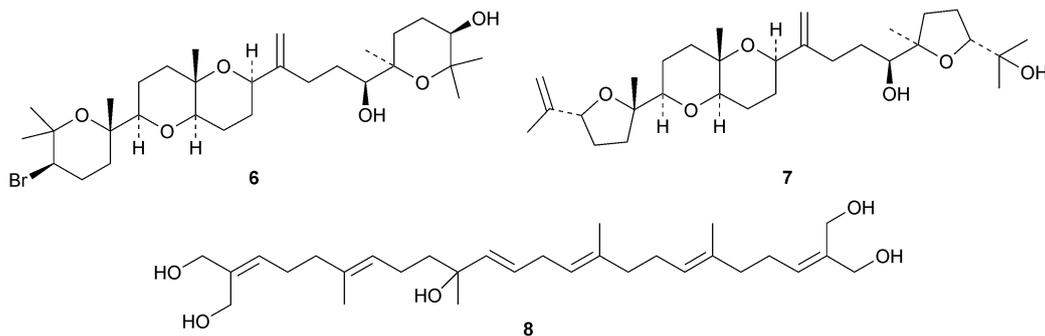
15-Dehydroxythyrserol A **1**, prethyrserol A **2** and 13-hydroxy-prethyrserol A **3** are new cytotoxic squalene derivatives from *Laurencia viridis*.²³ The related compounds 22-hydroxy-15(28)-dehydrovenustatriol **4**, secodehydrothyrseriferol **5**, iubol **6** and 1,2-dehydropseudodehydrothyrseriferol **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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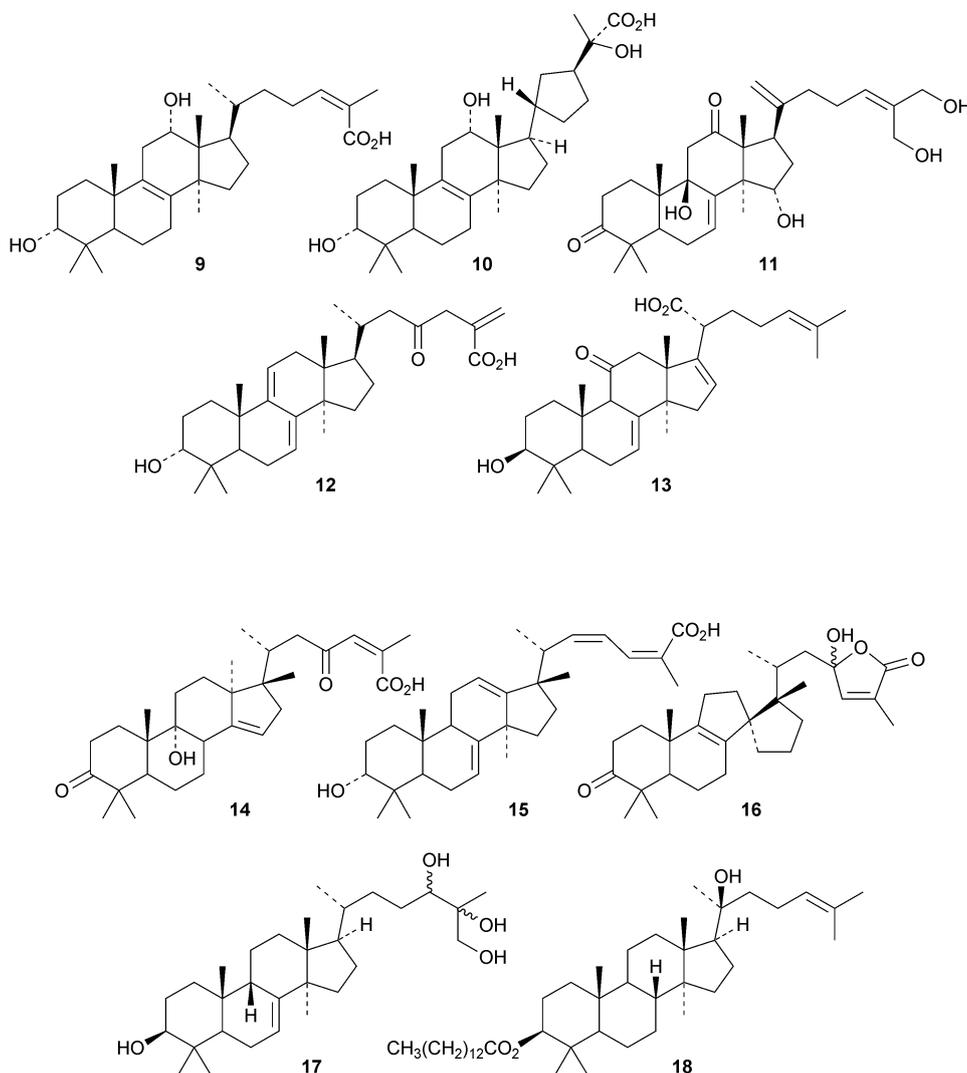


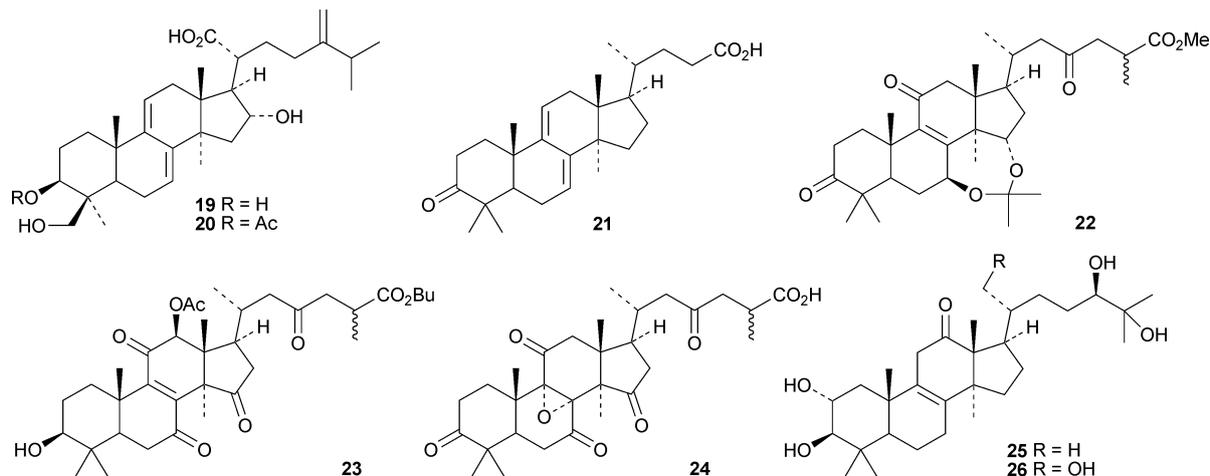
3 The lanostane group

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

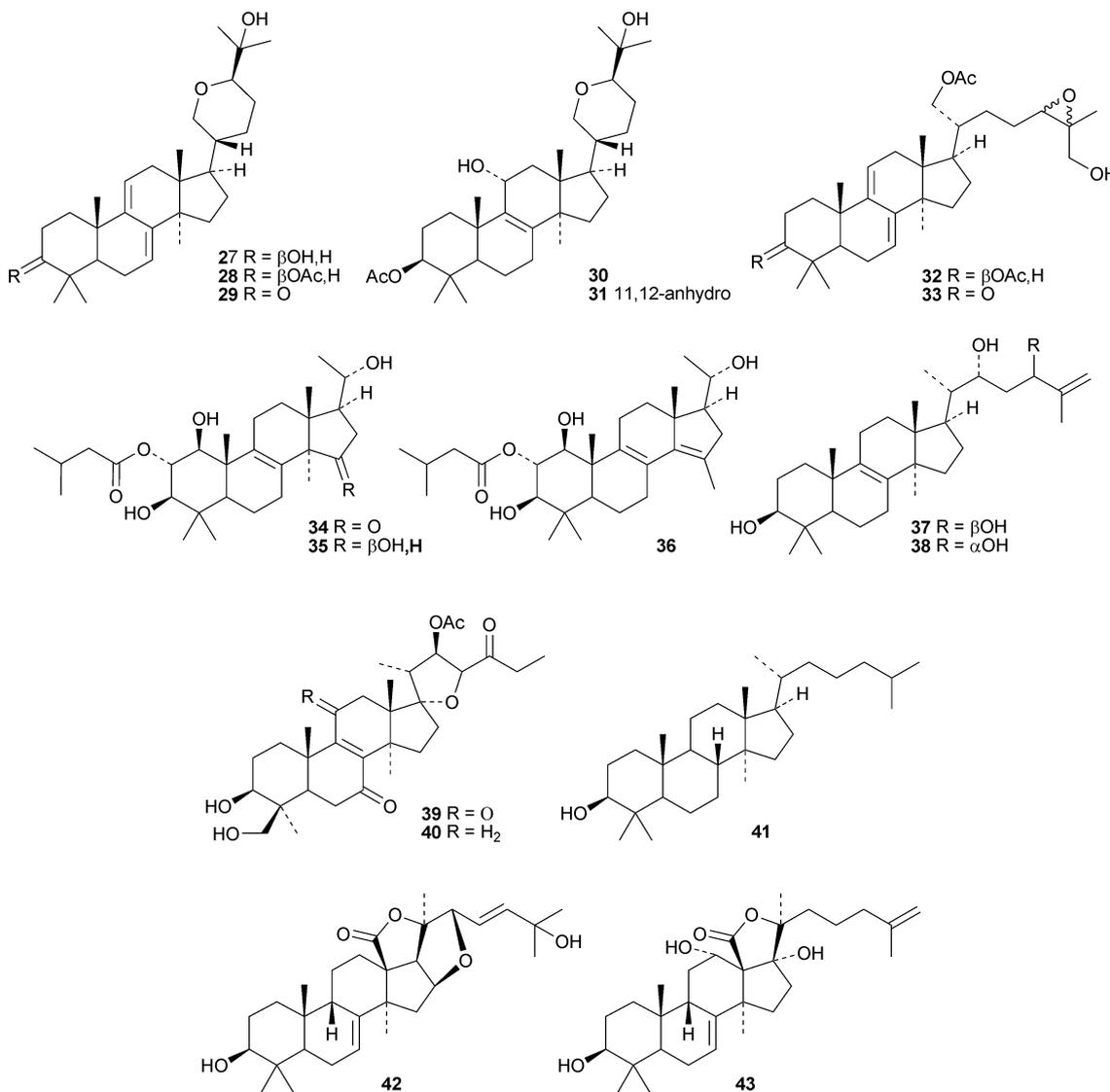
Bioactive lanostane derivatives from fungi include **19** and **20** from *Poria cocos*³¹ and 24,25,26-trinor-3-oxolanosta-7,9(11)-dien-24-oic acid **21**³² and methyl ganoderate A acetone **22** and butyl ganoderate H **23**³³ from *Ganoderma lucidum*. The epoxy-ganoderic acid **24** is also a constituent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





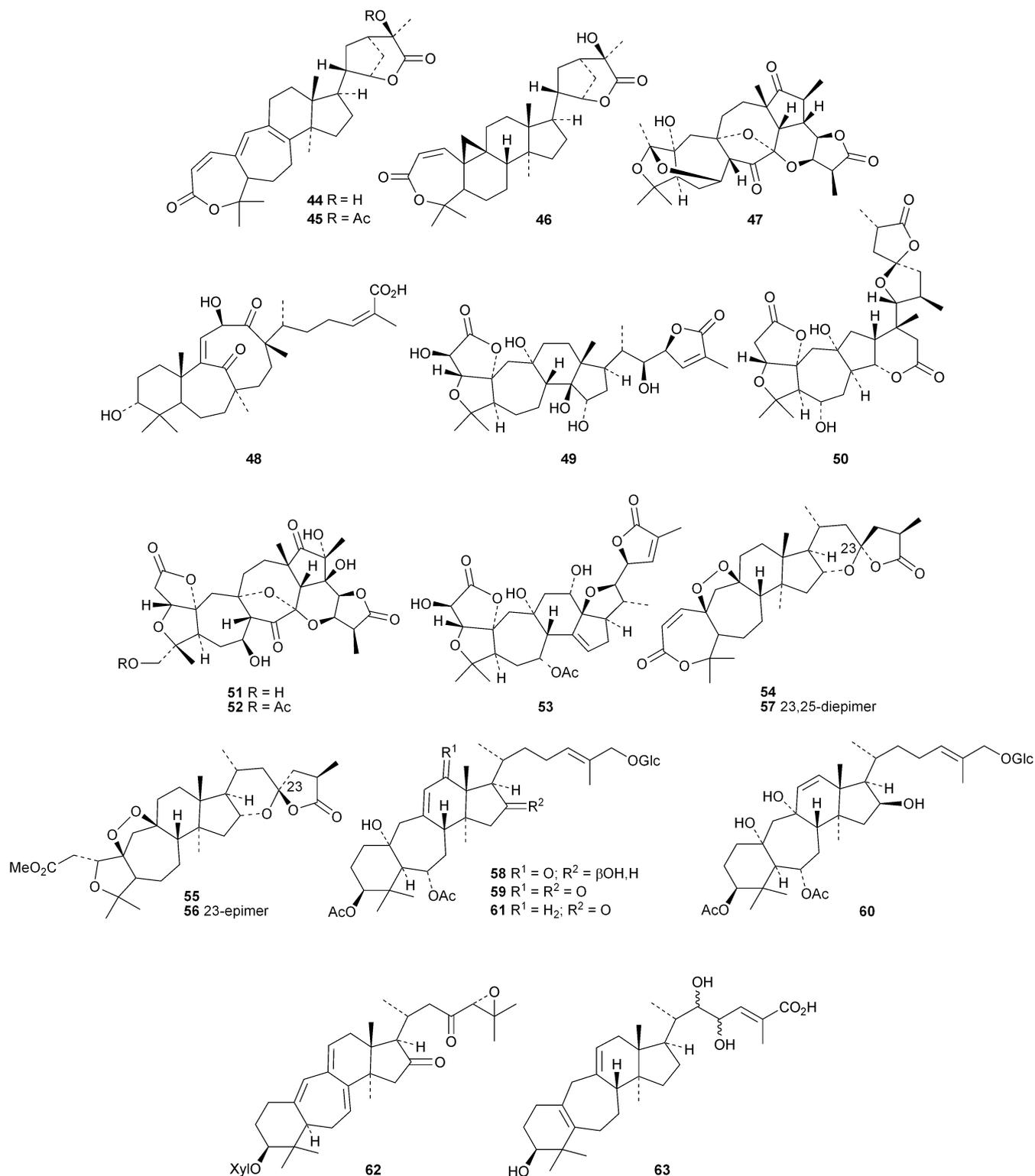
Fasciculols H 25 and I 26 are constituents of the Chinese mushroom *Naematoloma fasciculare*.³⁷ The entomopathogenic fungus *Hypocrella* sp. BCC 14524 is the source of the lanostanes hypocrellols A–G 27–33.³⁸ Xylariacins A 34, B 35 and C 36 have

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



Erylosides R₁, T₁, T₂, T₃, T₄, T₅ and T₆ 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-3 β -ol 41 is a new genin of a diglucuronide from the flowers of *Punica granatum*.⁴³

Cucumariosides H₅, H₆, H₇ and H₈ are new holostane glycosides from the sea cucumber *Eupentacta fraudatrix*.⁴⁴ Cucumarioside H₈ 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

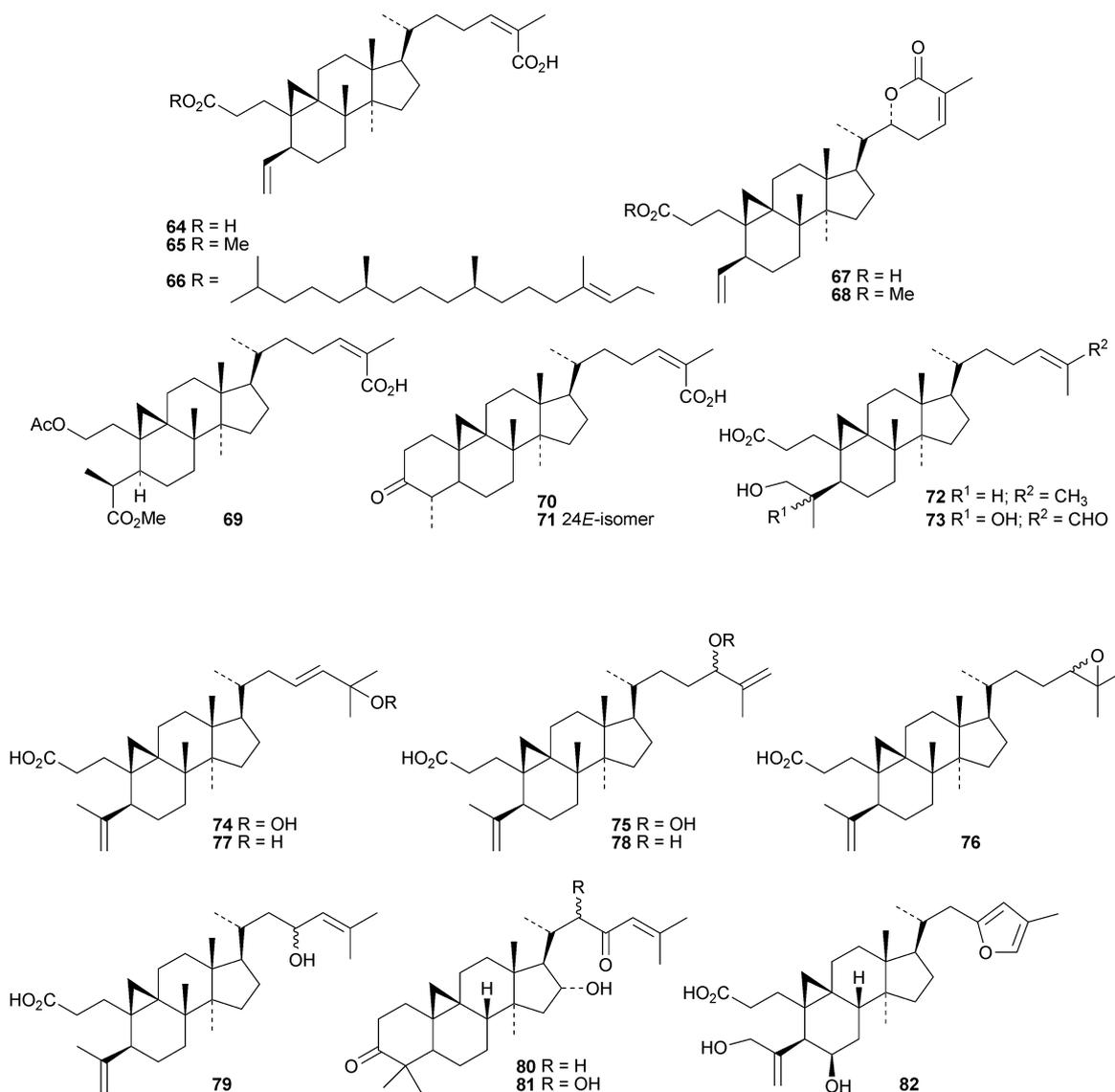


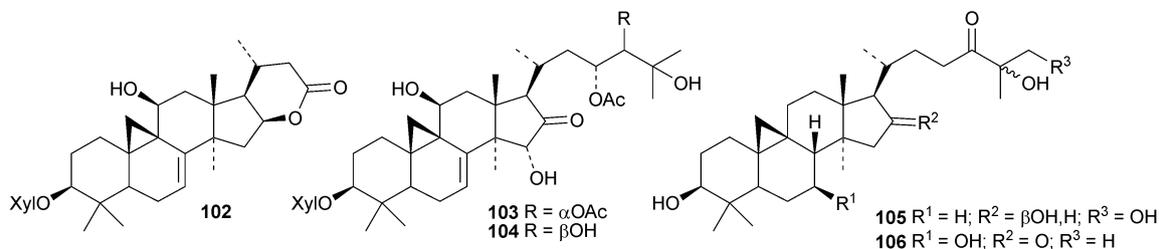
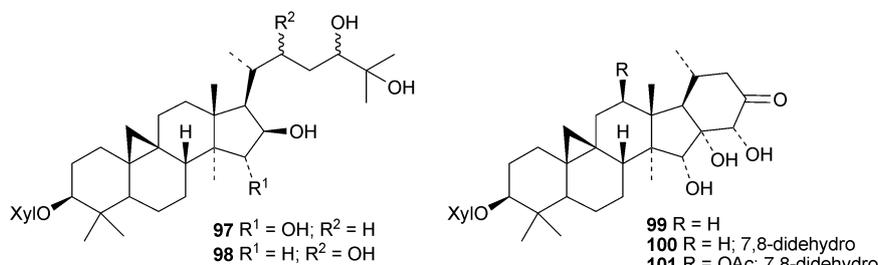
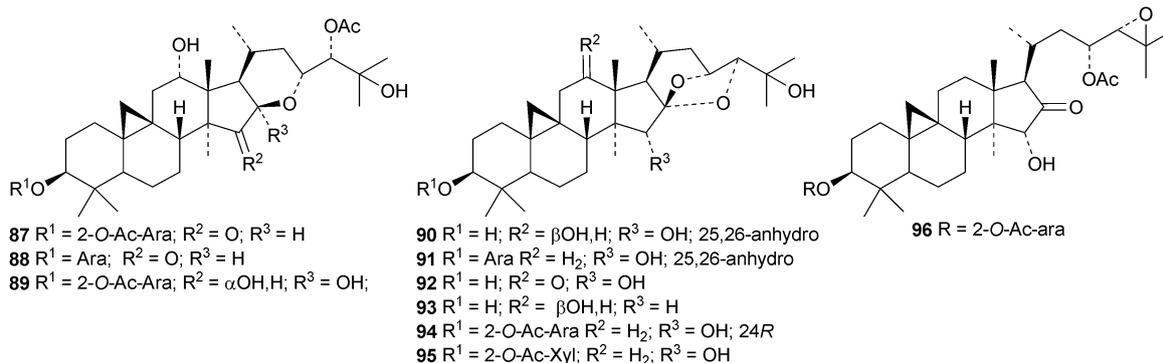
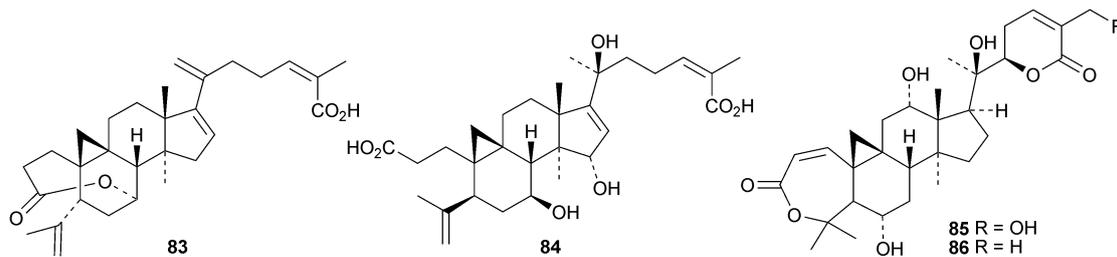
glycosides with known genins, liouvillosides A₄ and A₅, have been isolated from the sea cucumber *Staurocucumis liouvillei*.⁴⁶

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 bisnor-derivative 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 50⁵¹ and wilsoniadilactones D–F 51–53⁵² are new constituents of *Schisandra chinensis*, *Schisandra sphenanthera* and *Schisandra wilsoniana*, respectively. Four new peroxy-lactones, pseudodarolidides Q₂ 54, T₁ 55 and T₂ 56⁵³ 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 87–96⁶⁴ 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





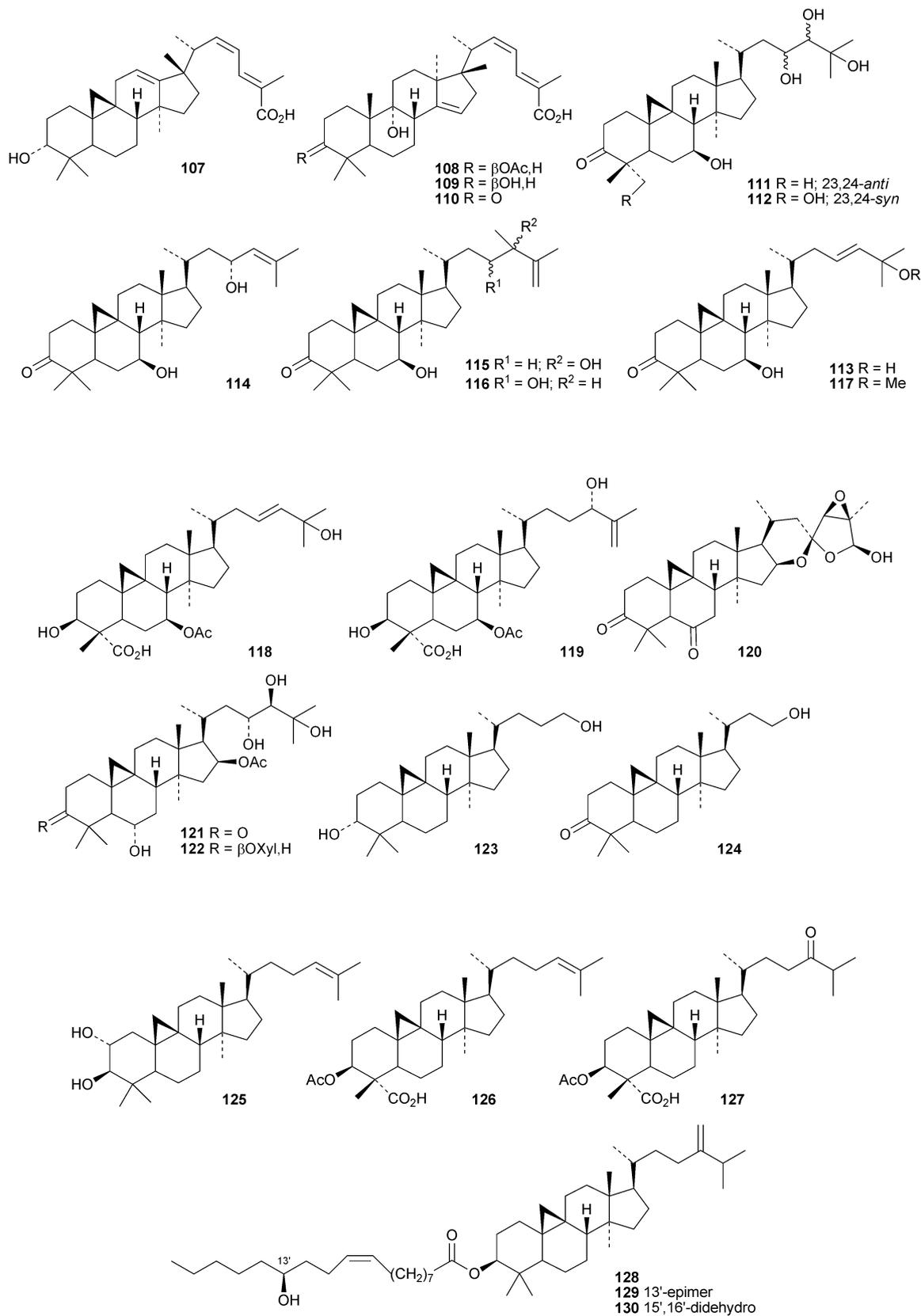
105 and **106**, from the leaves of *Tarenna gracilipes*.⁶⁷ Tarecilio-sides H–K have known gens.

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 quadrangulare*,⁶⁹ bicusposides D–F **120–122** from *Astragalus bicuspis*,⁷⁰ macrostachyosides A **123** and B **124** from *Mallotus macrostachyus*,⁷¹ cycloart-24-ene-2 α ,3 β -diol **125** from the stigma of *Zea mays*⁷² and boniatic acids A **126** and B **127** from *Radermachera boniana*.⁷³ Boniatic 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 gens 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 colocythins A, B and C, from 24S to 24R. Compounds **140** and **141**, from the roots of *Wilbrandia*

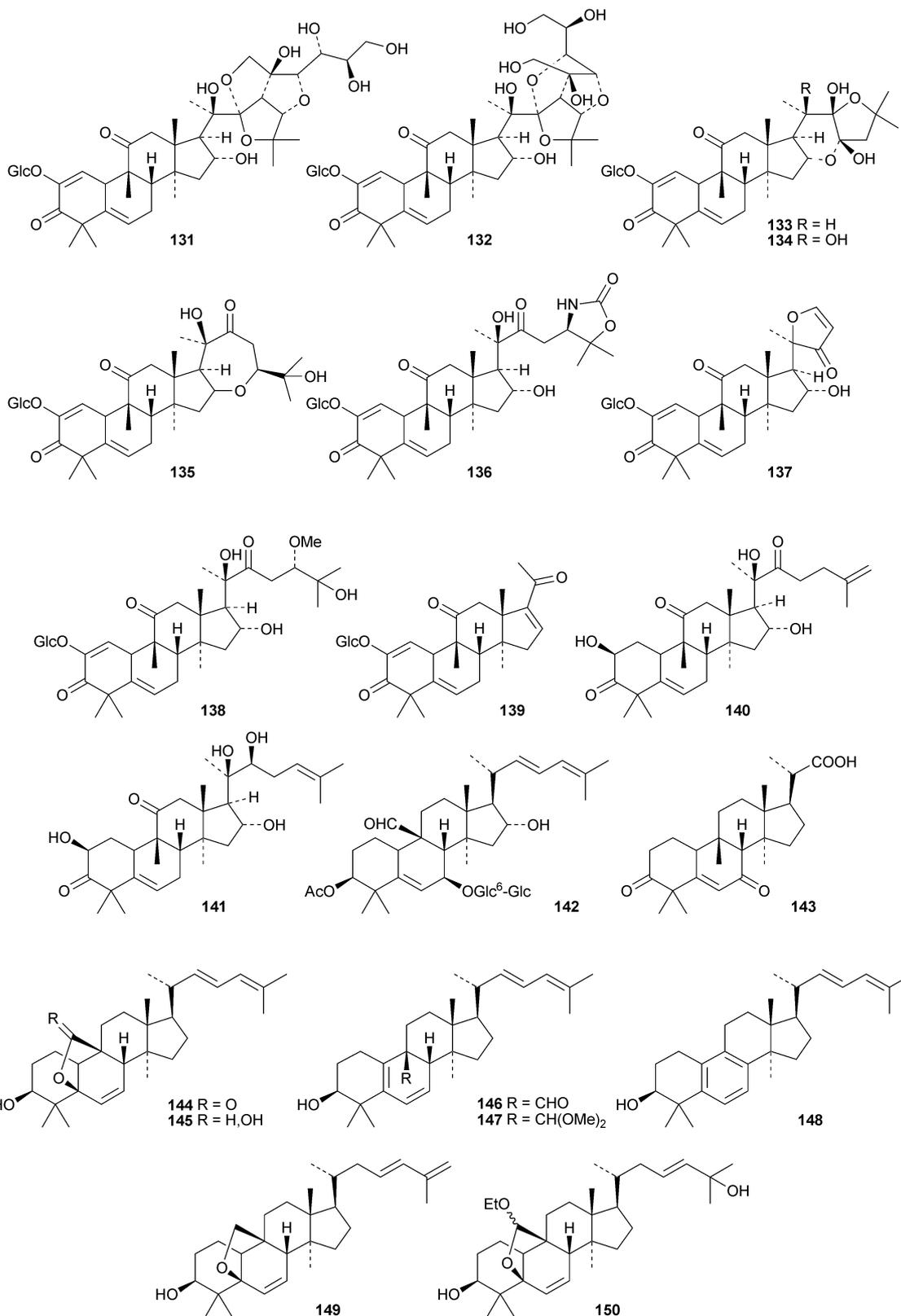




ebracteata, are reported to have cytotoxic activity.⁸² New cucurbitanes from *Momordica charantia* include the antioxidants taiwacins A 142 and B 143 from the stems and fruit,⁸³ 144–148⁸⁴

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





4 The dammarane group

Gypsapogenins A 151 and B 152 are modified dammaranes, with an unusual ring A, from *Gynostemma pentaphyllum*, where

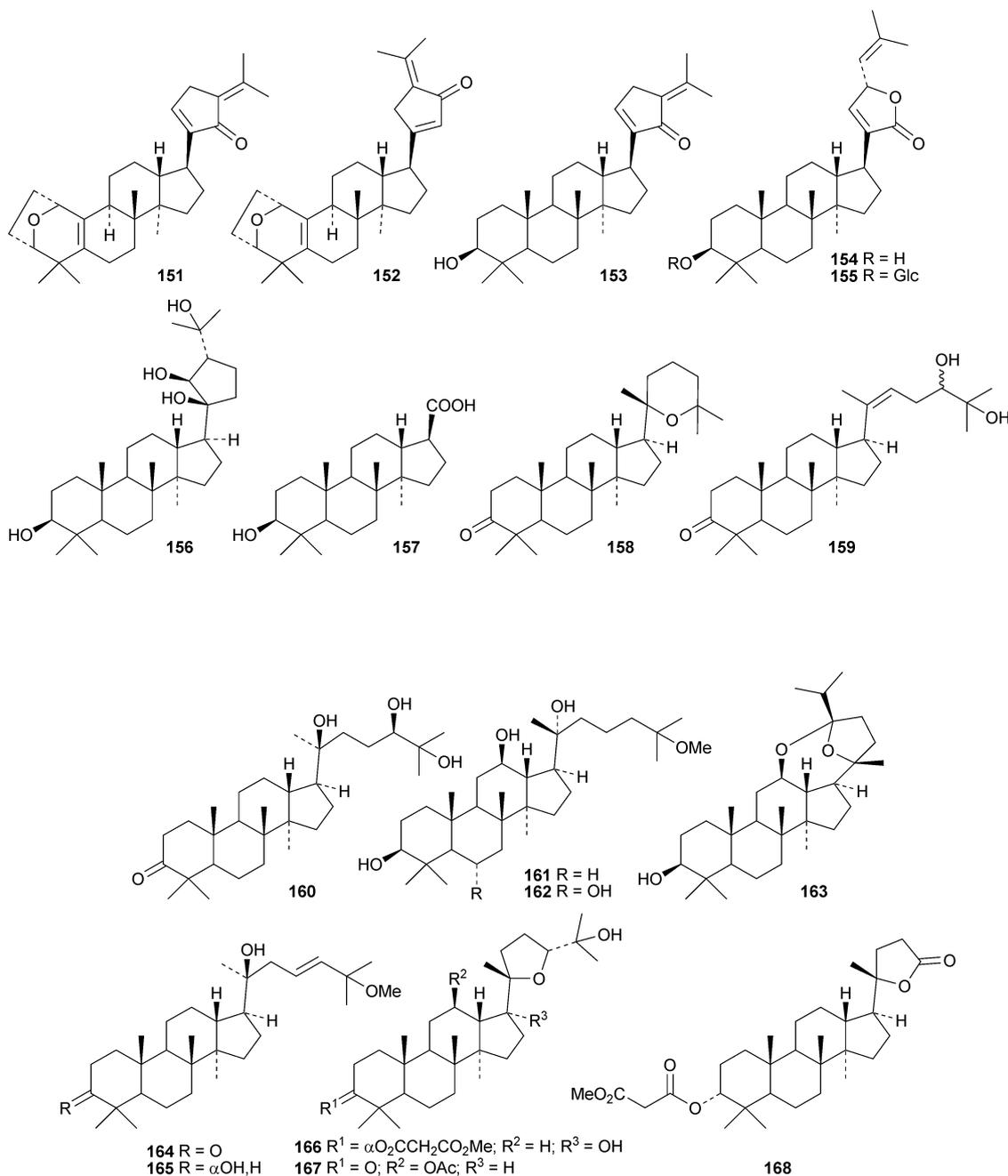
they are found with gypsapogenins C 153, D 154 and the glucoside 155⁸⁷ and the 21,24-cyclo derivative 156 and the nonandammarane 157.⁸⁸ The structure of gypsapogenin A 151 was confirmed by X-ray analysis. Other new dammaranes

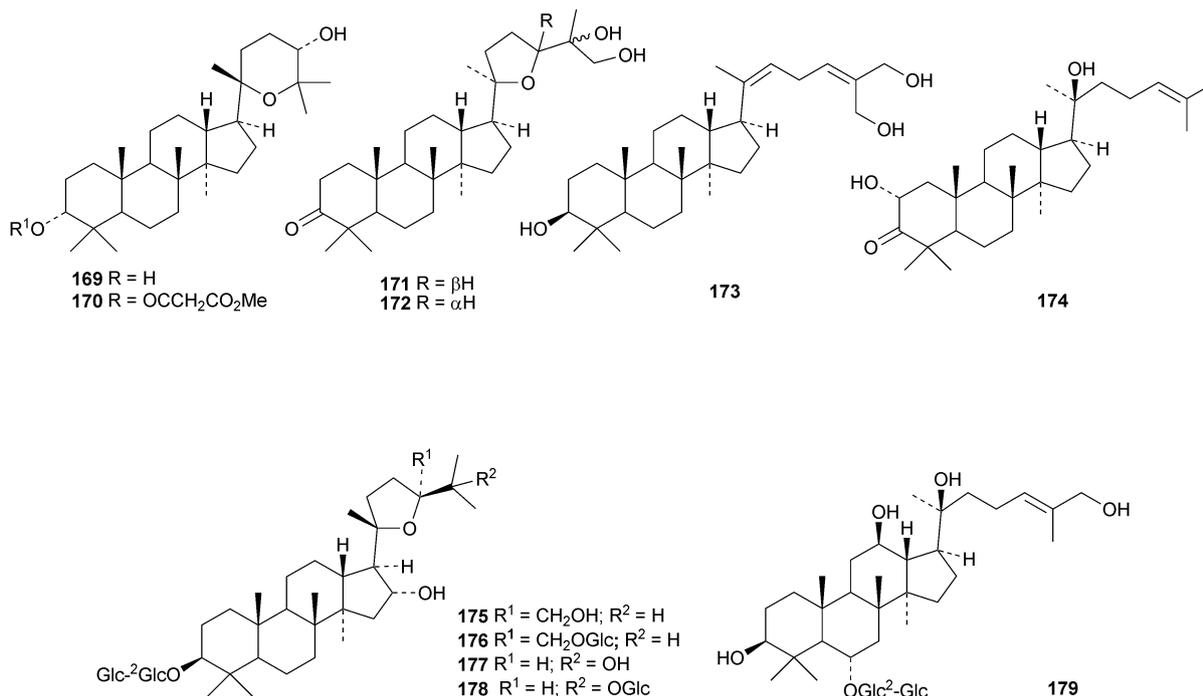


include gardaubryones A–C **158–160** from *Gardenia aubryi*,⁸⁹ **161–163** from the berries of *Panax ginseng*,⁹⁰ **164–170** from the floral spikes of *Betula platyphylla* var. *japonica*,⁹¹ the 24-epimers **171** and **172** from the apical buds of *Gardenia collinsae*,⁹² dammara-20(22),24-diene-3 β ,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 3 β -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 Re₁–Re₆ have been reported from the root of *Panax ginseng*, only ginsenoside Re₅ **179** has a new genin.⁹⁵ Panajaponol, from the roots of *Panax japonicus* var. *major*, is identical to ginsenoside Re₅ **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 betalnositides B and C from *Betula alnoides*,⁹⁹ centellosides A and B and ginsenosides Mc and Y from *Centella asiatica*,¹⁰⁰ ginsenosides Ra₄–Ra₉¹⁰¹ and 20R-ginsenoside ST₂¹⁰² from *Panax*

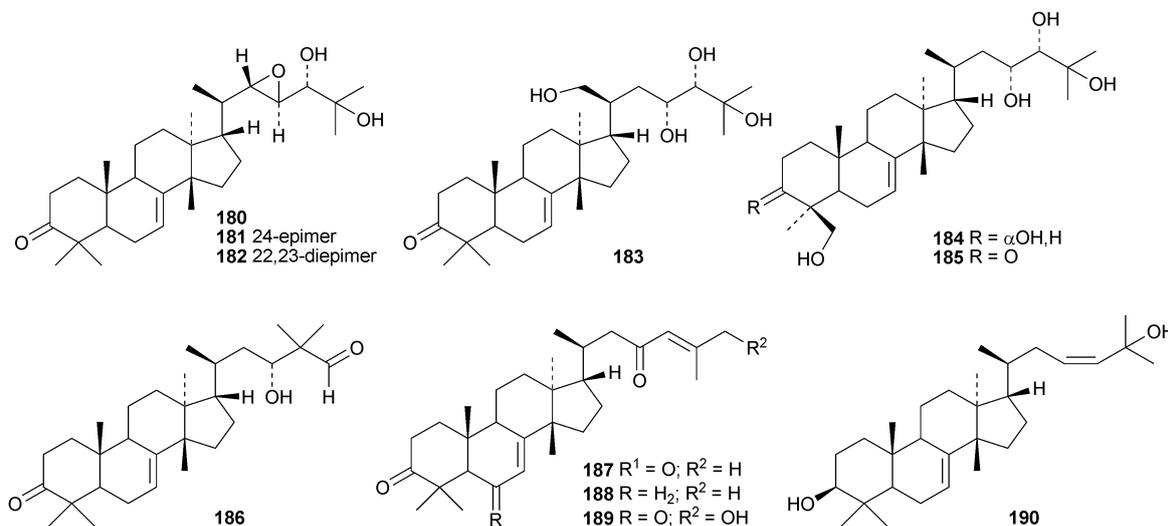


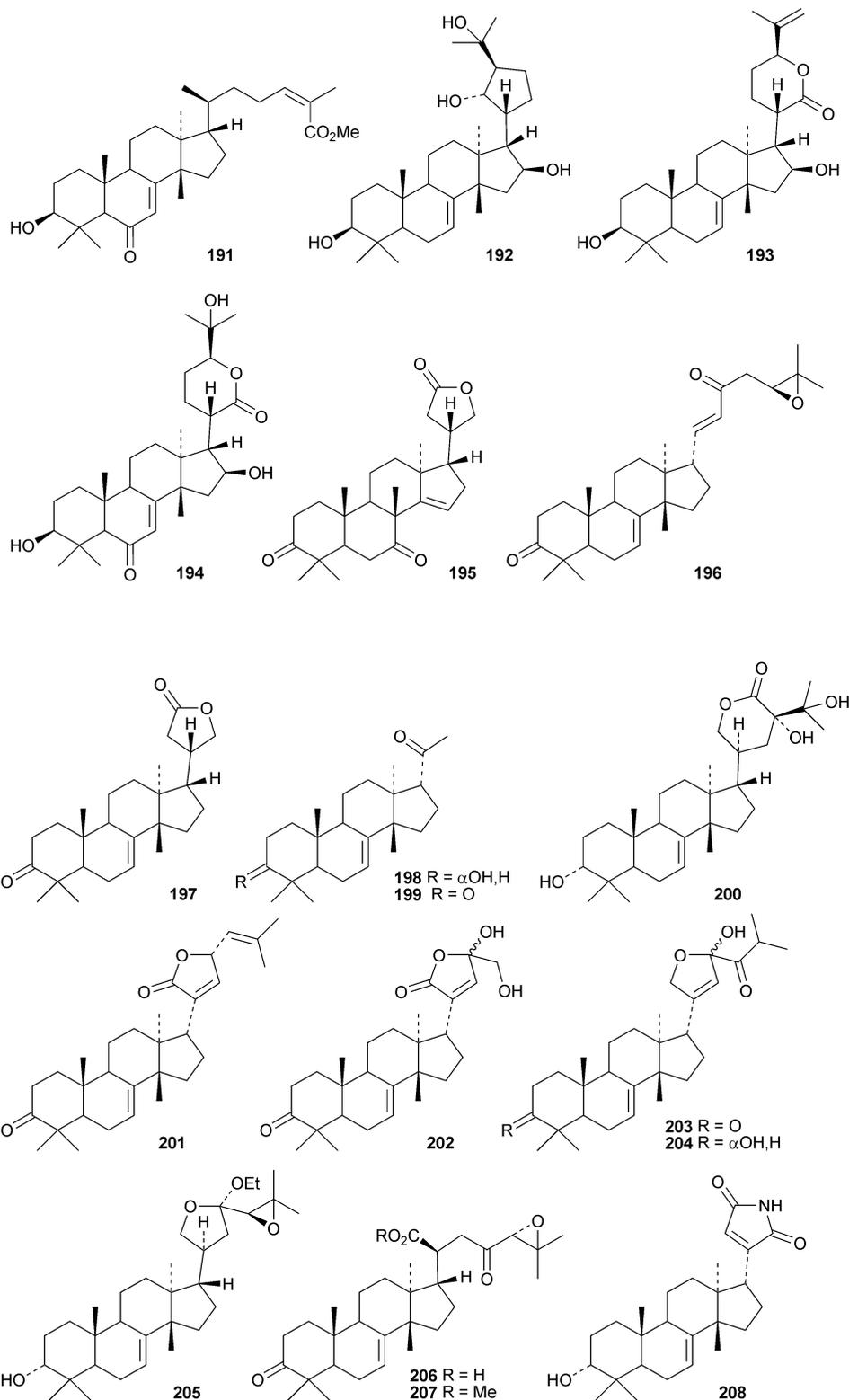


ginseng, gypenosides GC1–GC7 from *Gynostemma pentaphyllum*,¹⁰³ notoginsenosides SFT₁–SFT₄ from *Panax notoginseng*,¹⁰⁴ pseudoginsenosides G₁ and G₂ from *Panax quinquefolium*,¹⁰⁵ yesanchinosides R₁ and R₂ from *Panax japonicus*¹⁰⁶ and unnamed saponins from *Gynostemma pentaphyllum*.¹⁰⁷

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





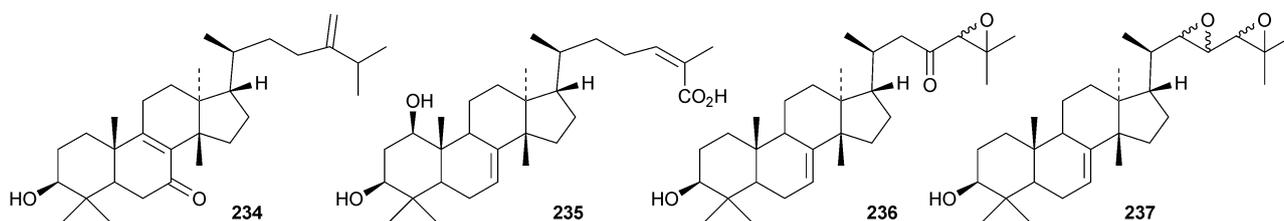
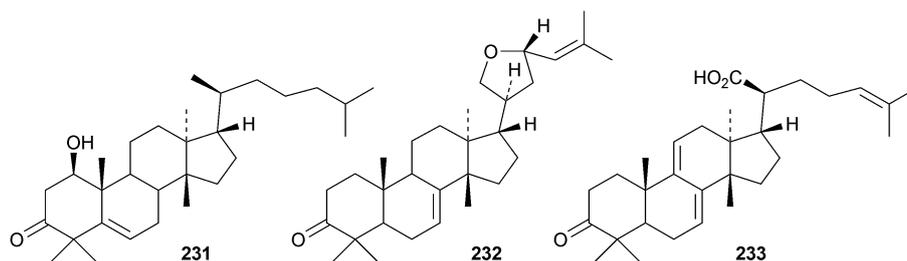
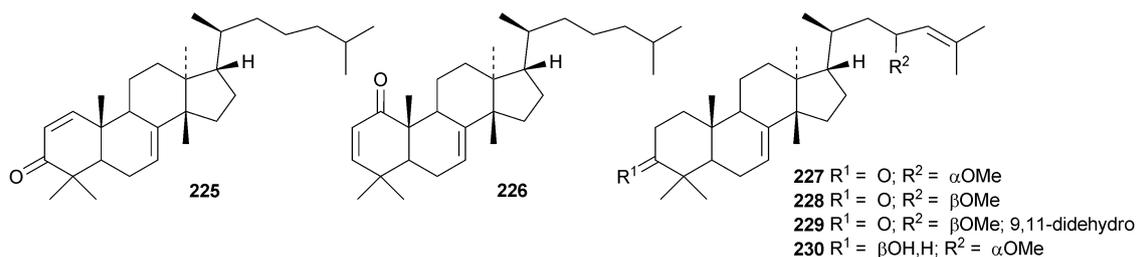
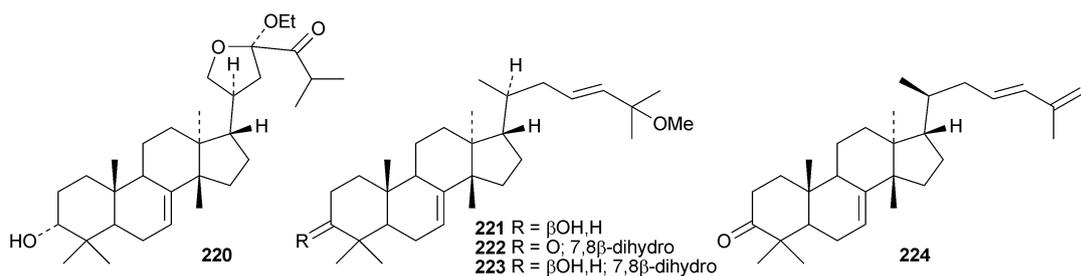
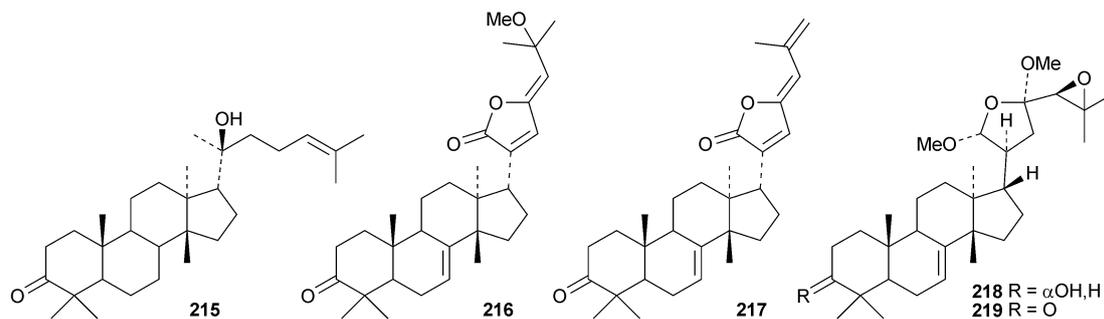
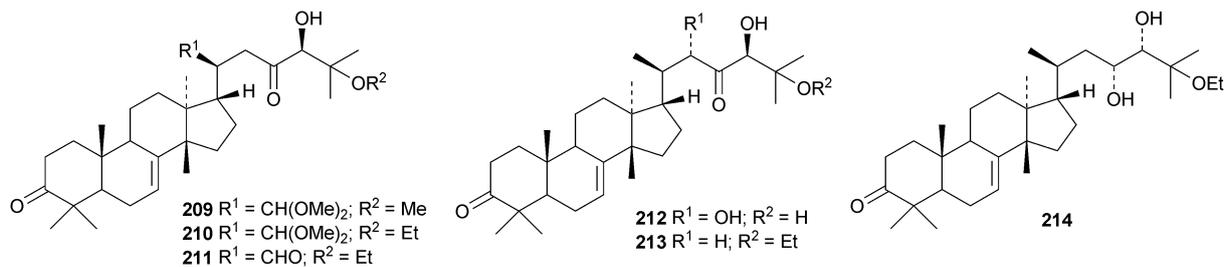
235 from Jordanian propolis¹¹⁷ and 236 and 237 from *Azadirachta indica*.¹¹⁸

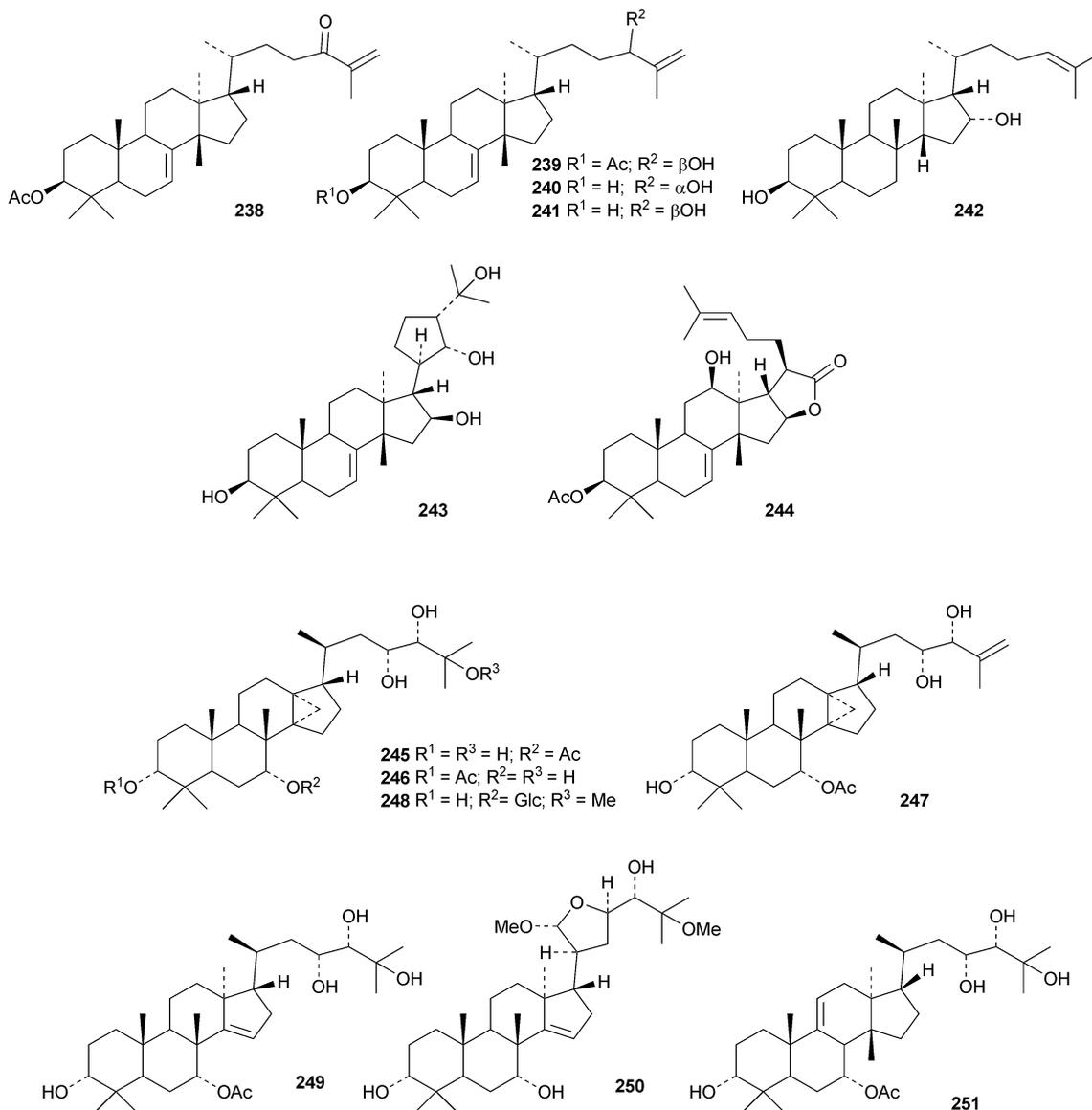
Only seven euphane triterpenoids have been reported. They are compounds 238–241 from the bark of *Broussonetia papyrifera*,¹¹⁹ nepetadiol 242 from *Nepeta suaveis*¹²⁰ and the 21,24-

cycloephane 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,







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

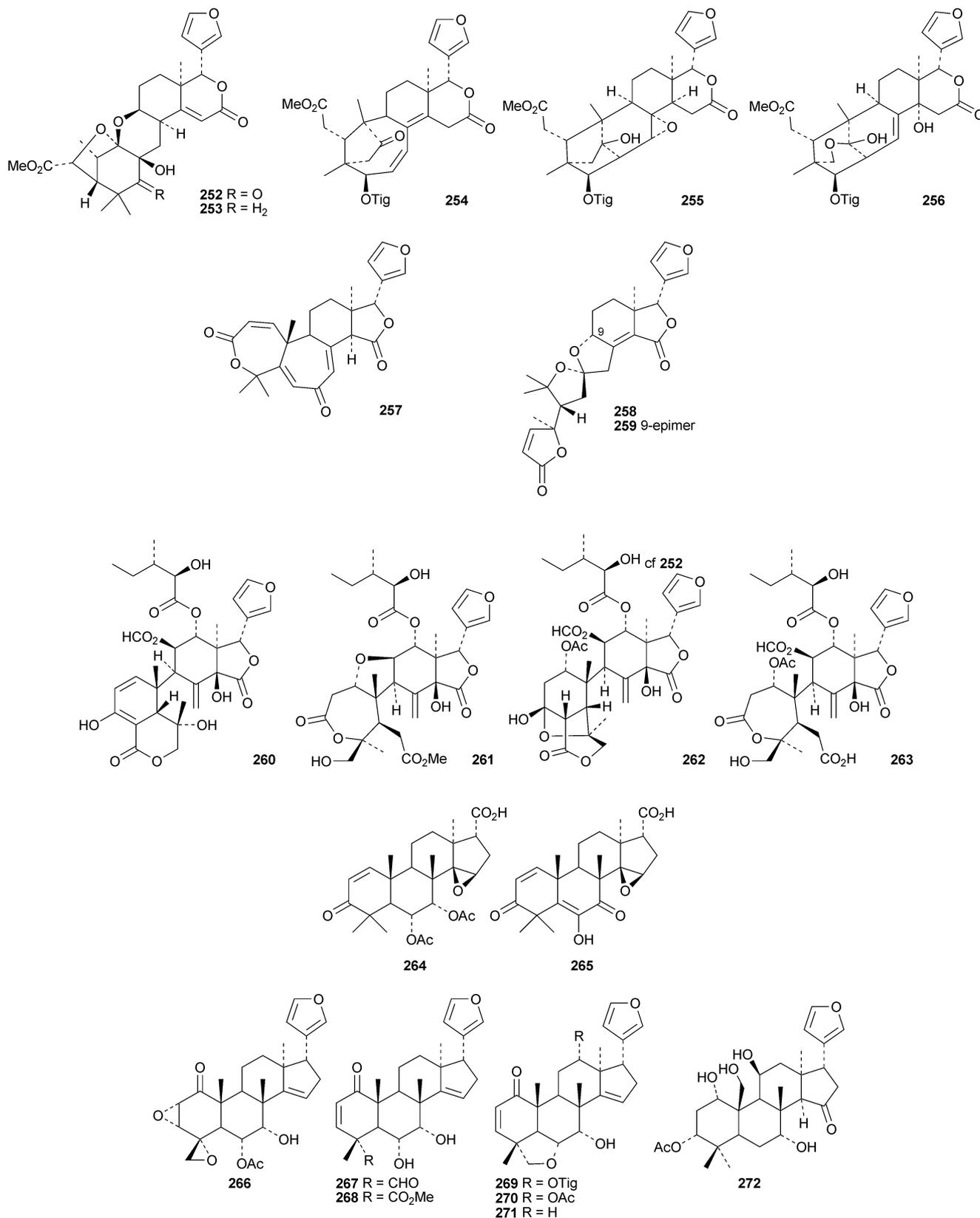
4.1 Tetranortriterpenoids

Reviews have appeared on limonoids from the Meliaceae¹²³ 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 aphapolytins 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 toonapubescic acids A **264** and B **265** from *Toona ciliata* var. *pubescens*.¹⁰⁸ The structure of the methyl ester of toonapubescic 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

Dasyllactones 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

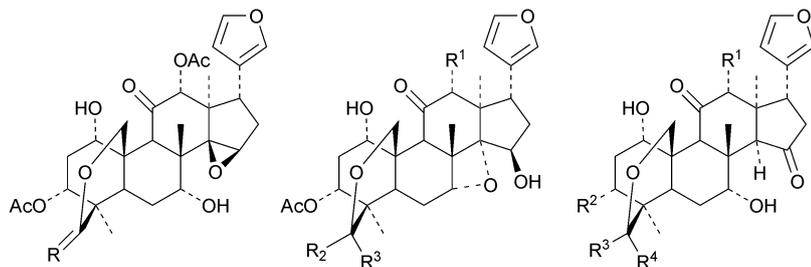




Three methyl angolensate derivatives **301–303** have been found in the root bark of *Entandrophragma angolense*, where they occur with the gedunin derivatives **304** and **305**.¹³⁷ Compound **301** is the same as moluccensin O which was published in 2010.

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.

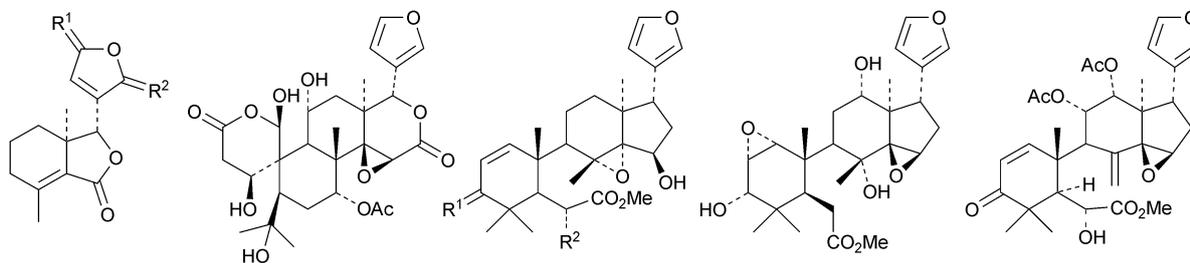




273 R = O
274 R = OMe, H

275 R¹ = OAc; R² = OMe; R³ = H
276 R¹ = R³ = OH; R² = H
277 R¹ = R² = OH; R³ = H

278 R¹ = R² = OAc; R³ = OMe; R⁴ = H
279 R¹ = OAc; R² = OH; R³ = OMe; R⁴ = H
280 R¹ = R² = OH; R³ = OMe; R⁴ = H
281 R¹ = OH; R² = OAc; R³ = H; R⁴ = OMe
282 R¹ = R² = OAc; R³ = H; R⁴ = OMe



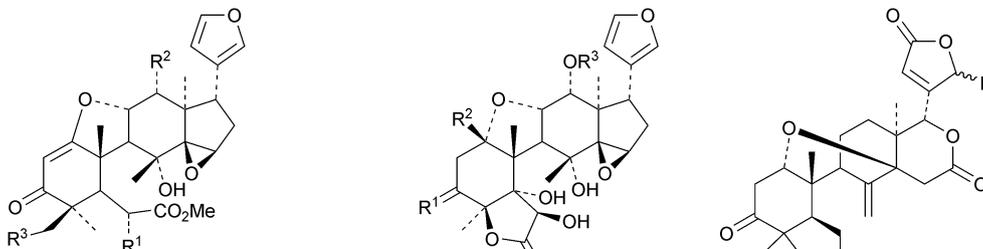
283 R¹ = O; R² = OH, H
284 R¹ = OH, H; R² = O

285

286 R¹ = α OH, H; R² = OH
287 R¹ = O; R² = OH
288 R¹ = O; R² = H

289

290



291 R¹ = H; R² = OH; R³ = H

292 R¹ = OAc; R² = OH; R³ = H

293 R¹ = H; R² = R³ = OAc

294 R¹ = OAc; R² = OH; R³ = H; 1 β ,2-dihydro

295 R¹ = OAc; R² = OH; R³ = OAc; 1 β ,2-dihydro

300 R¹ = OAc; R² = R³ = H

296 R¹ = β OH, H; R² = OH; R³ = H

297 R¹ = α OH, H; R² = OH; R³ = H

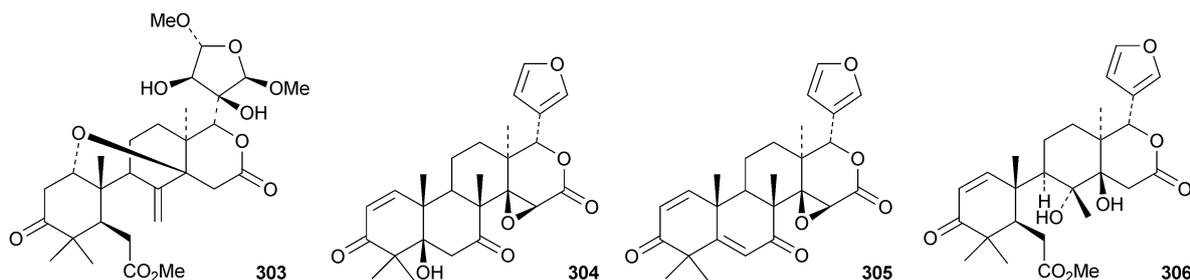
298 R¹ = O; R² = H; R³ = Ac

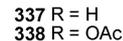
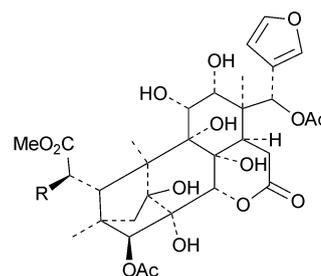
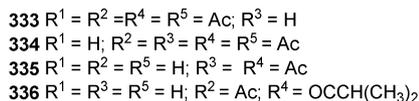
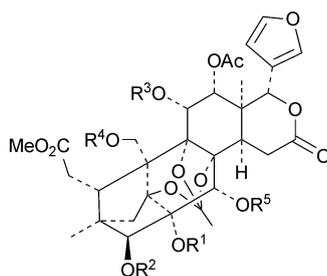
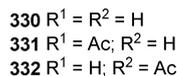
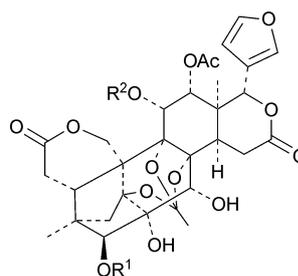
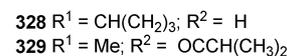
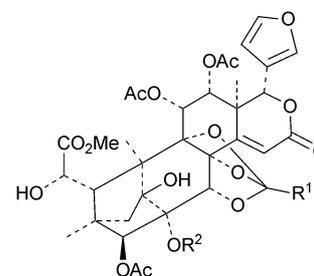
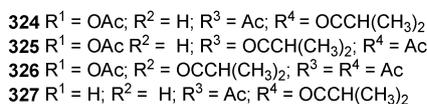
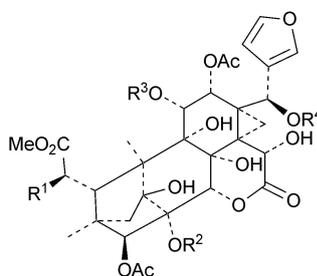
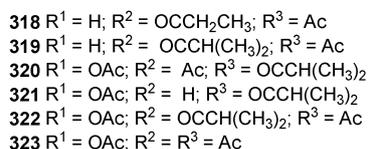
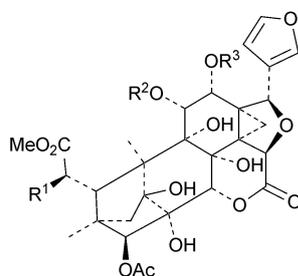
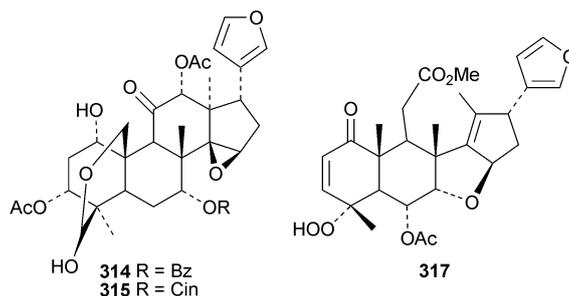
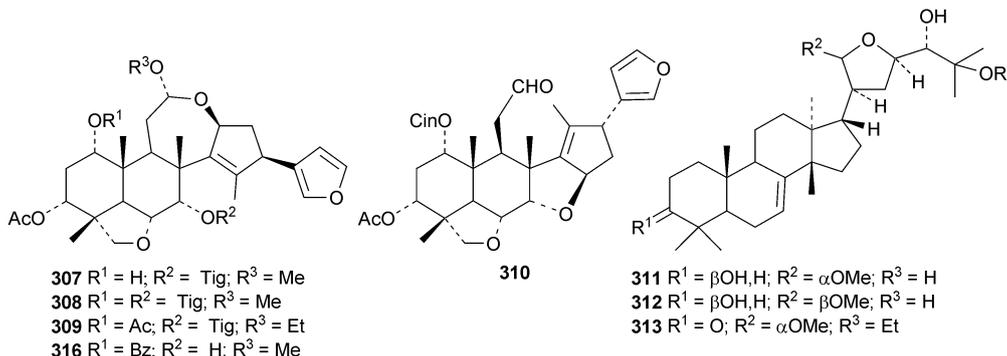
299 R¹ = α OH, H; R² = H; R³ = Ac

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





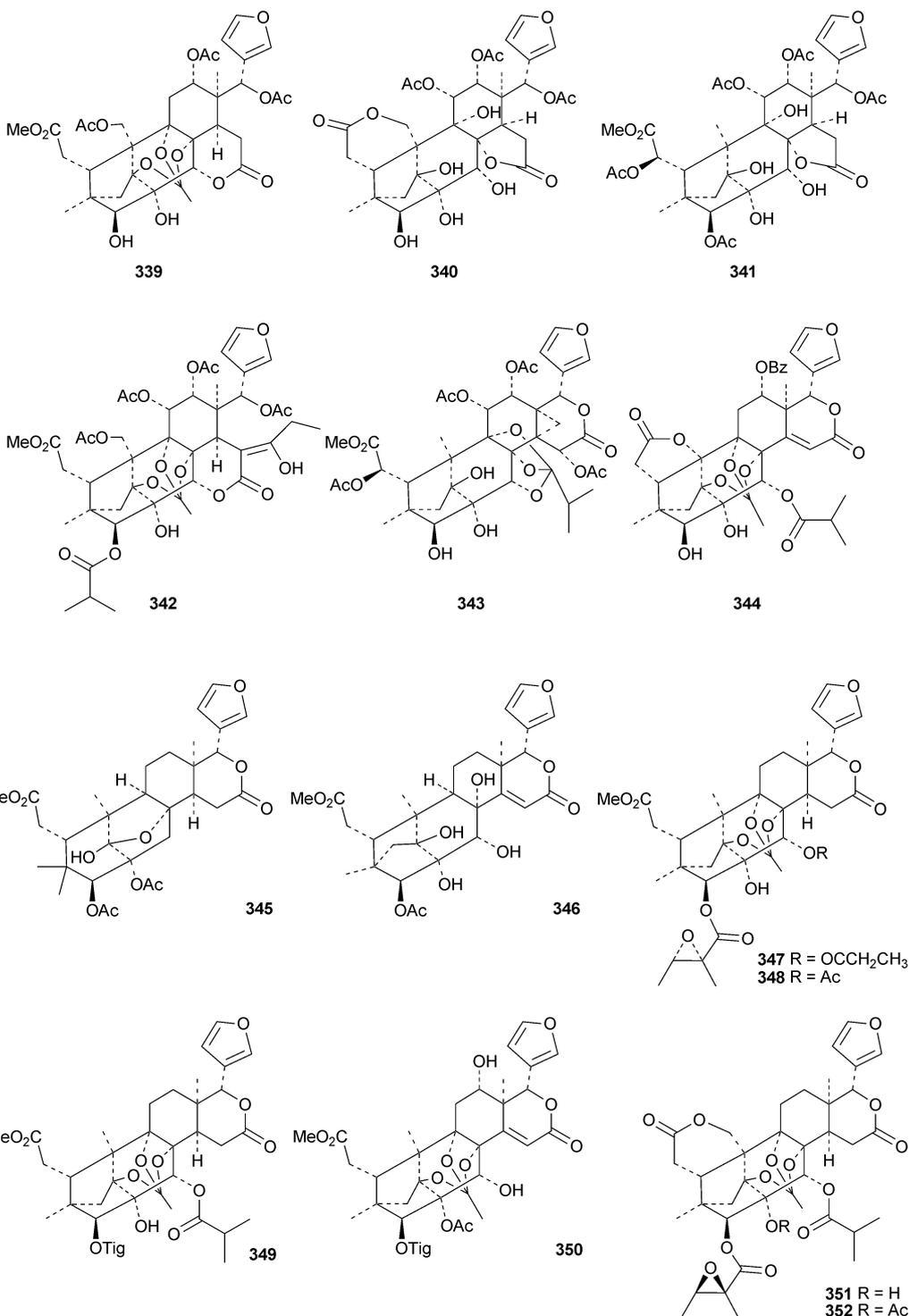
The flow of new mexicanolide and phragmalin derivatives continues unabated. *Chukrasia tabularis* var. *velutina* is a particularly rich source. The new derivatives reported from this

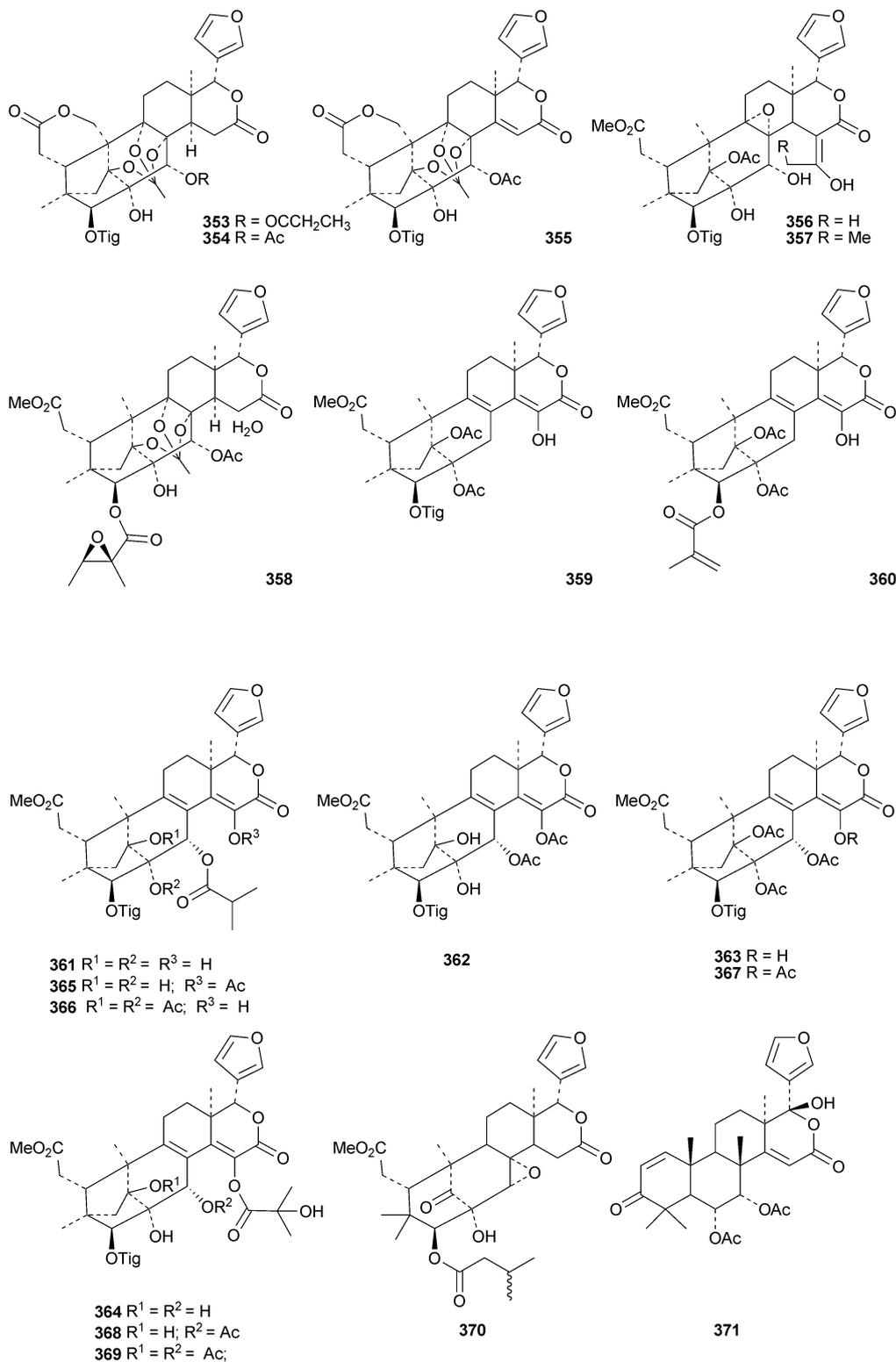
source include velutabularins A–J **318–327**,¹⁴¹ tabularides F–N **328–336**,¹⁴² tabularins A–E **337–341**,¹⁴³ chukvelutilide H **342** and tabularis R **343**,¹⁴⁴ tabulvelutins A **344** and B **345**¹⁴⁵ and



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

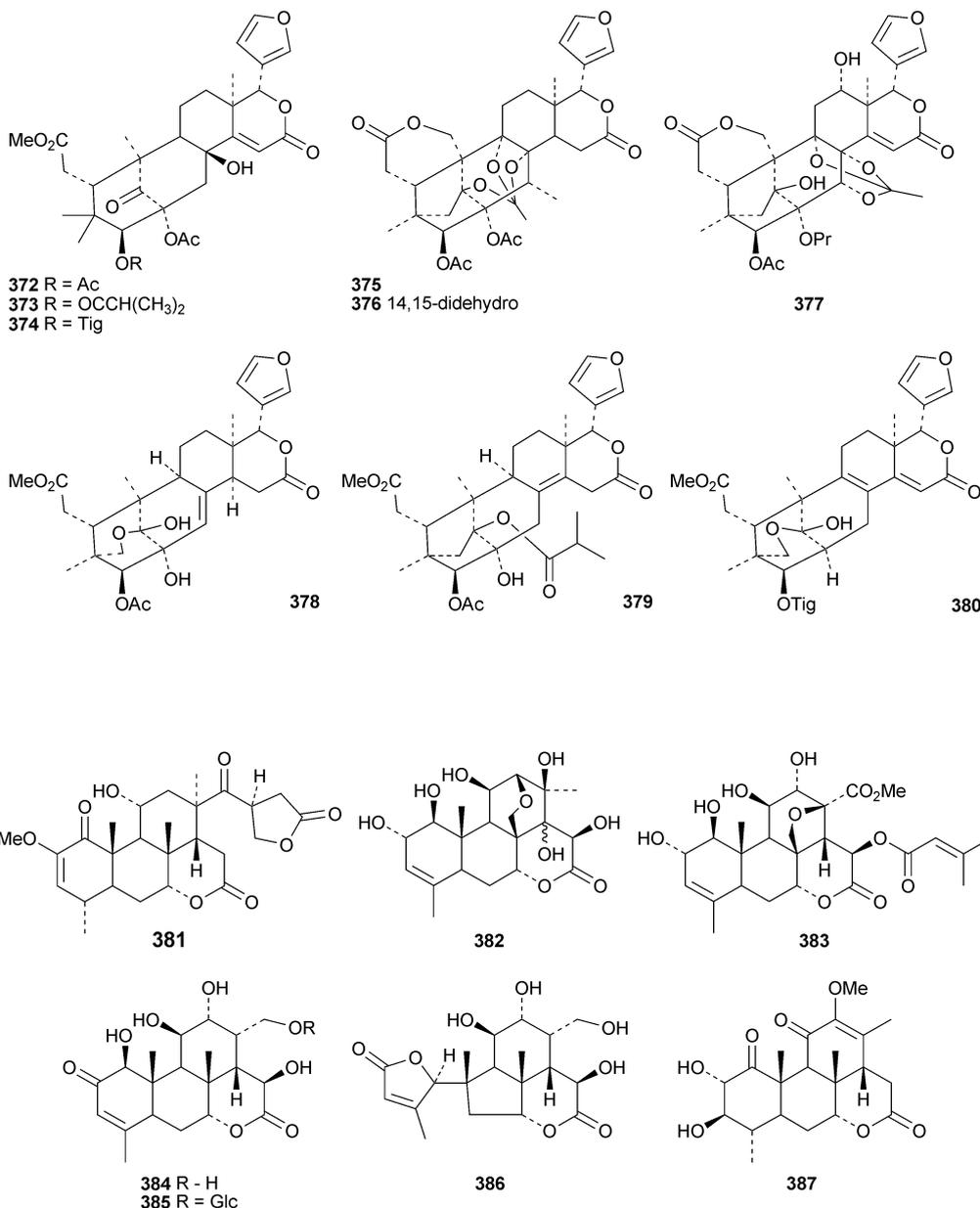




of *Carapa guianensis*.¹⁴⁹ The structure of andirolide E 375 was confirmed by X-ray analysis. Other phragmalin derivatives include thaimoluccensins B 378 and C 379 from the seeds of Thai *Xylocarpus moluccensis*¹³⁸ and godvarin K 380 from the Godvari mangrove *Xylocarpus moluccensis*.¹⁵⁰

New quassinoids are few in number. They include 2'-isopirasin A 381 from the stems of *Picrasma quassinoides*,¹⁵¹ bruceines K 382 and L 383 from the ripe fruit of *Brucea javanica*,¹⁵² yadanzliolides T-V 384–386 from the stems of *Brucea mollis*¹⁵³ and nothospondin 387 from *Nothospondias staudtii*.¹⁵⁴



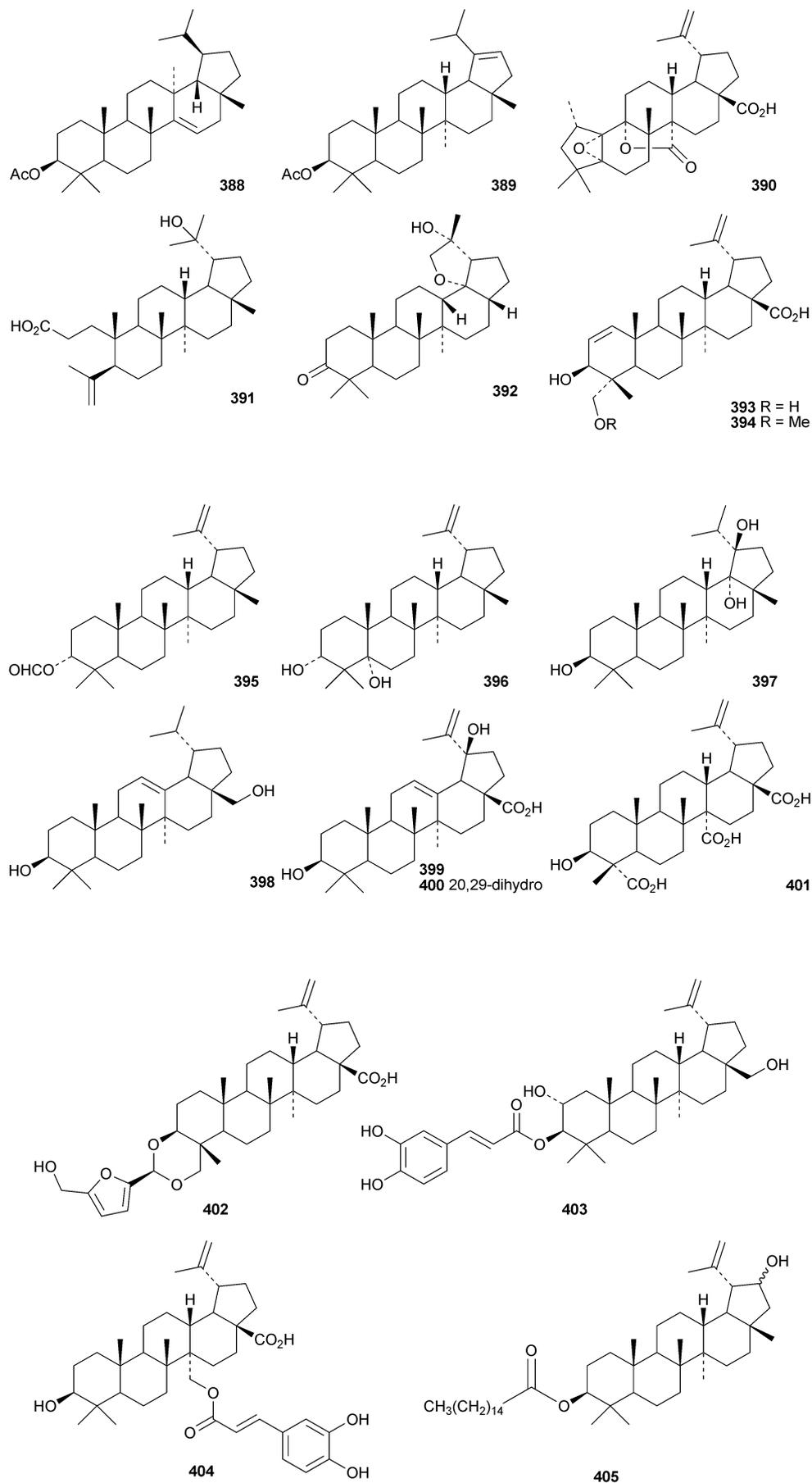


5 The lupane group

The pharmacological activities of lupeol¹⁵⁵ and lupane saponins¹⁵⁶ 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-3 β -yl acetate **389**. Breyneanthanolic 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 18 α ,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-3 β ,18 α ,19 β -triol **397** from *Garcinia tetralata*,¹⁶³ lup-12-ene-3 β ,28-diol **398** from roots of *Diospyros virginiana*,¹⁶⁴ the 3 β ,19 β -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 3 β ,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 *Rauwolfia vomitoria*.¹⁷⁰ The 21-configuration of **405** has not been established. Seven lupane saponins with known genins have been isolated from *Stryphnodendron fissuratum*.¹⁷¹



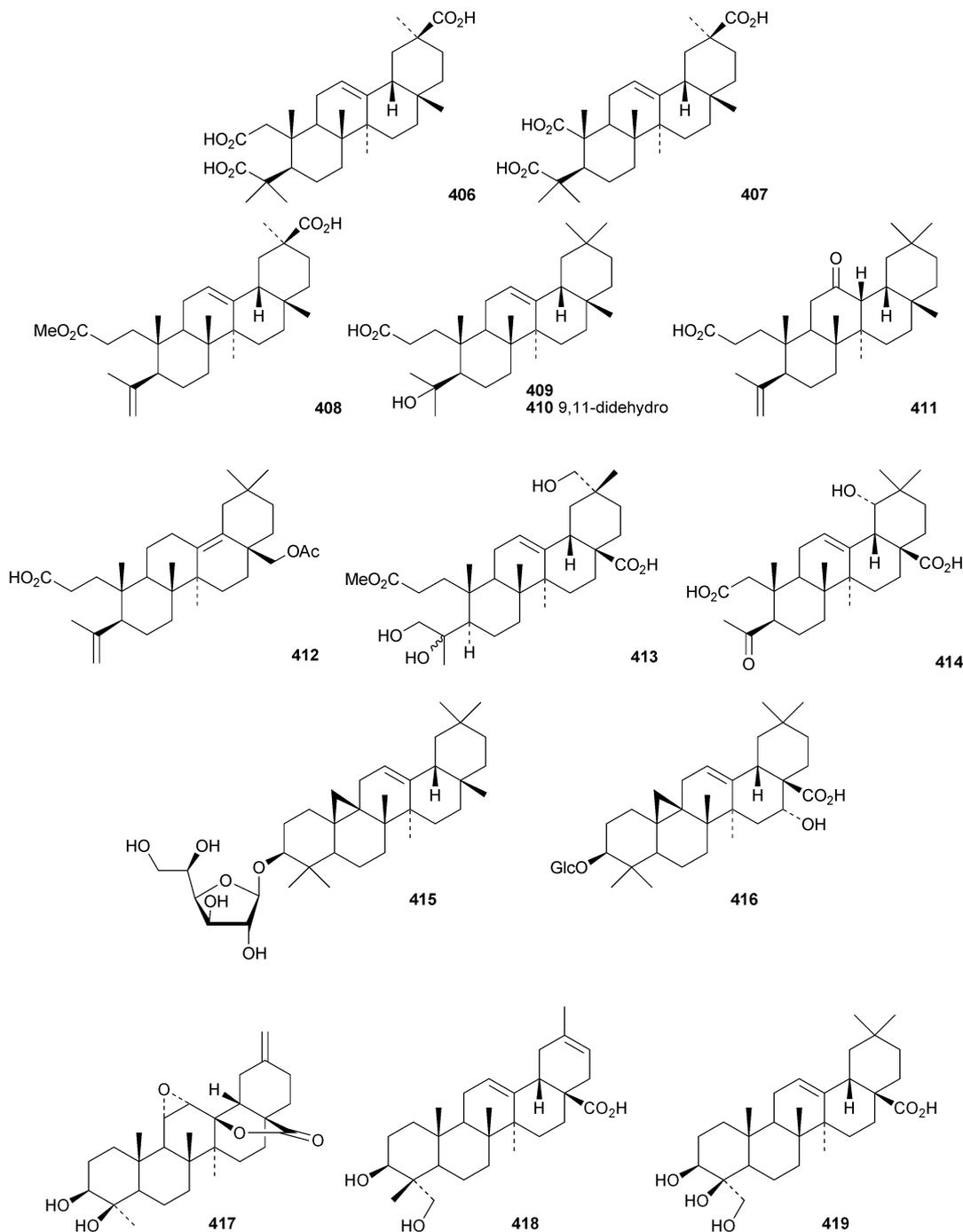


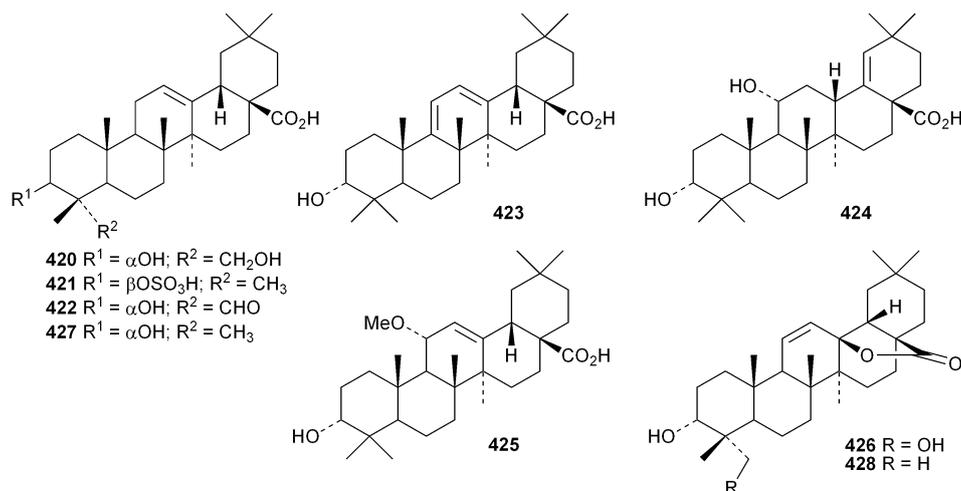
6 The oleanane group

Several ring-A *seco*-oleanane triterpenoids have been isolated, including the 2,3-*seco*-oleanenetriolic 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 ivorenigenin B **414** from *Terminalia ivorensis*.¹⁷⁵ The unusual 9,25-cycloolean-12-en-3 β -yl β -D-glucopyranoside **415** has been reported to be a constituent of *Celestris australis*¹⁷⁶ and the same group has identified 9,25-cyclo-3 β -(β -D-glucopyranosyloxy)-16 α -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. 15 α -Hydroxysoyasapogenol B **429**, 7 β ,15 α -hydroxysoyasapogenol B **430** and 7 β ,29-dihydroxysoyasapogenol **431** are metabolites of the

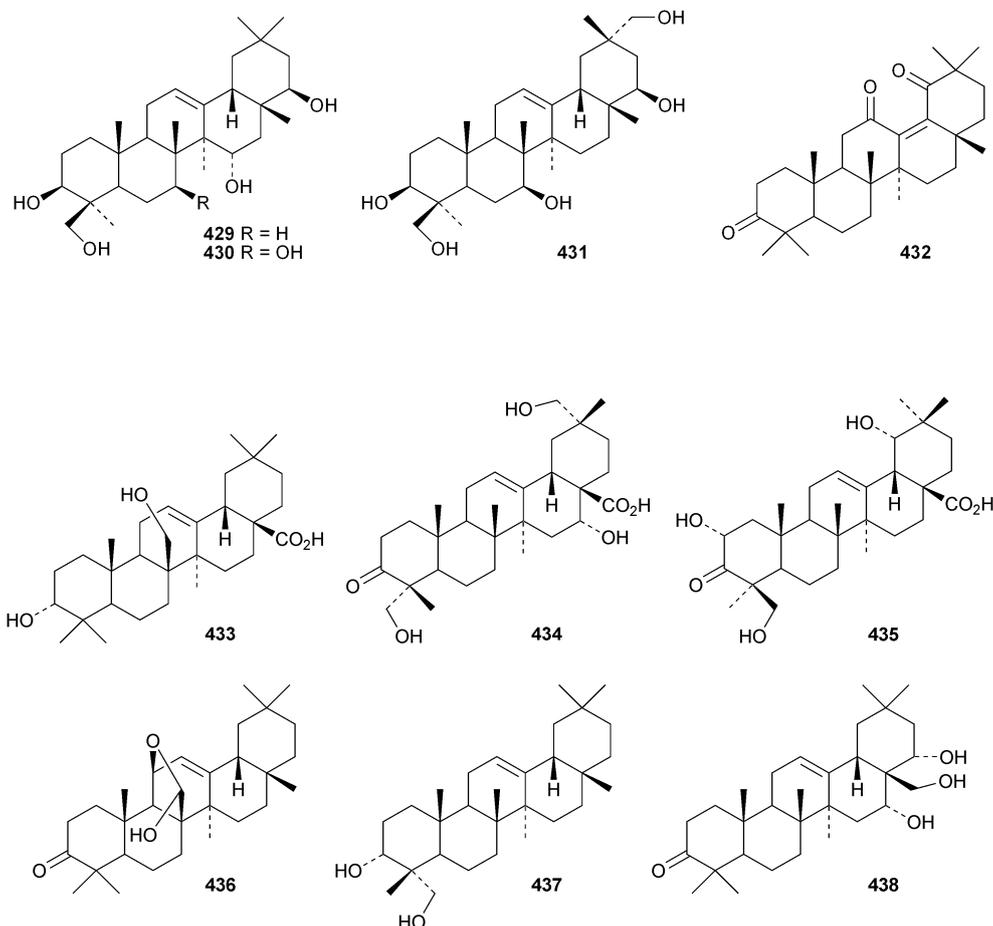


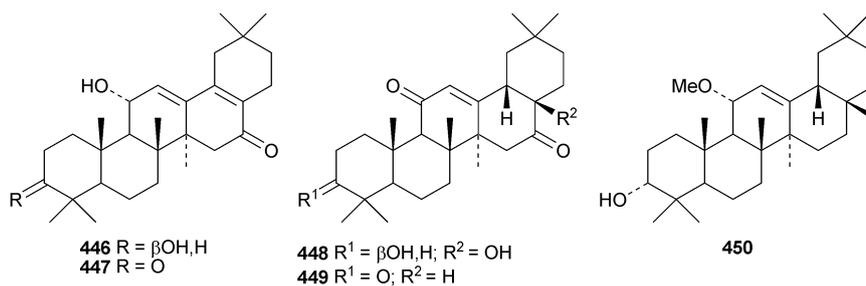
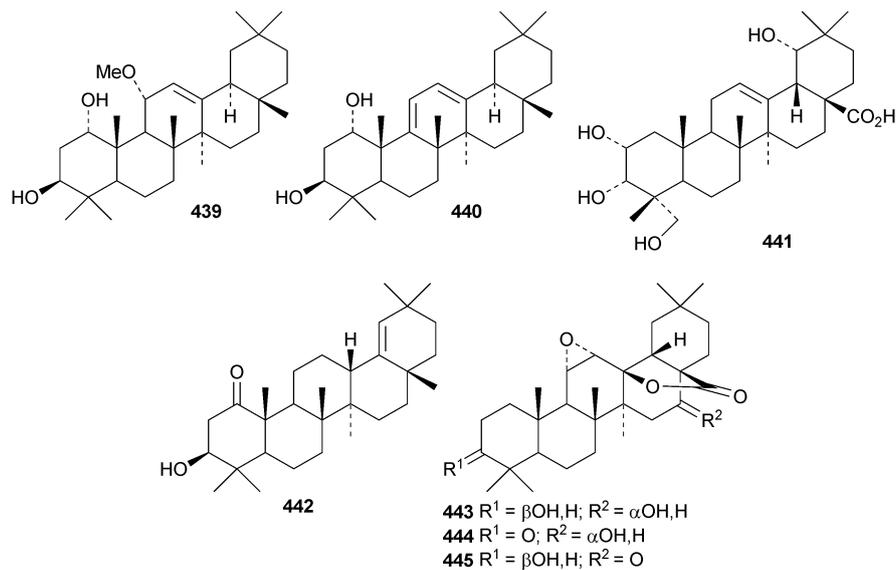


endophytic fungus *Pestalotiopsis clavispora*, isolated from *Bru-guiera sexangula*.¹⁸² The structure of 15 α -hydroxysoyasapogenol B **429** was confirmed by X-ray analysis. The structure of olean-13(18)-ene-3,12,19-trione **432**, from *Sedum linare*, was also established by X-ray analysis.¹⁸³

Other new simple oleanane derivatives include ambradiolic acid A **433** from *Liquidambar formosana*,¹⁶⁰ 16 α ,23,29-trihydroxy-

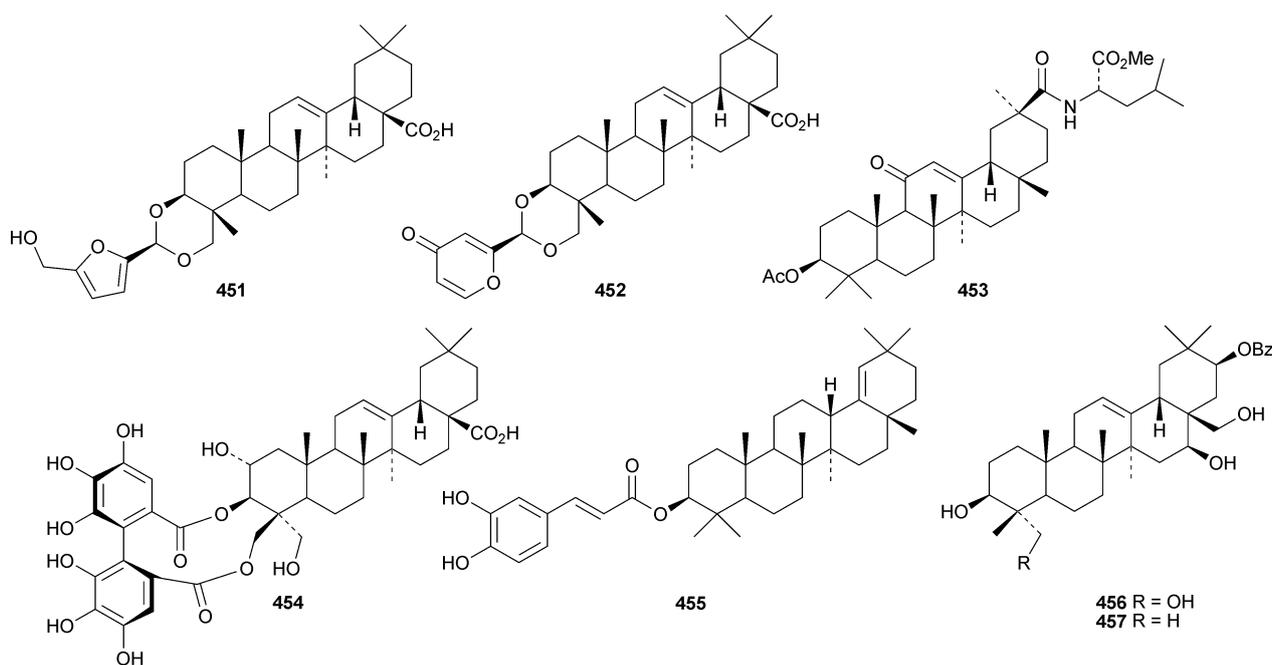
3-oxoolean-12-en-28-oic acid **434** from *Kalopanax pictus*,¹⁷⁴ ivorengenin A **435** from *Terminalia ivorensis*,¹⁷⁵ salacetal **436** from *Salacia longipes* var. *camerunensis*,¹⁸⁴ olean-12-ene-3 α ,23-diol **437** from *Salvia miltiorrhiza*,¹⁸⁵ camelliagenone **438** from *Barringtonia asiatica*,¹⁸⁶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

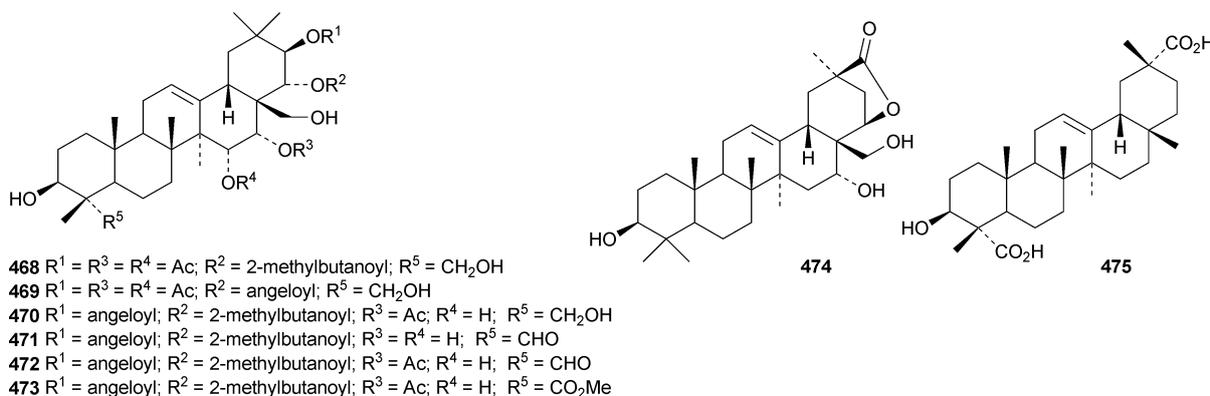
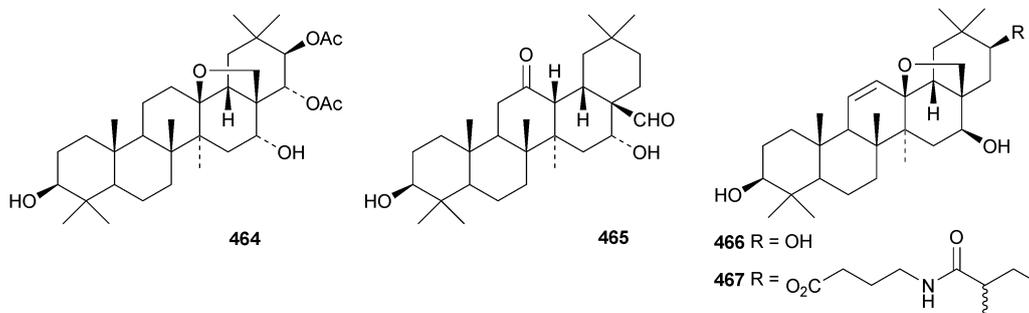
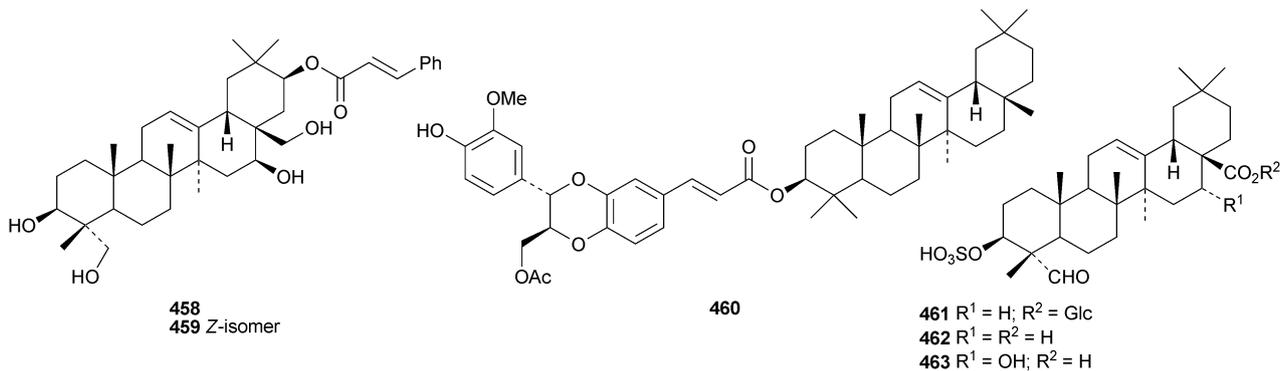




Juglans chinensis,¹⁸⁹ 443–449 from *Nannoglottis carpesioides*¹⁹⁰ and olibanumol E 450 from olibanum, the gum resin of *Boswellia carterii*.¹⁶²

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





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 *Gypsophila 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 heterogena*, is identical to clethroidoside F and it is found with heterogenoside E that has a

known genin.¹⁹⁷ The genins of glaucosides A and B, from *Atriplex glauca* var. *ifniensis*, are the new compounds **466** and **467** whereas glaucoside 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 ardiscrenoside 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



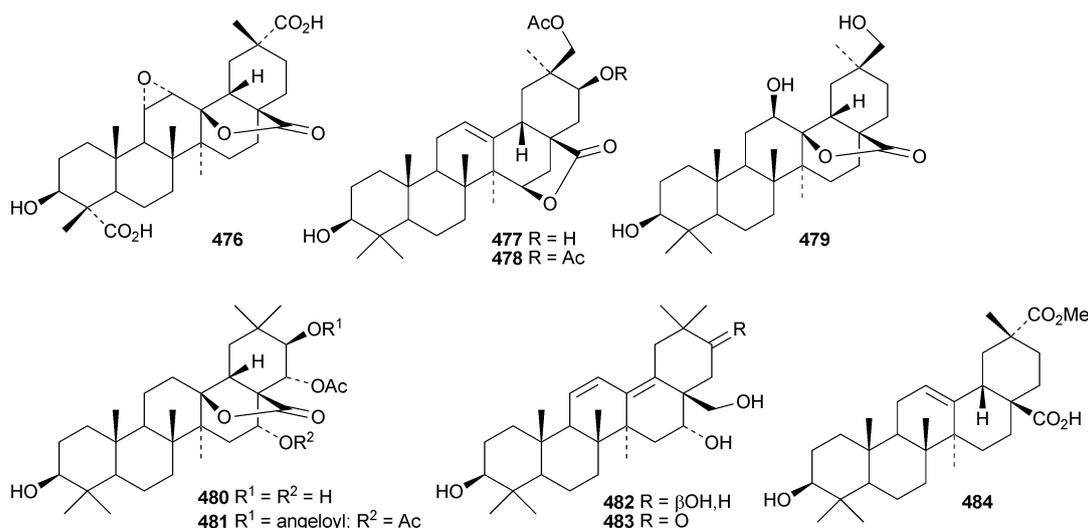


Table 1

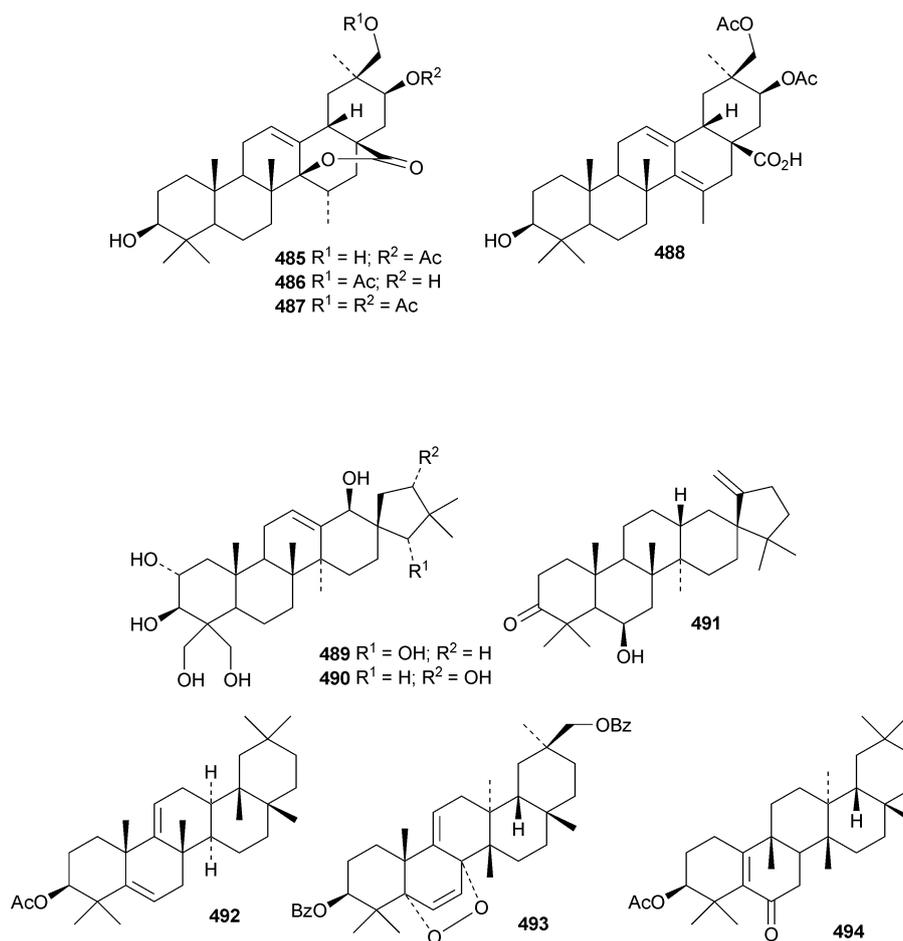
Trivial name	Plant species	Reference
Androsacin	<i>Androsace integra</i>	206
Apodytines A–F	<i>Apodytes dimidiata</i>	207
Ardisicrenosides I, J, M	<i>Ardisia crenata</i>	208
Ardisicrenoside N	<i>Ardisia crenata</i>	209
Azafrines 1, 2	<i>Crocus sativus</i>	210
Bifinosides A–C	<i>Panax bipinnatifidus</i>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

Table 2

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

478.²⁰¹ Other oleanane saponins with new gens 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 falcatum* and *Bupleurum rotundifolium*,²⁰⁴ and coryternic acid 484 from *Corydalis ternate*.²⁰⁵





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

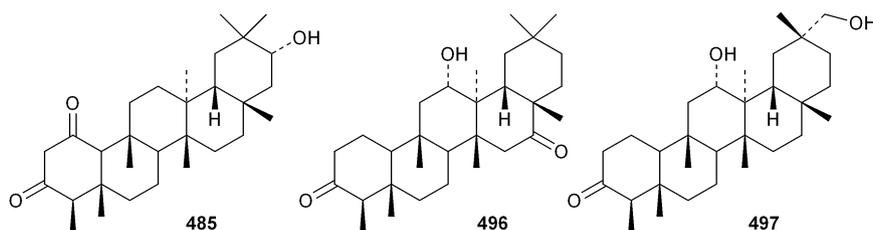
The sources of new oleanane saponins with known genins that have not been assigned trivial names are listed in Table 2.

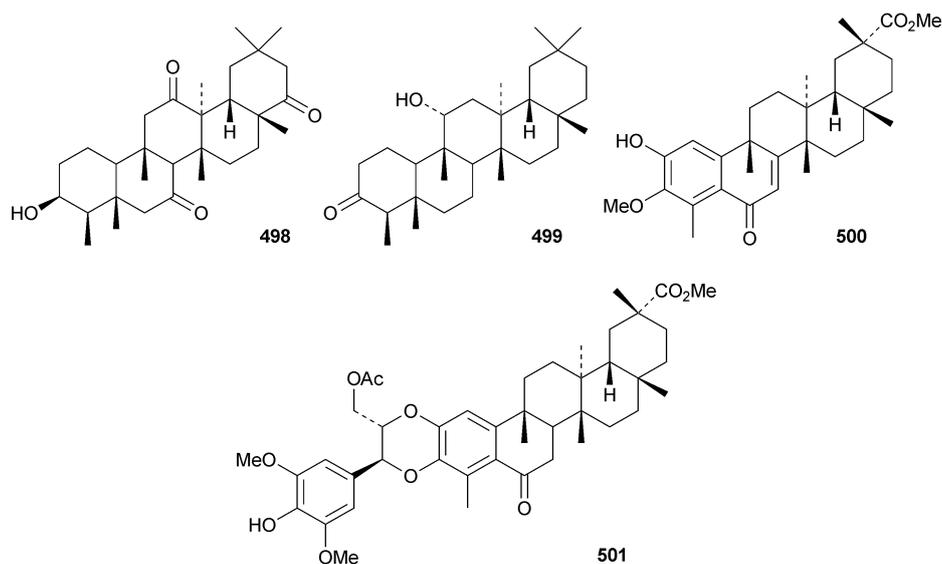
Pachanosides C1, E1, F1 and G1 are pachanane saponins from *Echinops macrogona* with the genins **485–488**, respectively.²⁰¹ The structure of pachanol C **485** has been revised.

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 3 β -Acetoxylglutin-5(10)-en-6-one **494** has been found in roots of *Scorzonera austriaca*.²⁶⁶

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



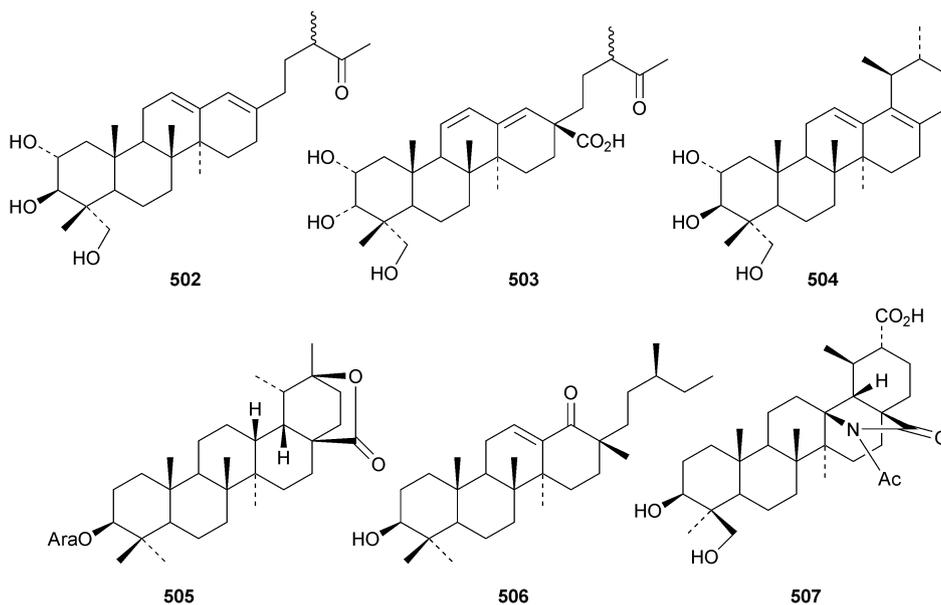


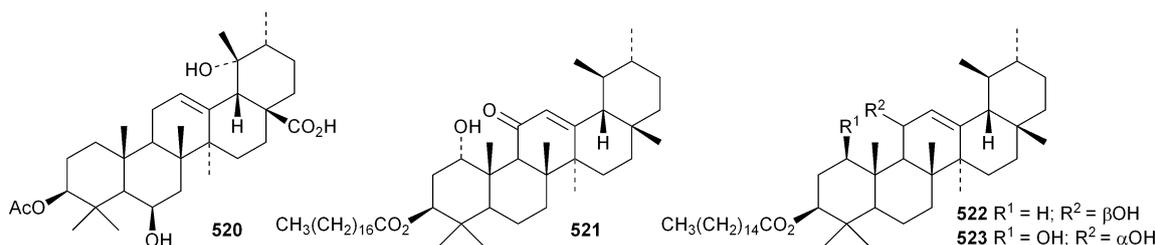
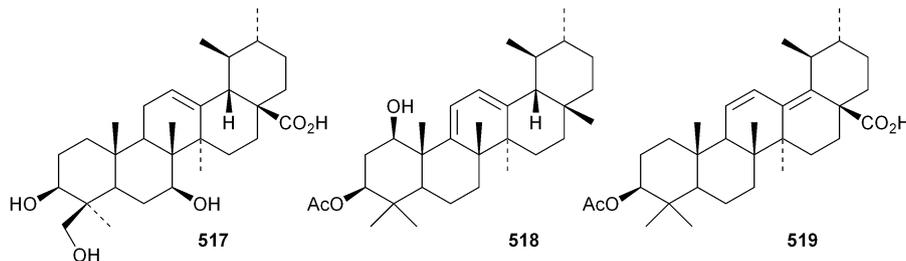
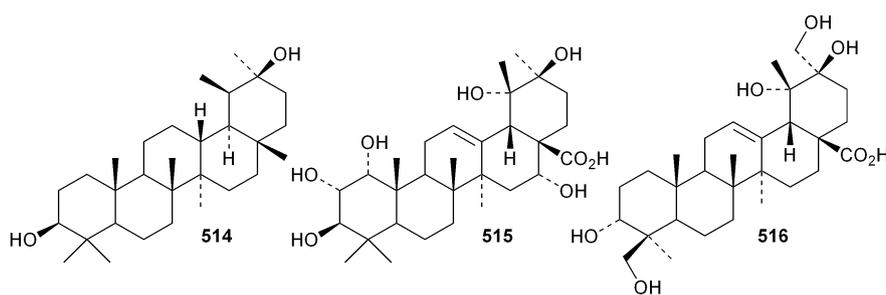
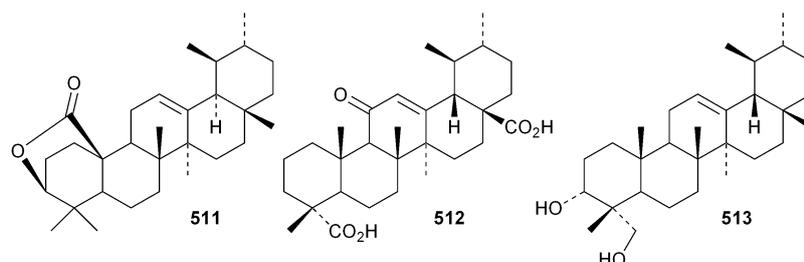
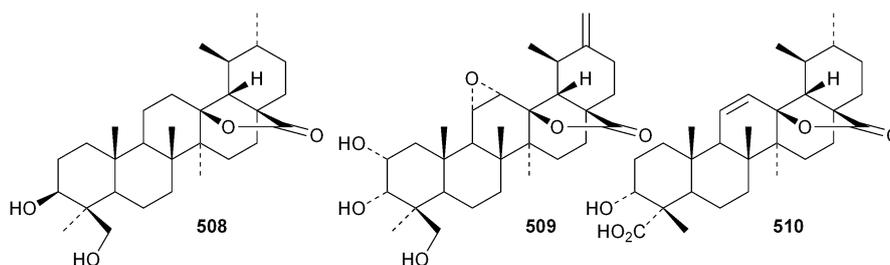
7 The ursane group

The 18,19-secoursane derivatives **502** and **503** have been isolated from *Rosa laevigata* together with 28-norursa-12,17-diene-2 α ,3 β ,23-triol **504** and the arabinoside **505** whose genin has an unusual 19 α -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 *Zygothymum eurypterum* where it is found with atriplicaide B **508** which is 3 β ,24-dihydroxyursan-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 18 α *H*-urs-12-en-25,3 β -olide.²⁷⁷ Other new simple ursane derivatives include cordinoic acid **512** from *Cordia latifolia*,²⁷⁸ urs-12-ene-3 α ,23-diol **513** from *Salvia miltiorrhiza*,¹⁸⁵ 18 α *H*-

ursene-3 β ,20 β -diol **514** from *Boswellia carterii*,¹¹⁶ 1 α ,2 α ,3 β ,16 α ,19 α ,20 β -hexahydroxyurs-12-en-28-oic acid **515** from *Pedicularis kansuensis*,²⁷⁹ glutinolic acid **516** from *Rehmannia glutinosa*,²⁸⁰ and 3 β ,7 β ,24-trihydroxyurs-12-en-28-oic acid **517** from *Saurauja roxburghii*.²⁸¹ New ursane ester derivatives include conrauidienol **518** from *Ficus conraui*,²⁸² 3 β -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 urs-9(11),12-diene-2 α ,3 β ,21 β ,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





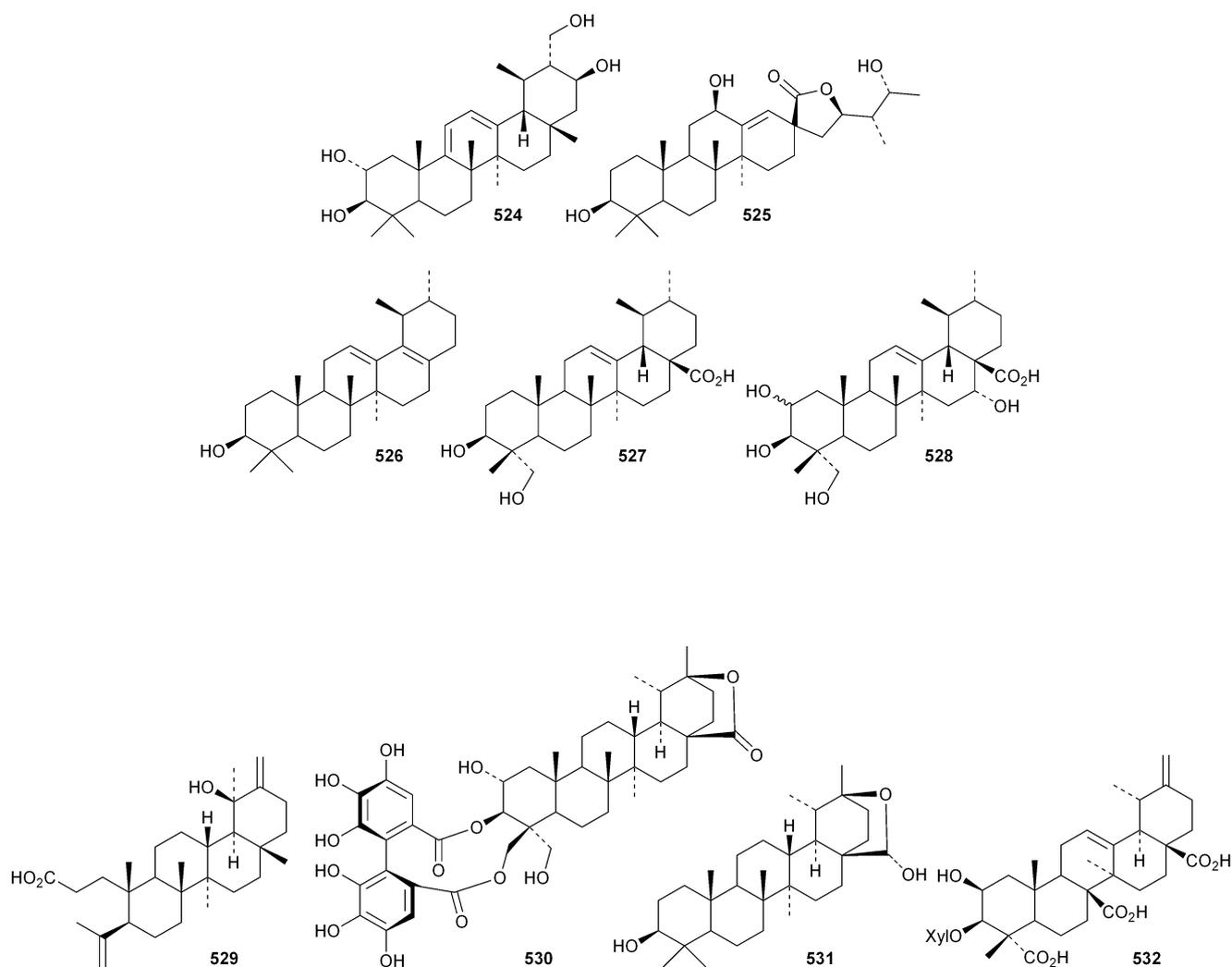
new genin 28-norursa-12,17-dien-2 β -ol 526.²⁸⁷ Other unnamed ursane saponins with the new genins include 3 β ,23-dihydroxyurs-12-en-28-oic acid 527 from *Juglans sinensis*,¹⁸⁹ and 2,3 β ,16 α ,23-tetrahydroxyurs-12-en-28-oic acid 528 from *Lathyrus aphaca*.²⁵¹

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–D²⁹⁰ and W²⁹¹ from *Ilex kudincha*, symplacosins 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

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

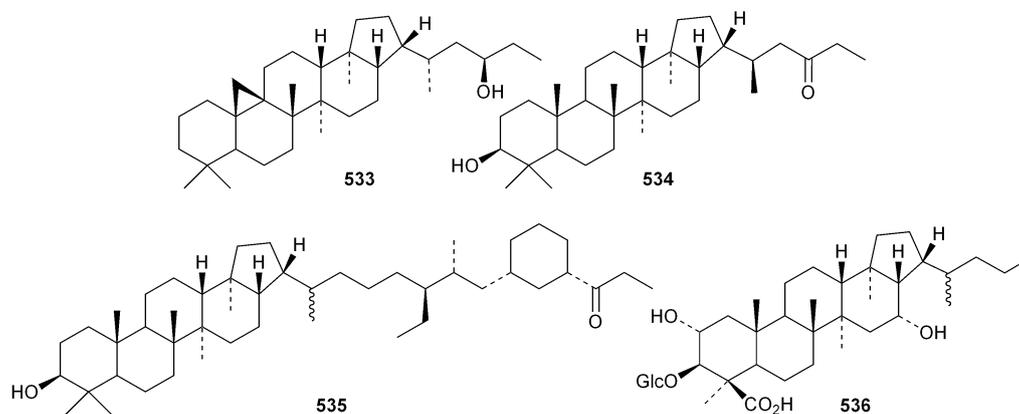


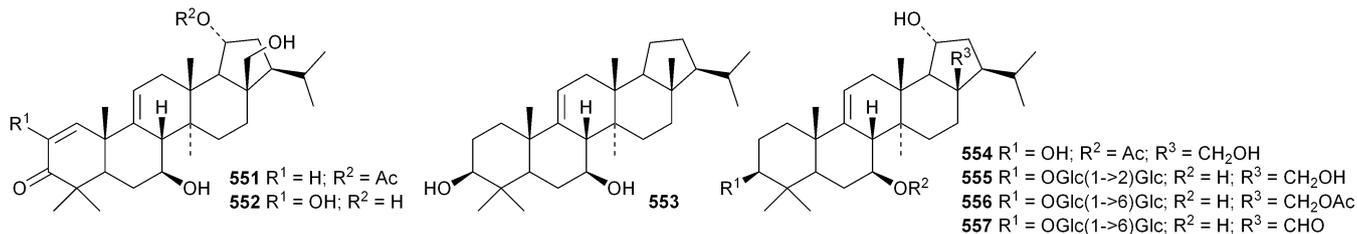
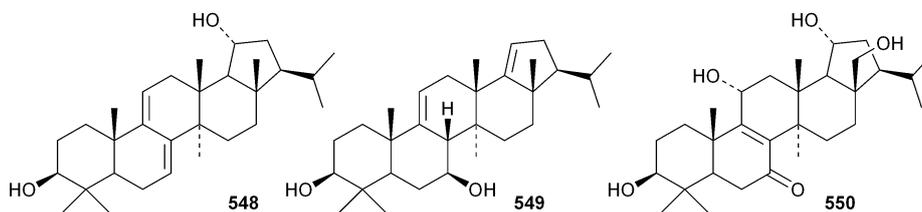
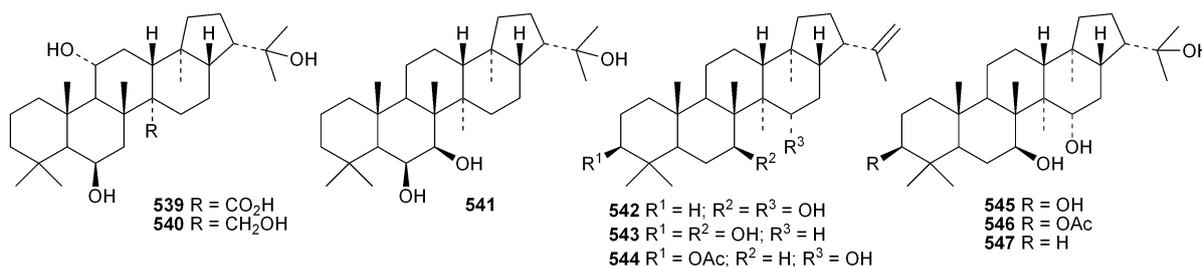
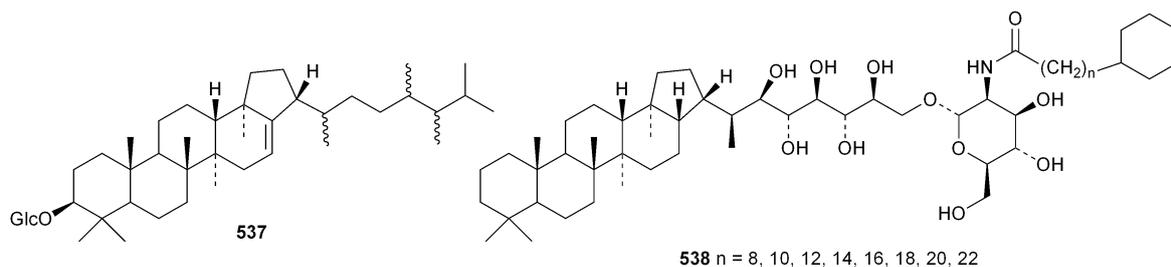


tannin ester **530** of $2\alpha,3\beta,23,24$ -tetrahydrotaraxastan-28,20 β -olide is a constituent of leaves of *Castanopsis fissa*.¹⁹² The taraxastane hemiacetal **531** has been found in *Geum japonicum*.²⁹⁵ Celosin F **532** appears to be a taraxastane xyloside from *Celosia argentea*.²¹⁸

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 3 β -hydroxy-29-propylhopan-31-one **534** have been identified in

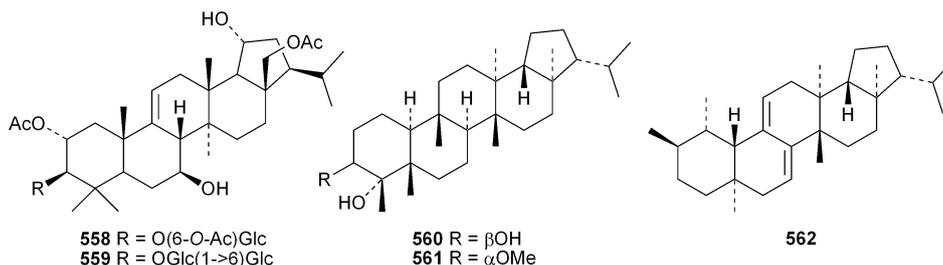




Celestria australis.¹⁷⁶ The same group claim that the cyclohexylhopane derivative 535 is also found in *Celestria australis*²⁹⁷ and that the 29-ethylhopane derivative 536 and 32,33,34-trimethylbacteriohopan-3 β -yl β -D-glucopyranoside 537 are constituents of *Symplocos paniculata*.¹⁷⁷ Several *N*-acylated bacteriohopanehexol mannosamine derivatives 538 have been identified in the thermophilic bacterium *Alicyclobacillus*

acidoterrestis.²⁹⁸ The simple hopane derivatives 539–541²⁹⁹ and 542–547³⁸ are metabolites of the entomopathogenic fungi *Conioideocrella 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-dihydroxyrubiarbonol A 553, rubiarbonol A 7-acetate 554, the



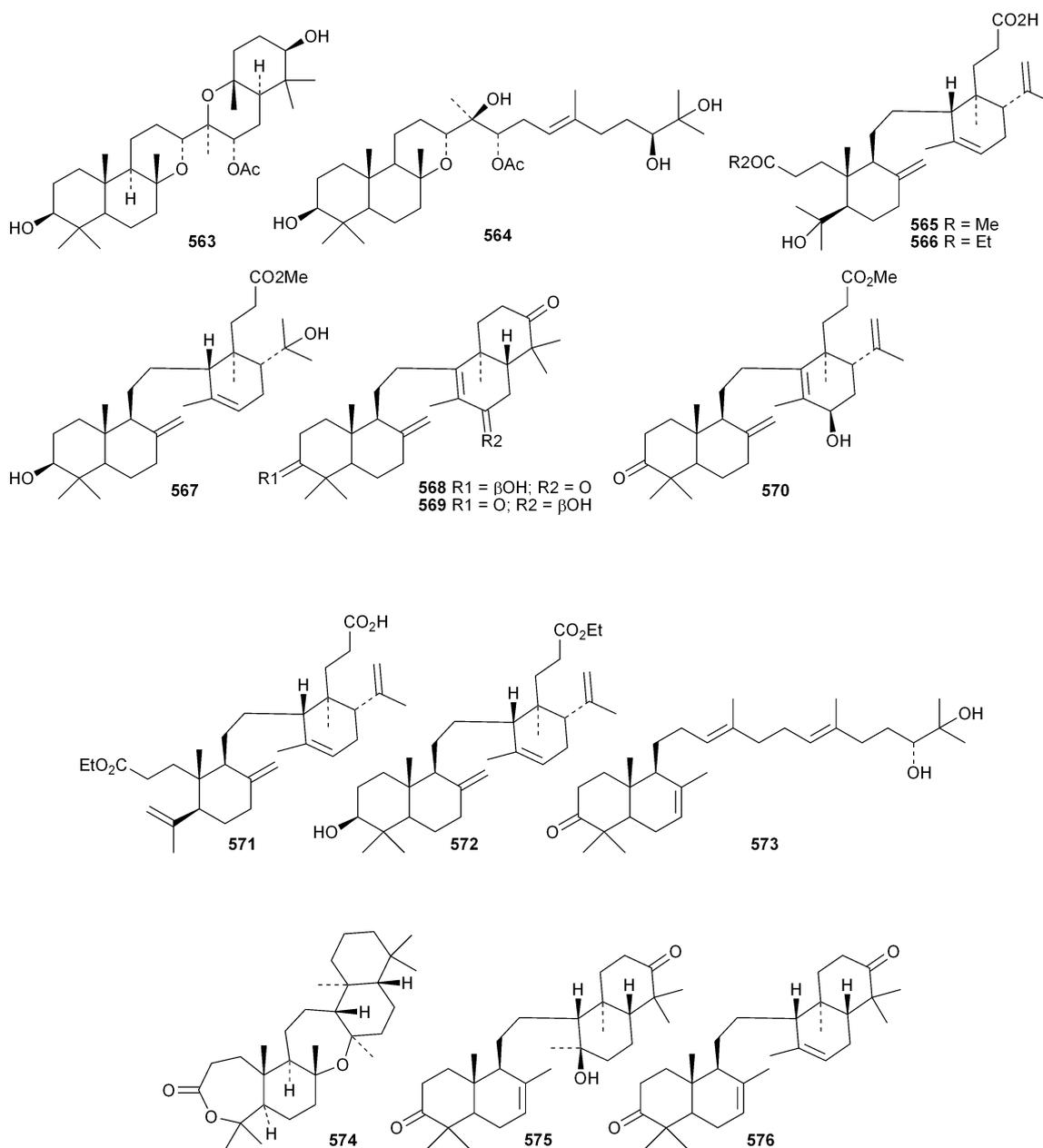
rubiaronol A glycoside 555, rubiarboside G 28-acetate 556, rubiarboside G 28-aldehyde 557, 2 α -acetoxyrubiaronol 28-acetate 558 and the rubianol E glycoside 559.³⁰⁰ *Adiantum capillus-veneris* is the source of filicane-3 β ,4 α -diol 560 and the corresponding 3 α -methyl ether 561.³⁰¹ Canarene 562 is 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.

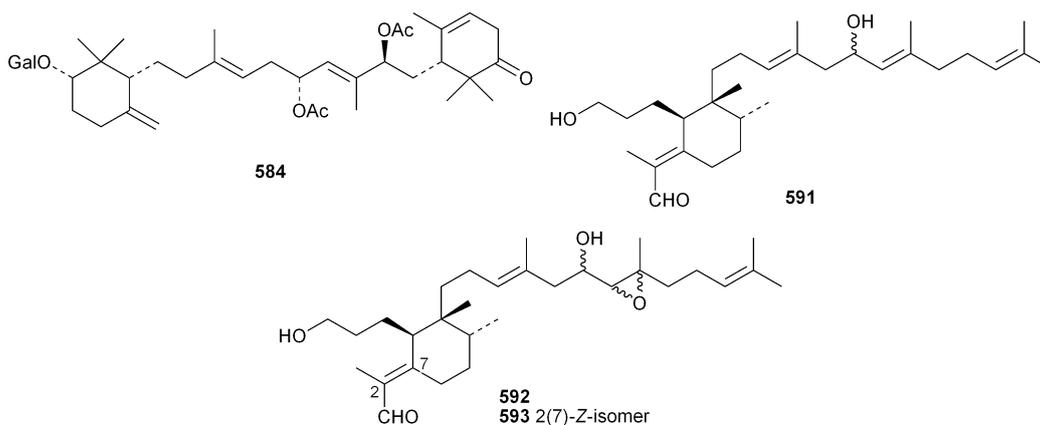
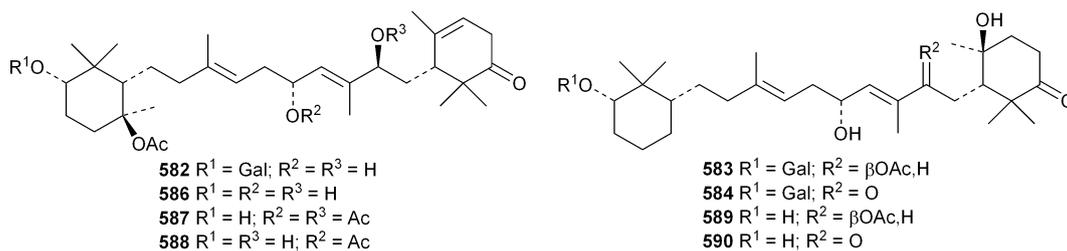
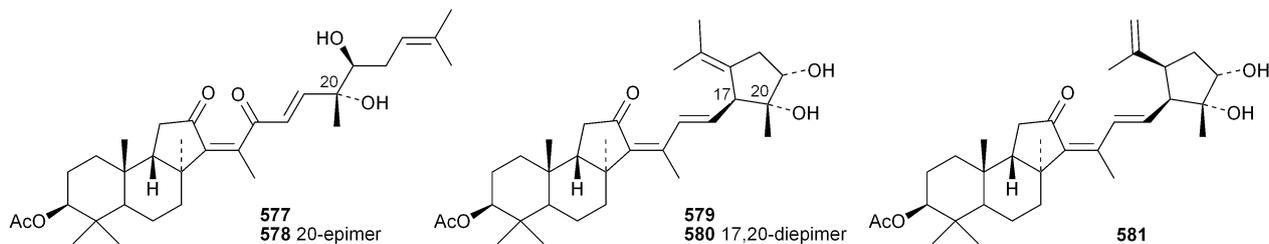
9 Miscellaneous compounds

Phyteumosides A and B, from *Phyteuma orbiculare*, have as aglycones the partially cyclised onocerane triterpenoid 563 and the polyopodane 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 lamsic acid 571 and ethyl lamsiolate 572 together the polyopodane 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





586–590.³⁰⁷ Three iridal triterpenoids 591–593 have been isolated from *Iris delavayi*.³⁰⁸

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