




Triterpenoids

Cite this: *Nat. Prod. Rep.*, 2020, **37**, 962 Robert A. Hill * and Joseph D. Connolly

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

Received 7th November 2019

DOI: 10.1039/c9np00067d

rsc.li/npr

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.

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1. Introduction

Reviews have been published on the biological properties of triterpenoids including hypoglycaemic,¹ antiparasitic² and immunomodulatory³ activities and neutrophil elastase inhibition.⁴ Triterpenoid saponins have been highlighted for a range of bioactivities⁵ 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**–**5**, have been found in the compass plant *Silphium laciniatum*.¹⁶ A compound

from cultures of the basidiomycete *Antrodia 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 epoxythysiferol **A 12** and its 15*R*,16*S*-isomer epoxythysiferol **B**. A new pathway for the synthesis of squalene in bacteria has been discovered and the responsible genes identified.²⁰

3. The lanostane group

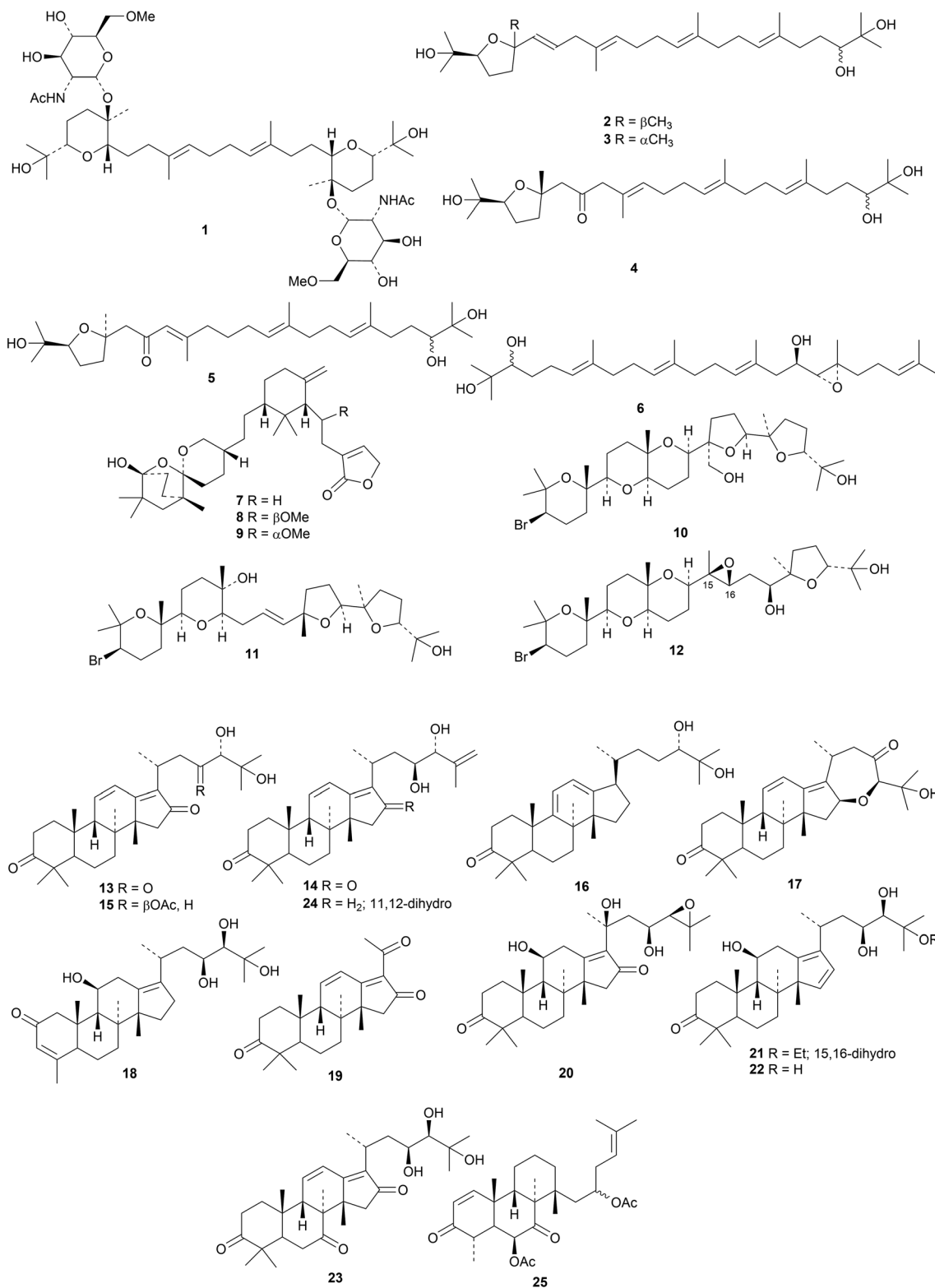
A range of protostane derivatives from the rhizomes of *Alisma orientale*, that show inhibitory effects on human carboxylesterase 2, includes alismanols **A 13**–**G 19**, 20-hydroxylisol **C 20**, 25-*O*-ethylisol **A 21** and compounds **22**–**24**.²¹ The helvolic acid-related compound **25**, from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

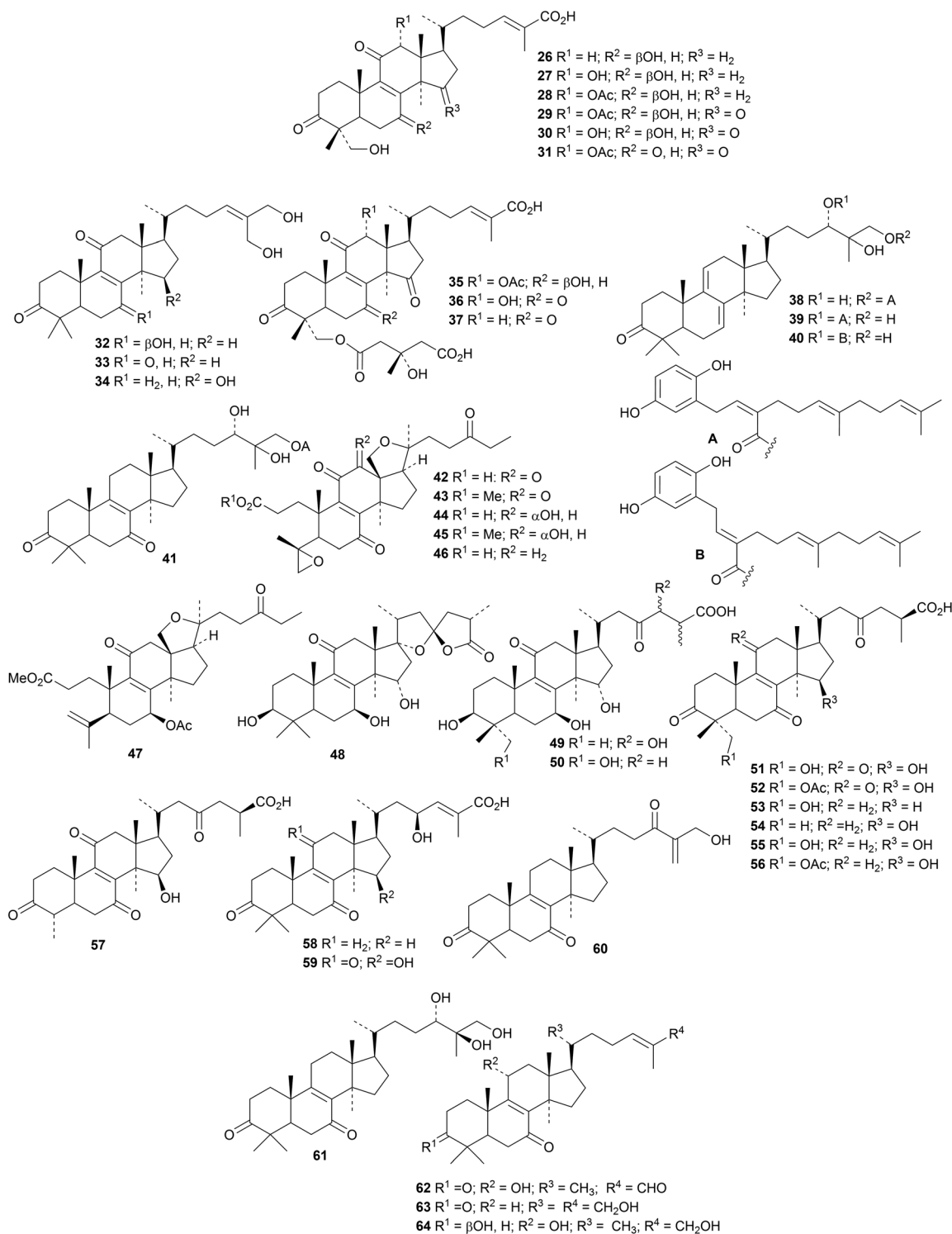
The Tibetan medicinal mushroom *Ganoderma leucocontextum* is full of lanostanes including ganoleucoins **A 26**–**L 37** and the meroterpenoid esters ganoleucoins **M 38**–**P 41**.²³ Many of these compounds inhibit HMG-CoA reductase and α -glucosidase. Ganoboninones **A 42**–**F 47** are secolanostanes from the medicinal mushroom *Ganoderma boninense* that show antiplasmodial activity.²⁴ Constituents of *Ganoderma tropicum* include²⁵ compounds **48**, **49**, and **50** while *Ganoderma hainanense* contains²⁶ 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 ganoderoids **A 71**–**G 77**,³⁰

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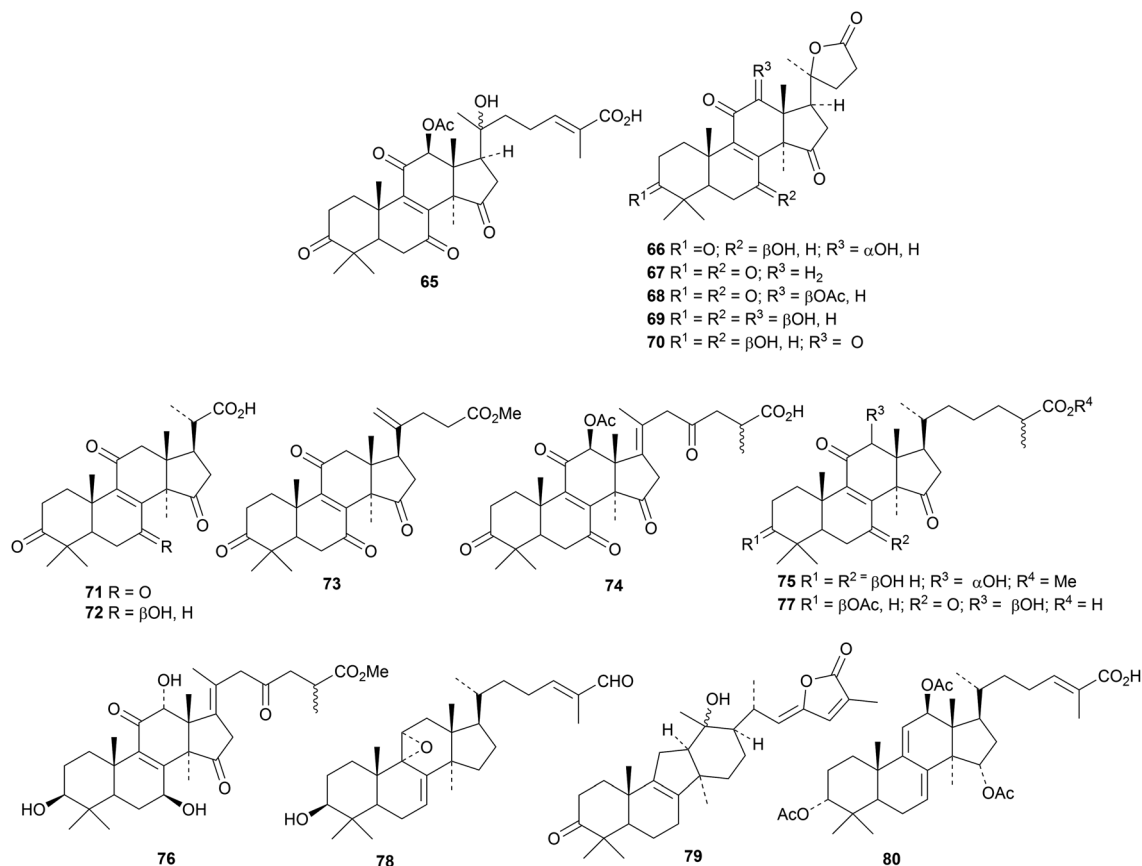


compounds **78** and **79** from the fruiting bodies³¹ and the triacetate **80**.³² Ganocochlearic acid **81** is an interesting rearranged hexanorlanostane from the fruiting bodies of *Ganoderma cochlear* where it occurs with cochlate **82**, cochlearic acids **83** and **84** and ganodercochlearins **85**–**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 **94**–**98** from the fruiting bodies of *Hexagonia apiaria*,³⁵ the 21-oic acid **99**, the 3,4-seco 3,21-dioic





acid **100** and its 3-methyl ester from the fruiting bodies of *Laetiporus sulphureus* var. *miniatus*³⁶ and astrasiate **101** and astrasiaine **102** from the edible mushroom *Astraeus asiaticus*.³⁷ The metabolites **103–111** of *Haddowia longipes* resemble those of *Ganoderma* species.³⁸ Compound **110** is lucidone H, which is a duplicate name, and **111** is the 3-acetate of ganoderatriol. *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

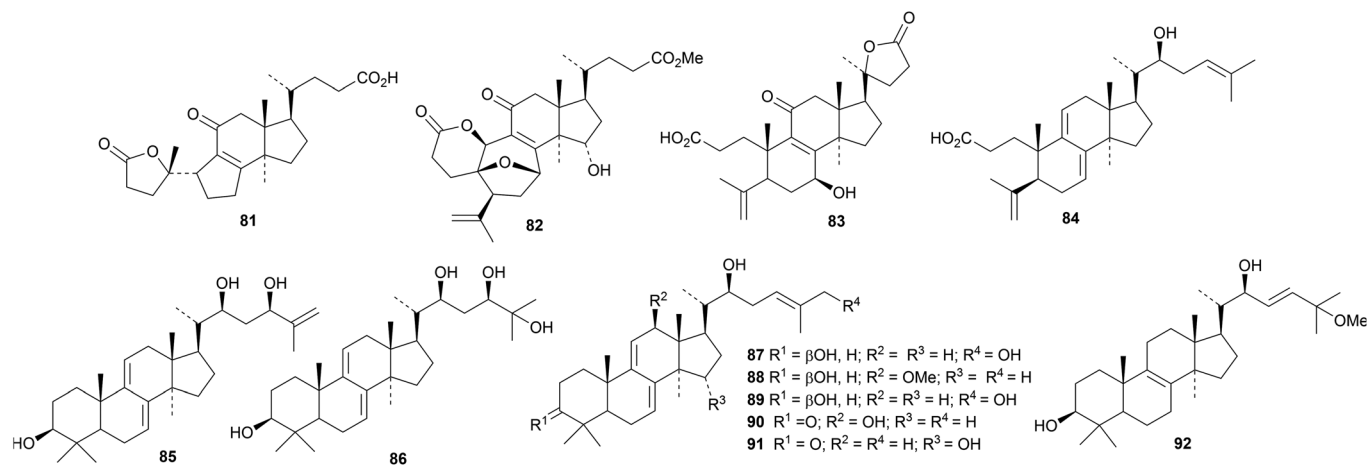
The 21,24-cyclised lanostanes inonotusanes A **125** and B **126** and the trinorderivatives inonotusane C **127** and obliquic acid **128** are constituents of *Inonotus obliquus*.⁴³ Scillascillol **129** and scillascillone **130** have been isolated from *Scilla scilloides*.⁴⁴ The aglycone **131** 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 monoterpene 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

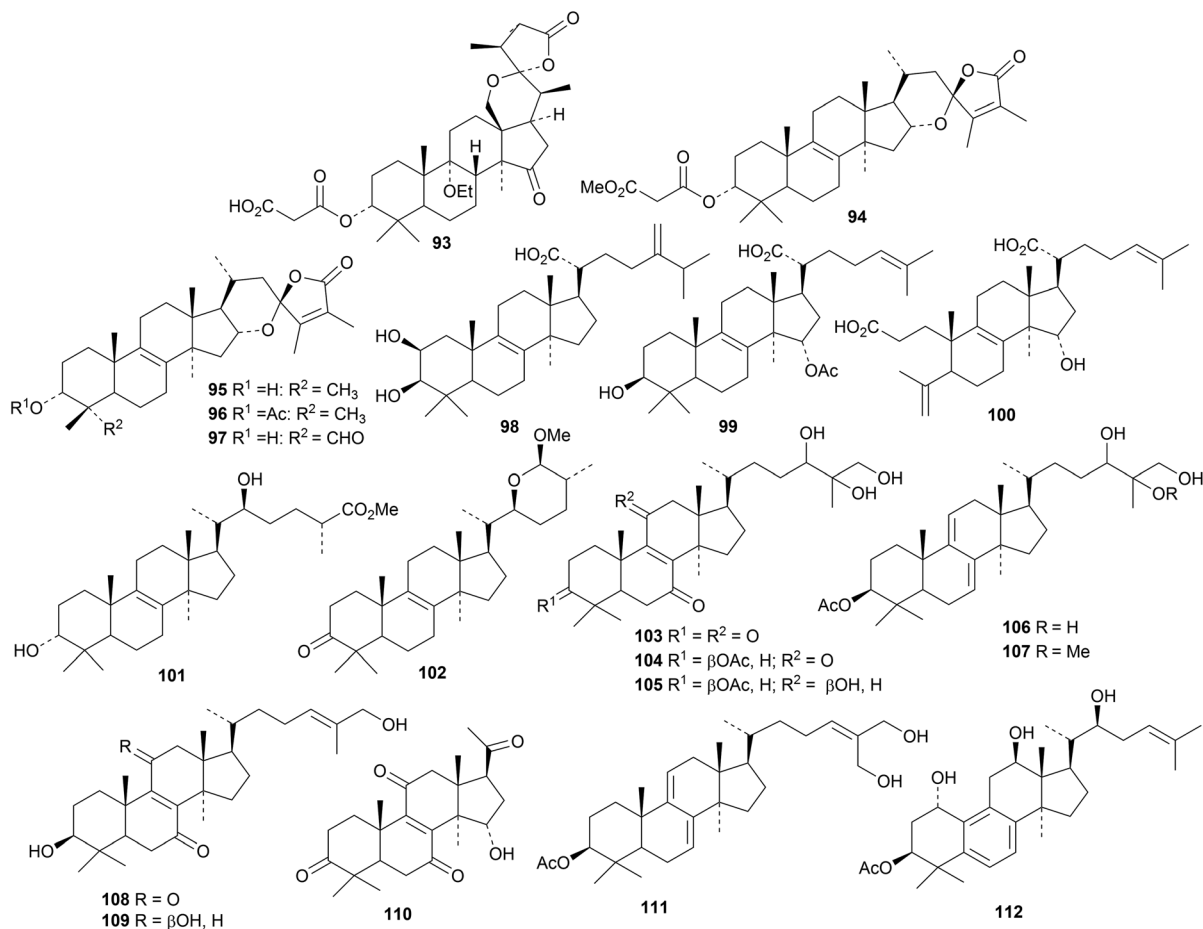


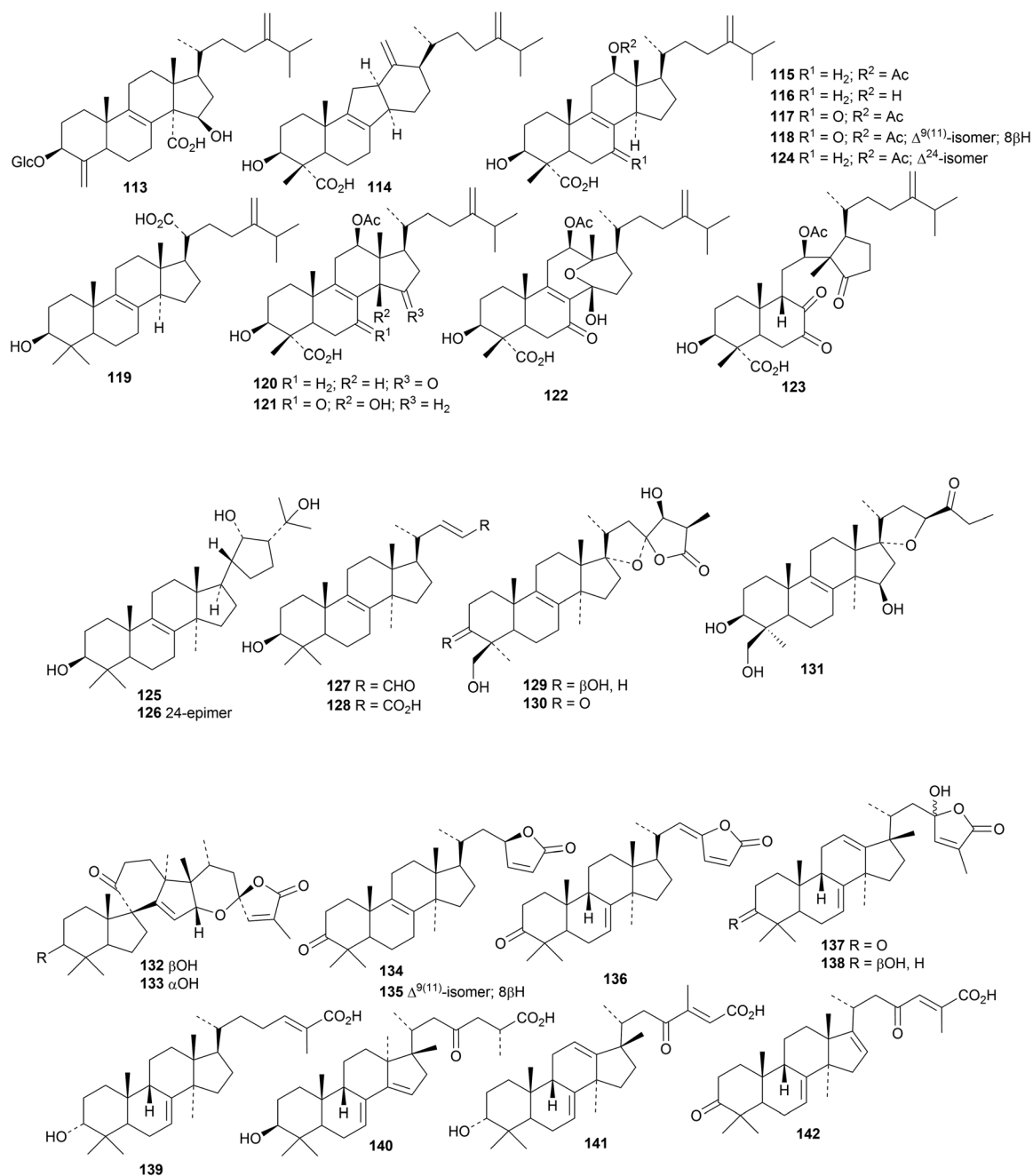


scillascolloside B1 from *Scilla scilloides*⁴⁴ and saponins from *Mussaenda luteola*.⁵⁵

The holostane saponins cladolosides C₃, E₁, E₂, F₁, F₂, G, H₁ and H₂, from the sea cucumber *Cladolabes schmeltzii*, have the new genins **178** (C₃), **179** (E₂, F₂, G, H₂) and **180** (E₁, F₁, H₁).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 B₁ and B₃ have the new genins **184** and **185** respectively whereas colochirosides B₂ and C have known genins.⁵⁸ The C-22 configuration of the

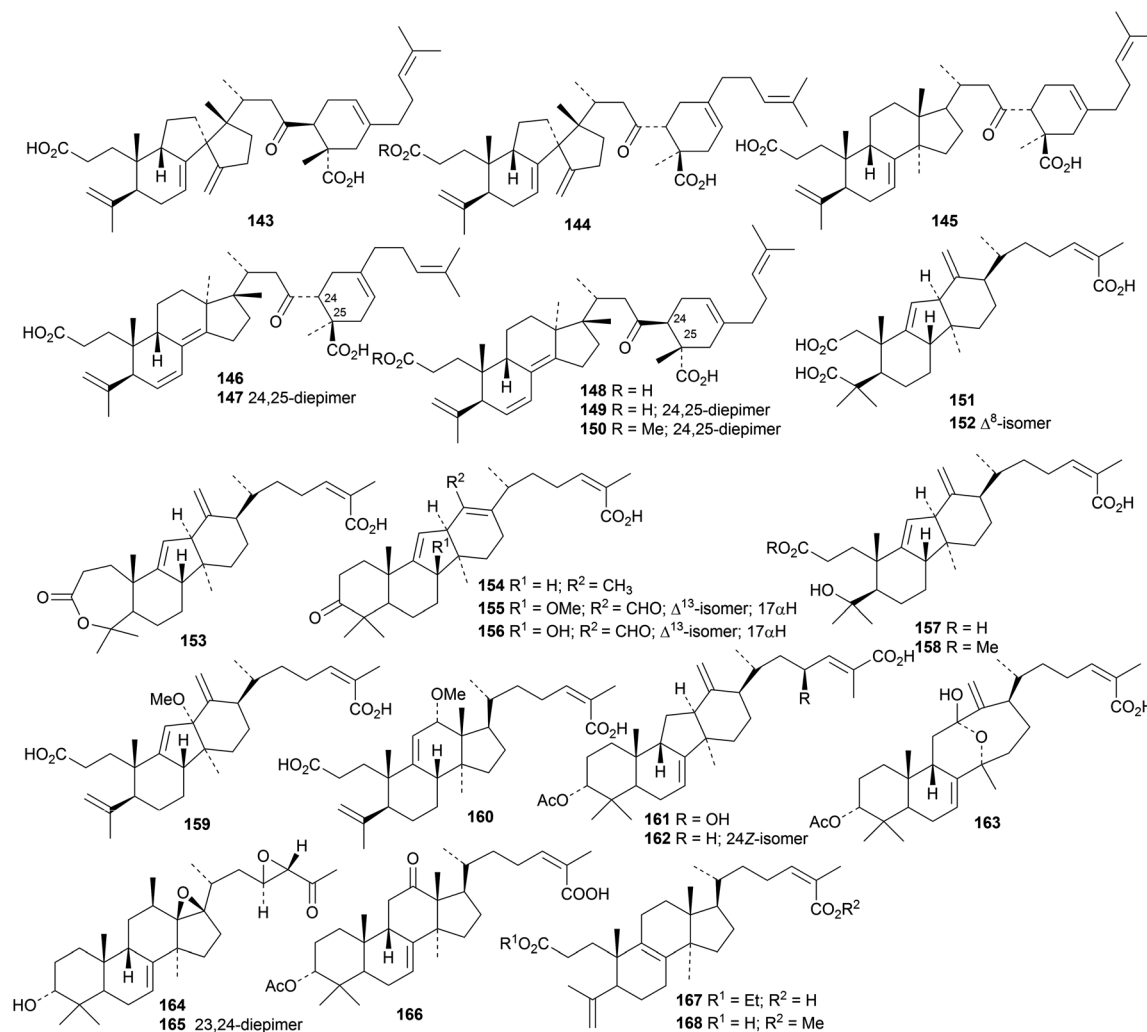




saponins of the sea cucumber *Cladolabes schmeltzii* has been assigned as *R*.⁵⁹ Other holostane saponins with known genins include cercodemasoides A–E from *Cercodemas anceps*,⁶⁰ cucumarioside E from *Cucumaria japonica*⁶¹ and moebioside A from *Holothuria moebii*.⁶² Reviews covering biological and taxonomic significance of sea cucumber holostane saponins⁶³ and their antitumour, anti-inflammatory and immunostimulatory properties⁶⁴ have been published.

Cimiyunnins 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. Cimiyunnin A **186** is a potent angiogenesis inhibitor. Ananosins A **190–E 194**, cycloartanes from *Kadsura ananosma*, have some unusual structures.⁶⁶

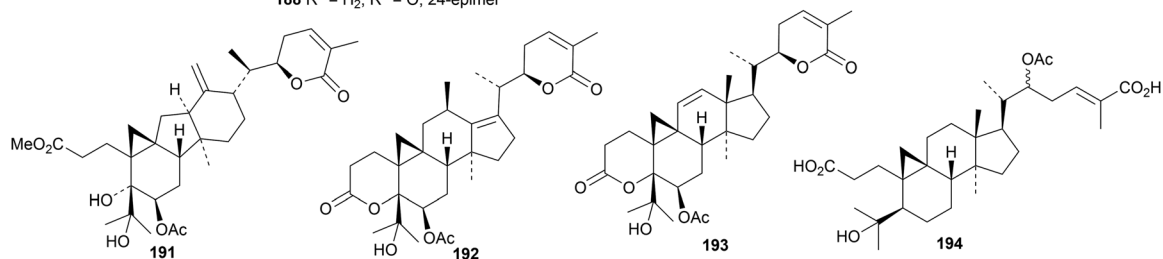
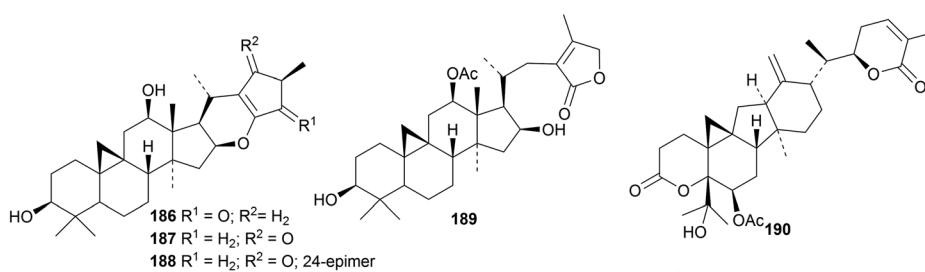
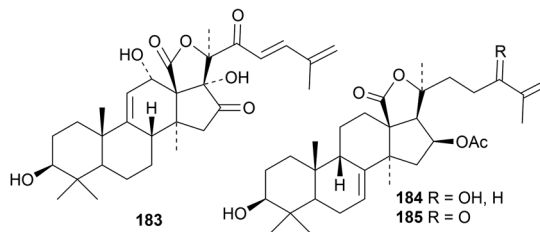
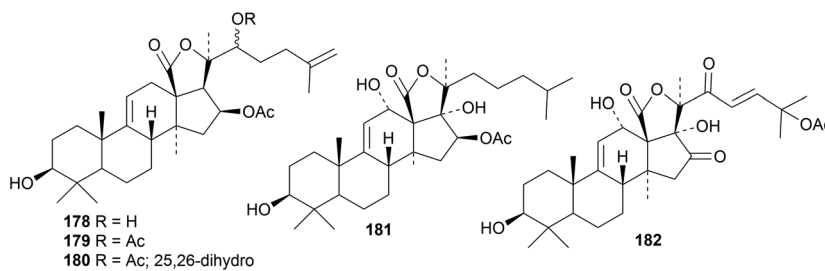
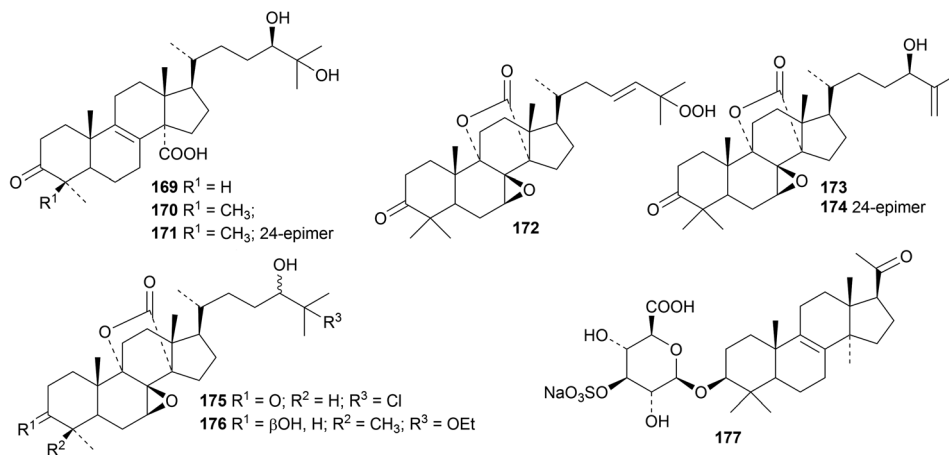


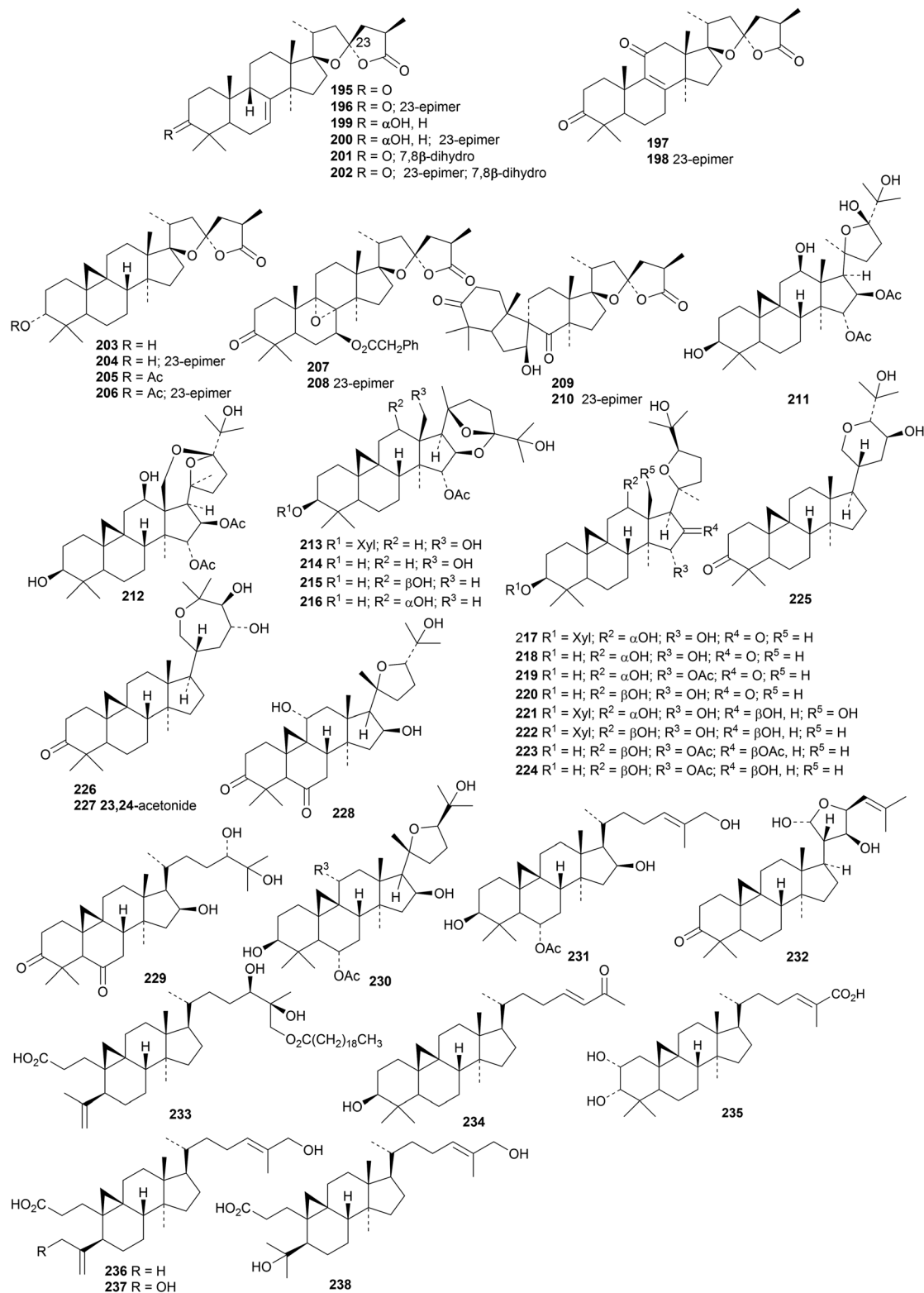


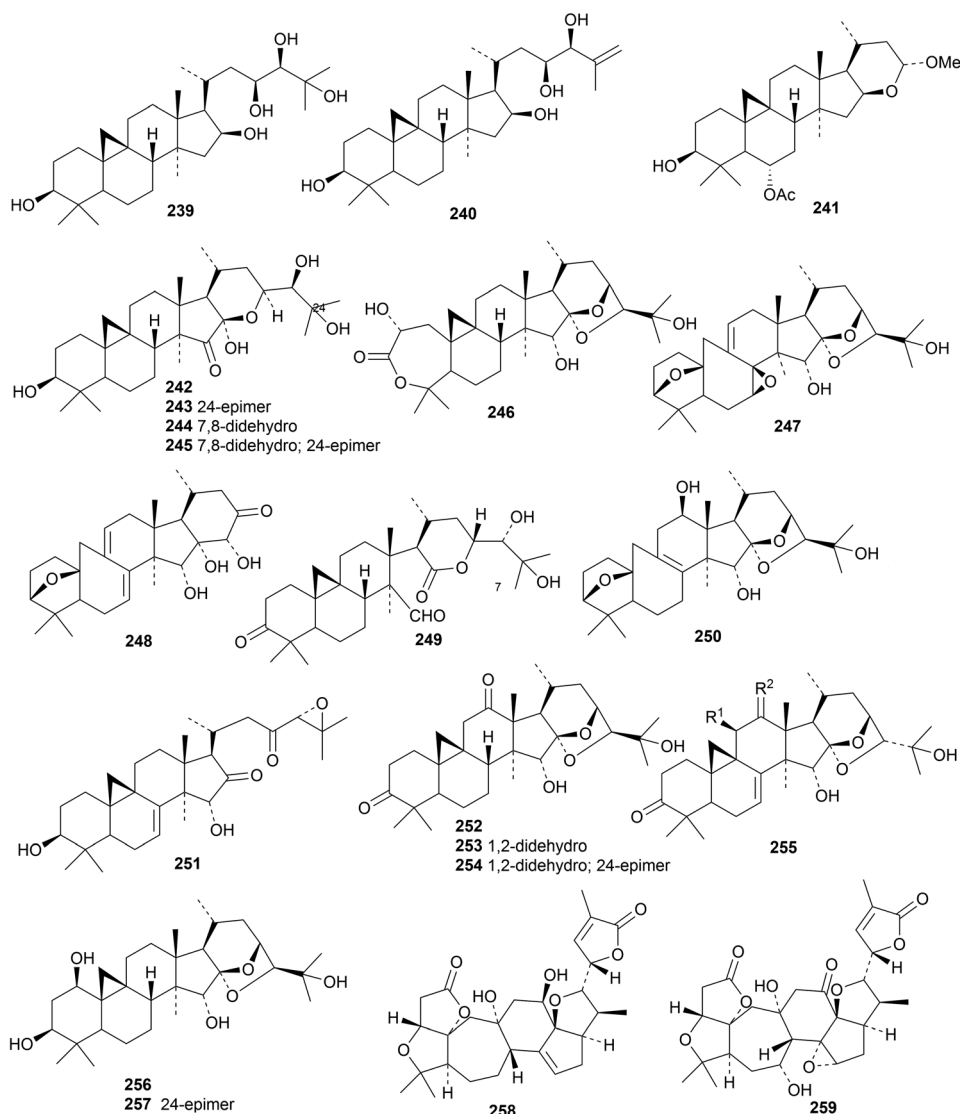
Abies faxoniana is the source of an impressive group of pairs of lanostane and cycloartane derivatives A₁/A₂ 195/196–H₁/H₂ 209/210, with epimeric spiro-side chains.⁶⁷ Fourteen new cycloartane derivatives, 211–216 (ref. 68) and 217–224,⁶⁹ have been isolated from *Beesia calthifolia*. Other cycloartanes 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 cimihacleins A 246–D 249, 12 β -hydroxyacerinol 250, 11-dehydroxy-15 α -hydroxycimicidanol 251, cimigenol-3,12-dione 252, the related enones 253 and 254, compound 255 and 1 β -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 *Schisandra* 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









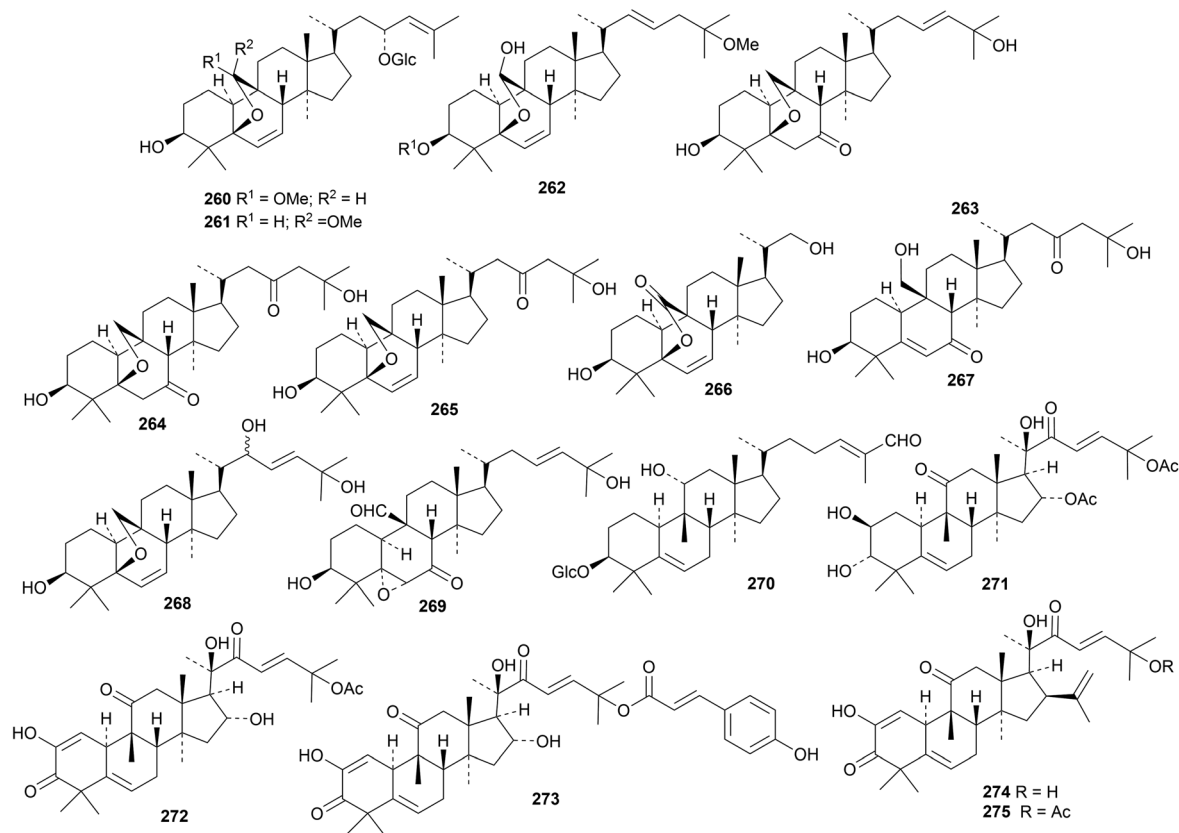
The cucurbitacins have interesting pharmaceutical potential.^{85,86} Cucurbitacin E has been investigated for a wide range of activities.⁸⁷ The biosynthesis of the bioactive mogrosides from *Siraitia grosvenorii* has been studied.⁸⁸ Three papers describe further cucurbitacin constituents of *Momordica charantia*, including taikugausins C 260, D 261 and E 262,⁸⁹ kuguacins II 263–VI 267 (ref. 90) and kuguacin 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 Hemsleyenside B 270 and the 16,25-diacetate 271 of cucurbitacin F have been isolated from *Hemsleya jinfushanensis*.⁹³ Hemsleyenside 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 VA₁ from *Siraitia grosvenorii*,⁹⁶ kaguaglycoside I⁹¹ and taikugausins A and B⁸⁹ from *Momordica charantia* and hemsleyensides 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 Rg₁₁, 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 pentaphyllum*,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 nordammaranes, 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 quinquifolioside 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 RF₂ 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

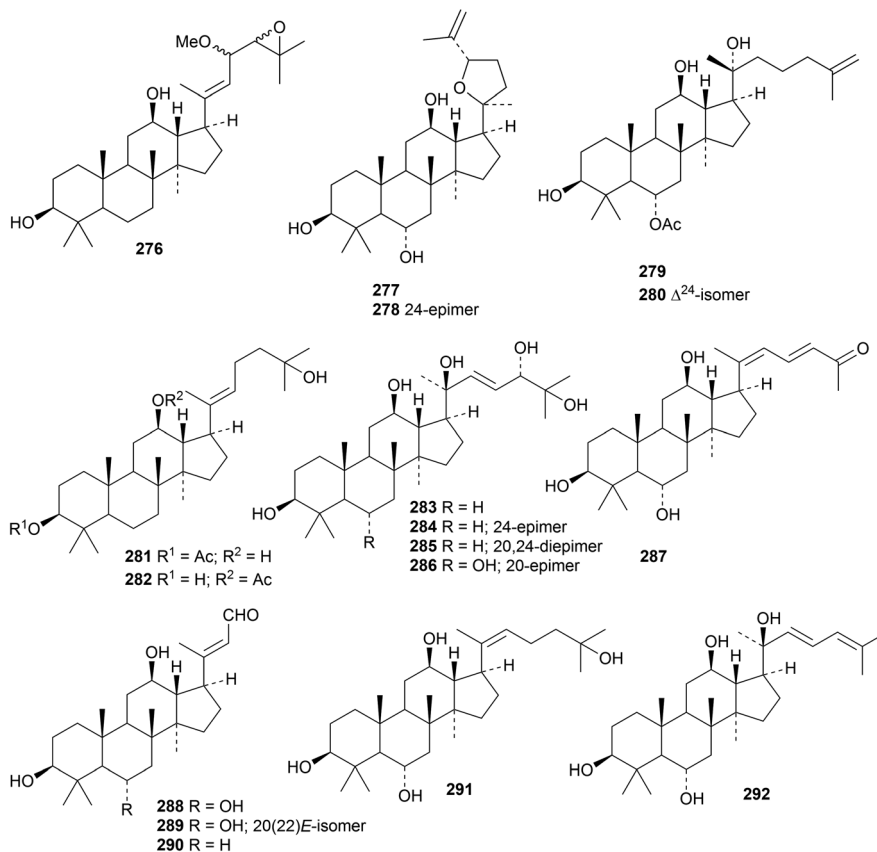
Panax ginseng.^{116–118} The current knowledge of the key enzymes involved in the biosynthesis of saponins from *Panax notoginseng* has been surveyed.¹¹⁹

Ricinidols A 318 and B 319 have a new rearranged euphane skeleton.¹²⁰ They occur in *Ricinodendron heudelotii* together with the euphane derivatives ricinidols 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-3 β -ol 327 from *Euphorbia pekinensis*.¹²³

New tirucallane derivatives include 3 β -*O*-tigloylmelianol 328 from *Guarea kunthiana*,¹²⁴ congoensins A 329 and B 330 from the bark of *Entandrophragma congoense*,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

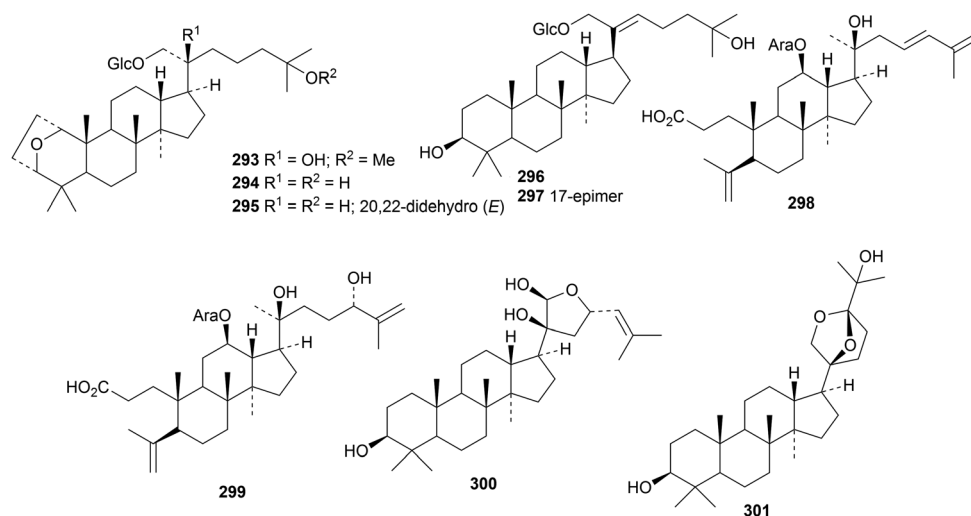
Polygonifoliol 346, from the latex of the seaside sandmat *Euphorbia polygonifolia*, is an apotirucallane with an 18(17 \rightarrow 14)-abeo rearrangement.¹³¹ Piscidinols H 347–L 351 are apotirucallane derivatives from the leaves of *Walsura trifoliata* that

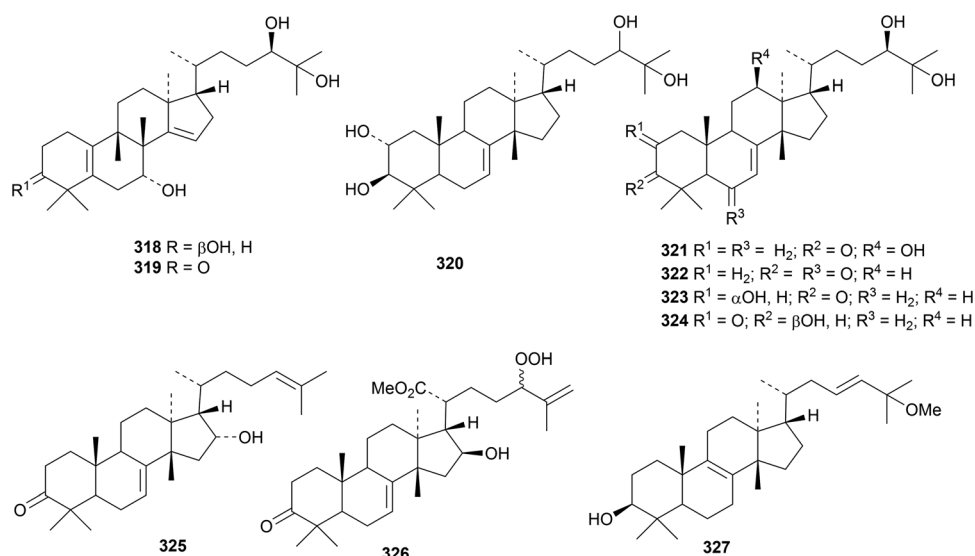
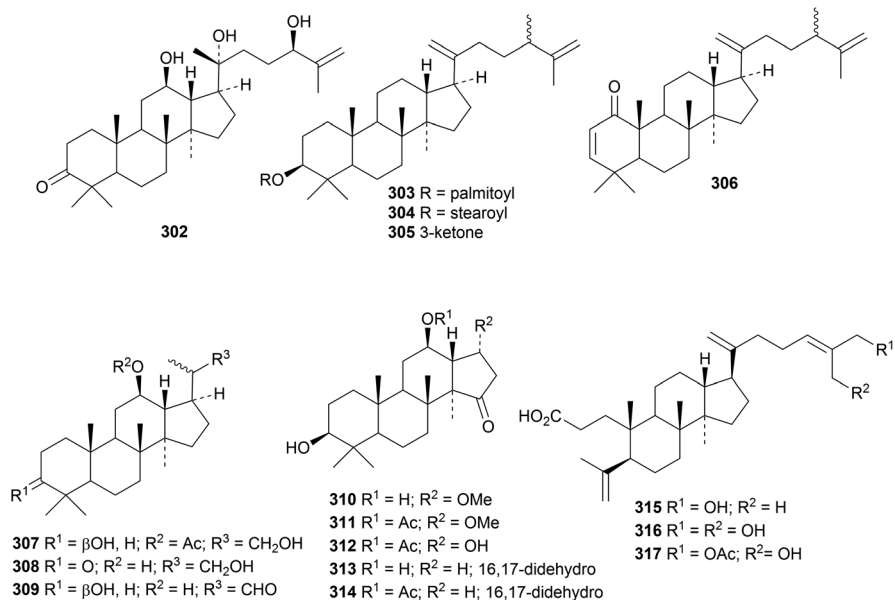




show moderate insecticidal activities.¹³² The apotirucallol derivative 352 has been isolated from the seeds of *Xylocarpus granatum*.¹³³

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





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*

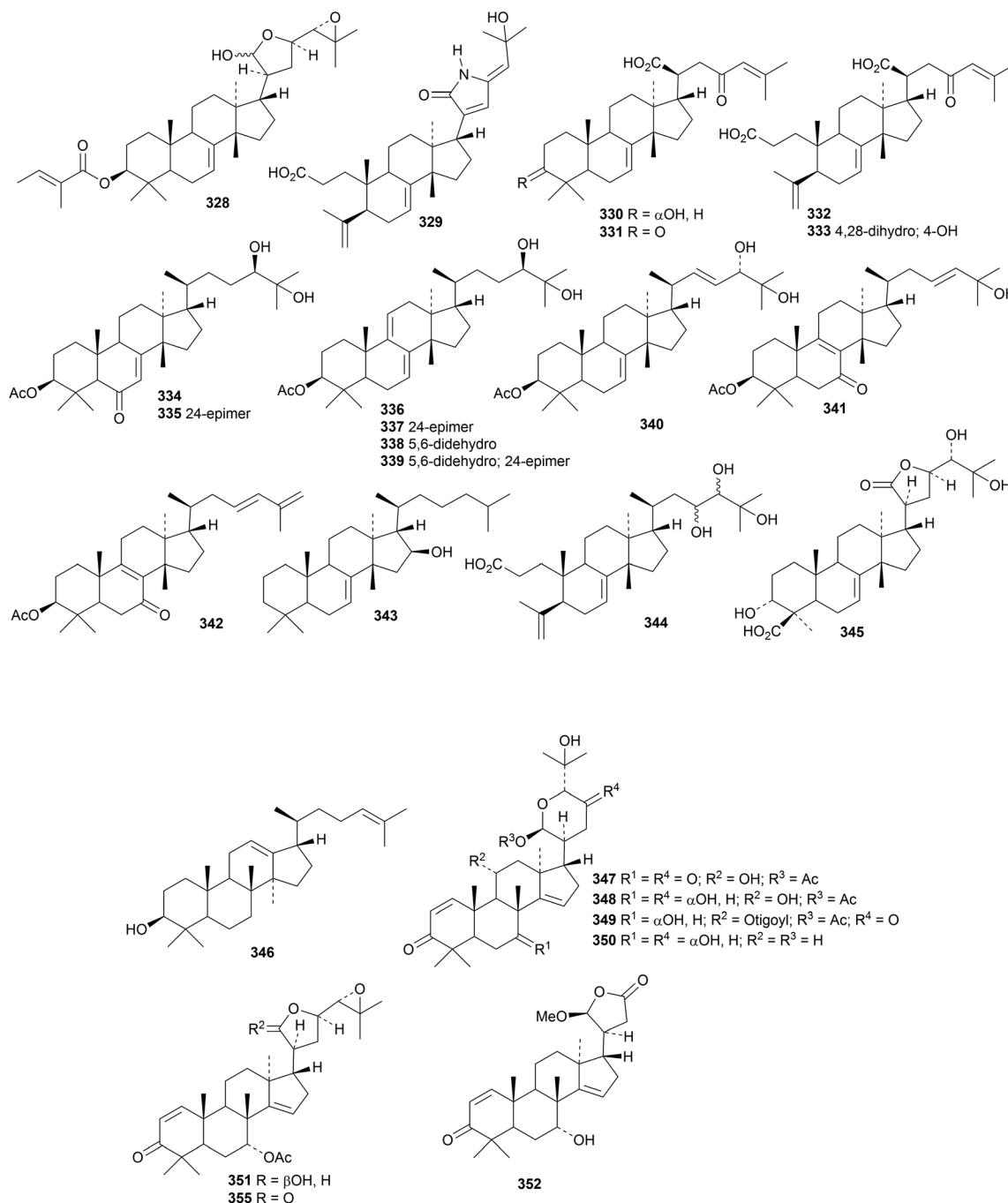
songboiensis with cytotoxic activity.¹³⁹

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.

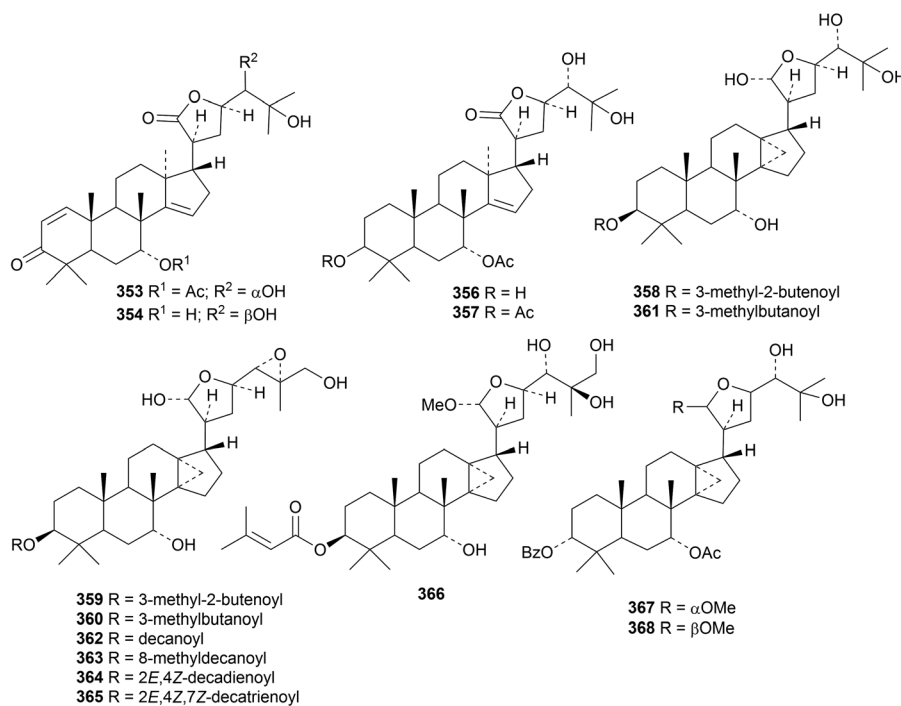




Munronins A 406–N 419 (ref. 142) and O 420, P 421 and Q 422 (ref. 143) are constituents of *Munronia henryi*. Unfortunately, the names munronins A–G have been used before and munronin L 415 is the known 23-O-methylvolkensin. The structure of munronin H 412 was confirmed by X-ray crystallographic analysis. 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 nimboldicin 438 and nimboicin 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 xylocensin U derivatives **465** and **466** and the mexicanolide derivatives **467** and **468**,¹⁵⁰ while the seeds of Indian *Xylocarpus moluccensis* yielded proceranolide propanoate **469** and deacetylangustidienolide **470**.¹⁵¹ 2,3-Dideacetylxylocensin S **471** and 30-deacetylxylocensin 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 oil¹⁵⁶ 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.

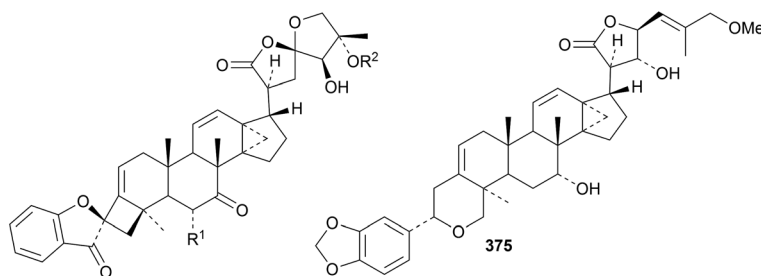
4.2. Quassinoids

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

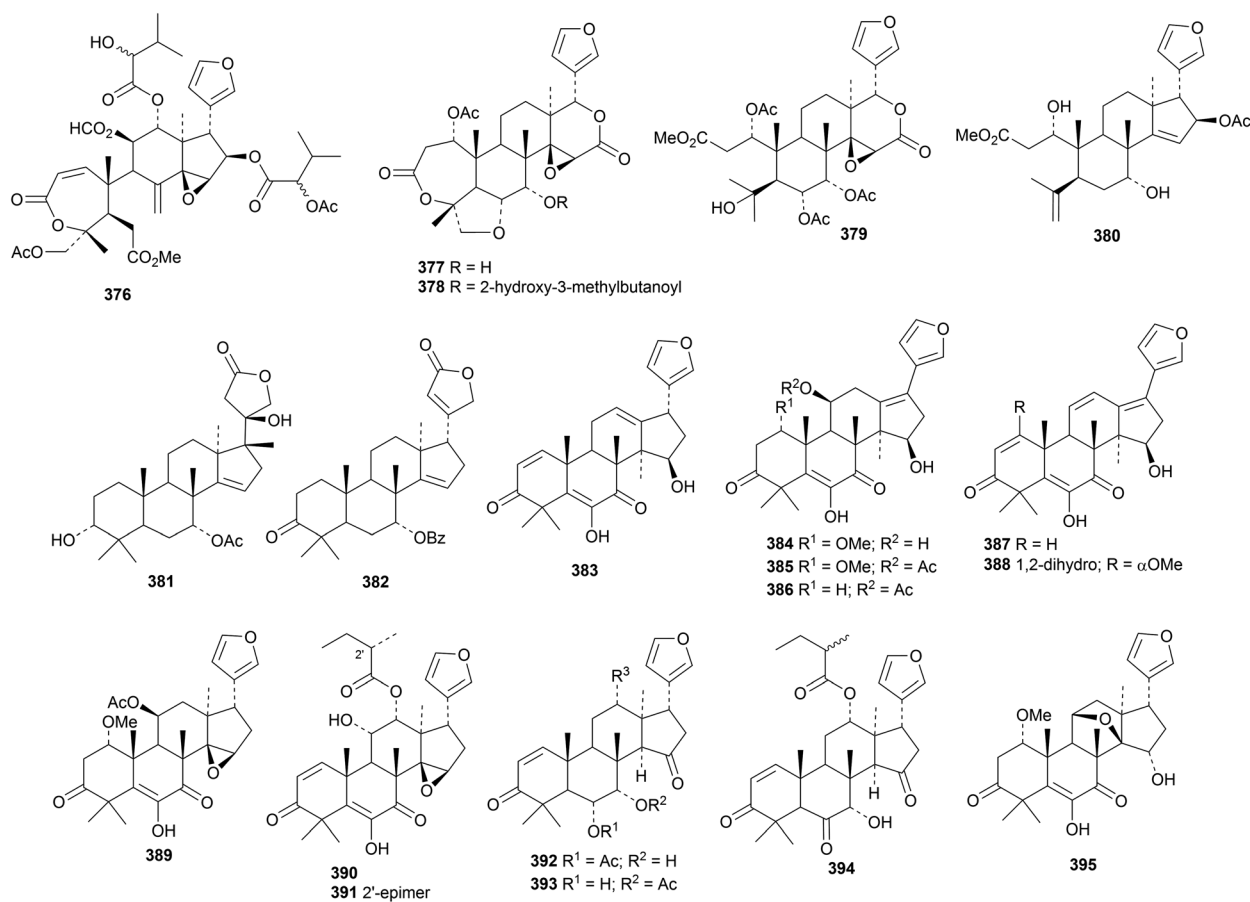
5. The lupane group

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





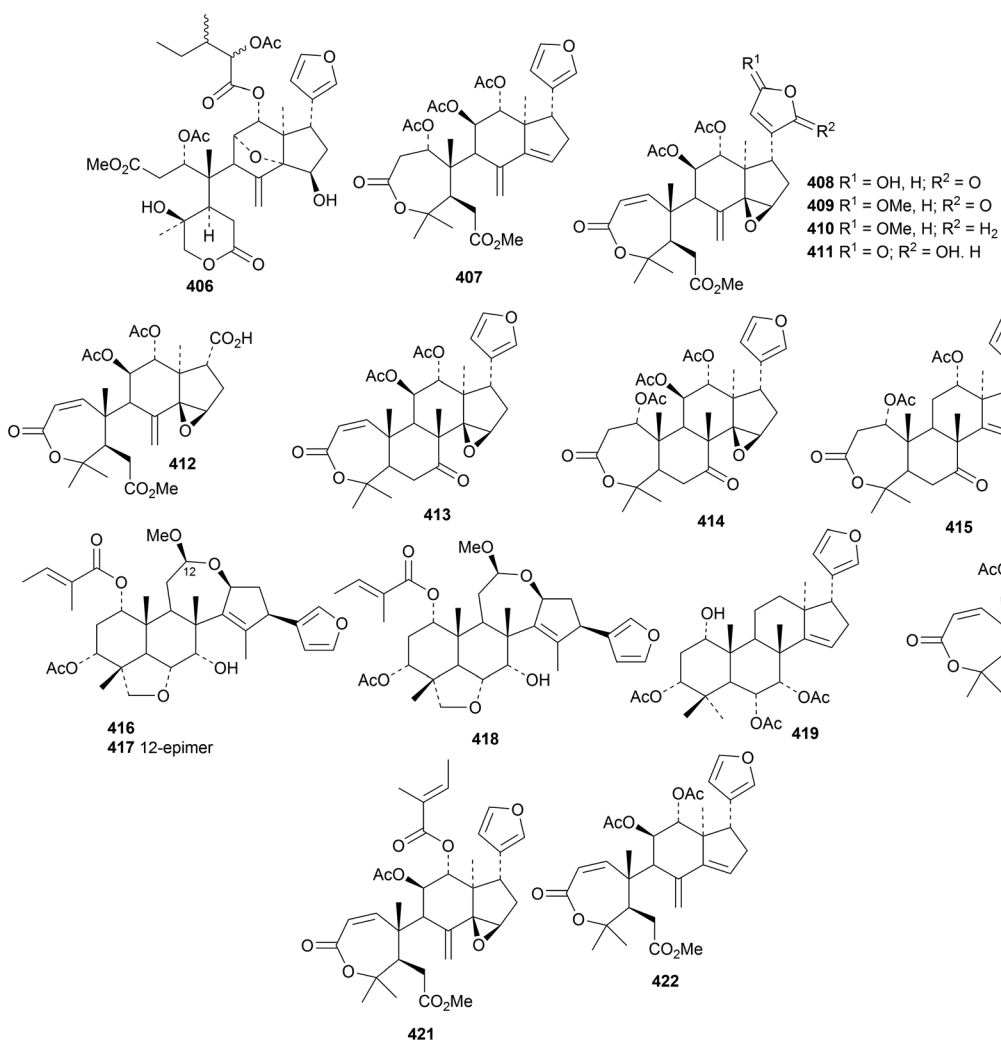
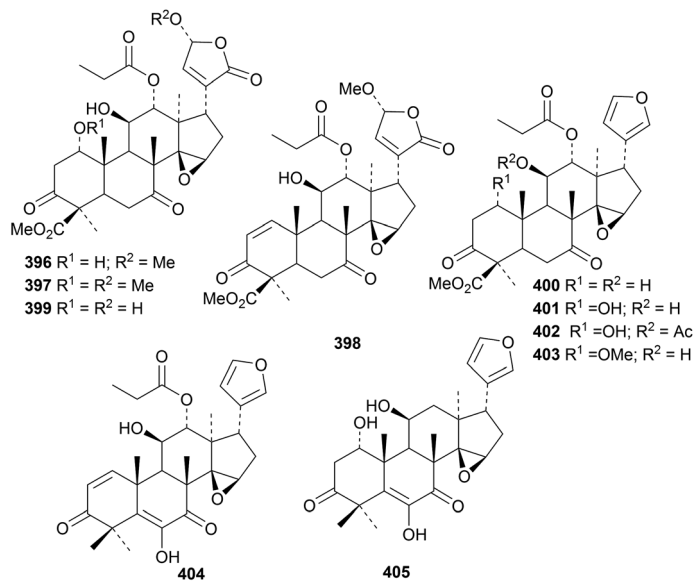
- 369 $R^1 = R^2 = H$
 370 $R^1 = OH; R^2 = H$
 371 $R^1 = OH; R^2 = Me$
 372 $R^1 = OH; R^2 = 6\text{-hydroxyhexanoyl}$
 373 $R^1 = OH; R^2 = 4\text{-hydroxy-3}R\text{-methoxybutanoyl}$
 374 $R^1 = OH; R^2 = 3R,4\text{-dimethoxybutanoyl}$

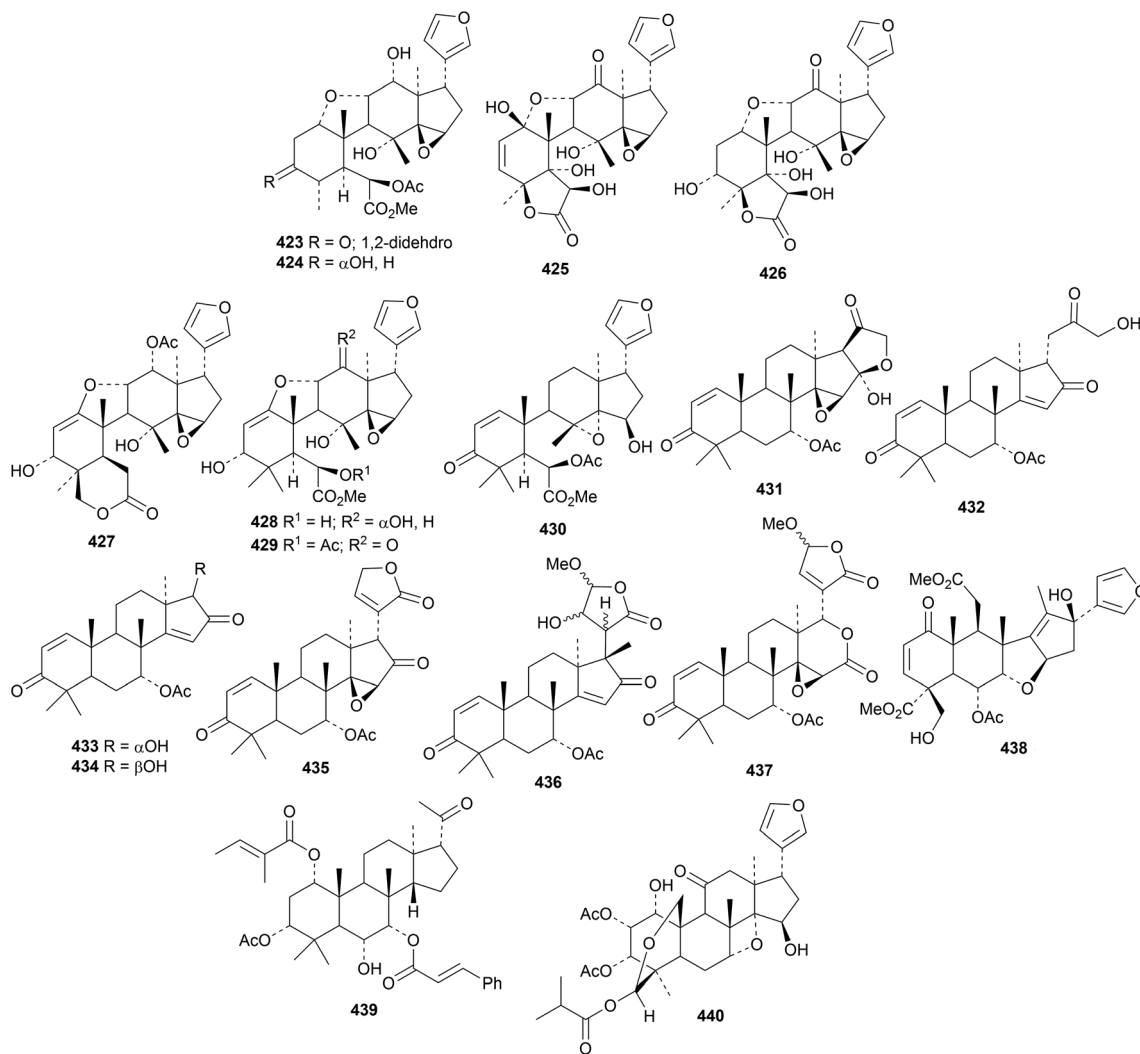


related compounds 547 and 548 have been found in Egyptian apple peel (*Malus domestica*).^{167,168} *Cassine xylocarpa* is the source of four new lupane derivatives 549–552 and a further

two, 553 and 554, are from *Maytenus cuzcoina*.¹⁶⁹ Other new lupane derivatives include the antibacterial 3 β -hydroxy-9(11),12-lupadien-28-oic acid 555 from *Sonneratia alba*¹⁷⁰ and





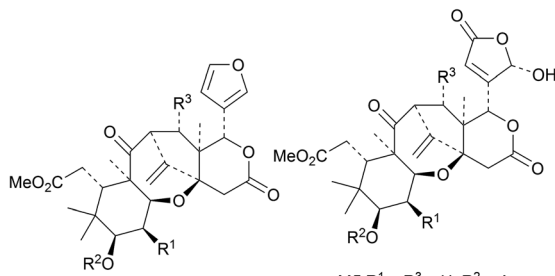


3 β -hydroxy-7-oxo-20(29)-lupen-28-oic acid **556** from *Manilkara zapota*.¹⁷¹ Novel lupane esters include the 3-hexadecanoyl ester **557** of 20(29)-lupene-3 β ,7 β -diol from *Scurrula parasitica* parasitic on *Nerium indicum*,¹⁷² the 4-hydroxy-3-methoxybenzoyl ester **558** from *Paullinia pinnata*,¹⁷³ the cafeoyl ester **559** from *Celastrus stylosus*¹⁷⁴ and the 2-benzoyl ester of aliphatic acid from *Rubus innominatus*¹⁷⁵ Hancokinoid, 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

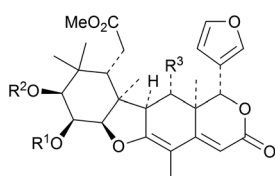
Three 24-noroleananes, **560**, **561** and **562**, have been isolated from biogas slurry.¹⁷⁹ The structure of 24-nor-12-oleanene-3,22-dione **562** was confirmed by X-ray crystallographic analysis. The related dione **563** has also been found in biogas slurry.¹⁸⁰ The 3,4-seco-oleanane derivative **564**, 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 2 α ,3 β ,21 β ,23-tetrahydroxy-12-oleanene-28,29-dioic acid¹⁸³ and



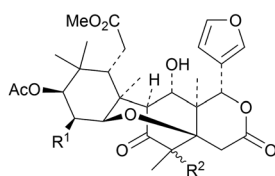


441 R¹ = OAc; R² = Ac; R³ = OH
 442 R¹ = OH; R² = Ac; R³ = OH
 443 R¹ = OH; R² = Ac; R³ = OAc
 444 R¹ = R² = R³ = H

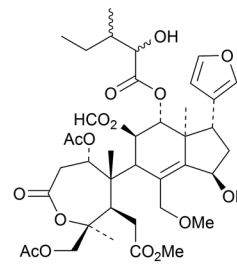
445 R¹ = R³ = H; R² = Ac
 446 R¹ = R³ = OAc; R² = Ac
 447 R¹ = H; R² = Ac; R³ = OAc



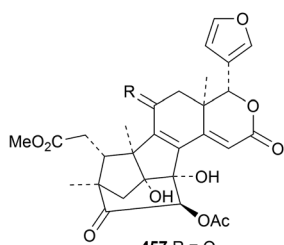
448 R¹ = H; R² = Ac; R³ = OH
 449 R¹ = R² = H; R³ = OH
 450 R¹ = R² = R³ = H



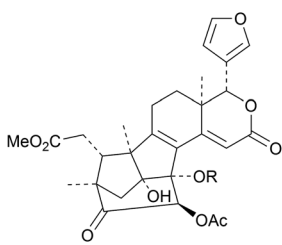
451 R¹ = H; R² = α H
 452 R¹ = OAc; R² = α H
 453 R¹ = OH; R² = α H
 454 R¹ = OAc; R² = β OH
 455 R¹ = OAc; R² = α OH



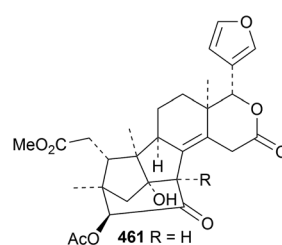
456



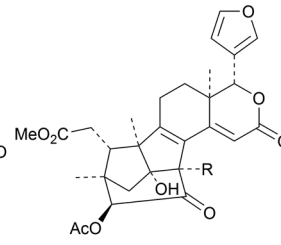
457 R = O
 458 R = H₂



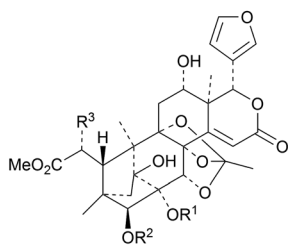
459 R = H
 460 R = Et



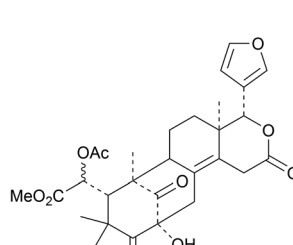
461 R = H
 462 R = OEt



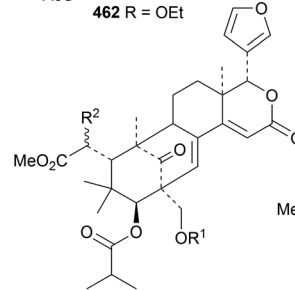
463 R = H
 464 R = Otigloyl



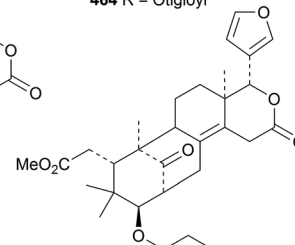
465 R¹ = R³ = H; R² = Ac
 466 R¹ = R² = Ac; R³ = H
 471 R¹ = R² = H; R³ = OH



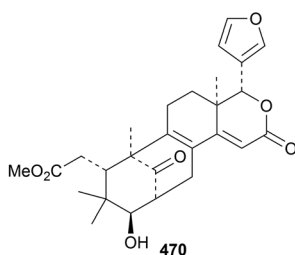
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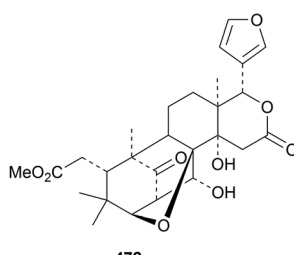
468 R¹ = H; R² = OAc
 474 R¹ = Ac; R² = H; 14 α ,15-dihydro



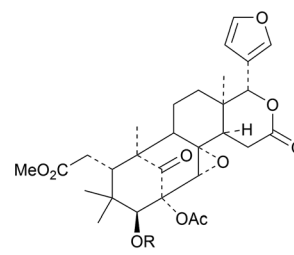
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470

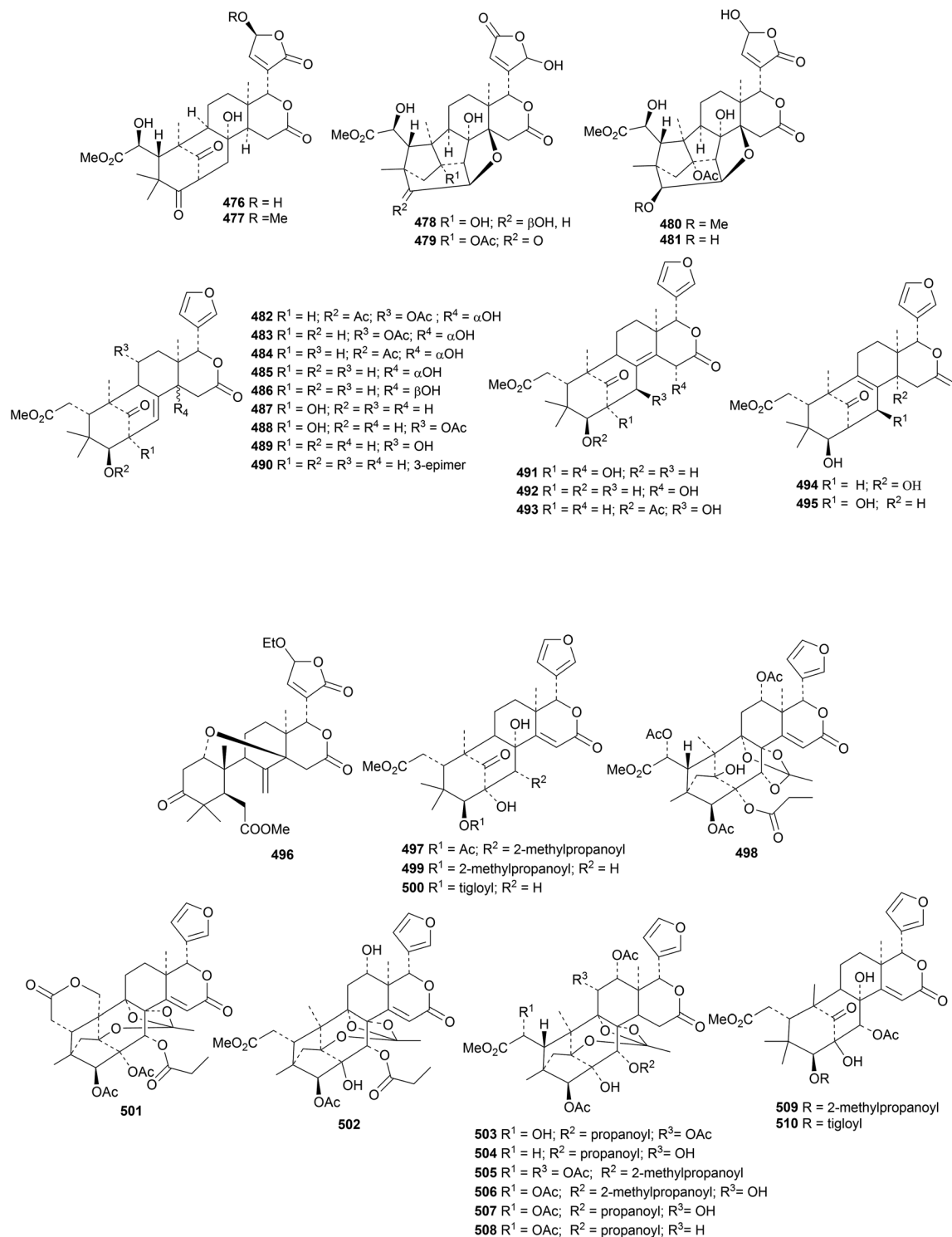


472



473 R = tigloyl
 475 R = 2-methylpropanoyl



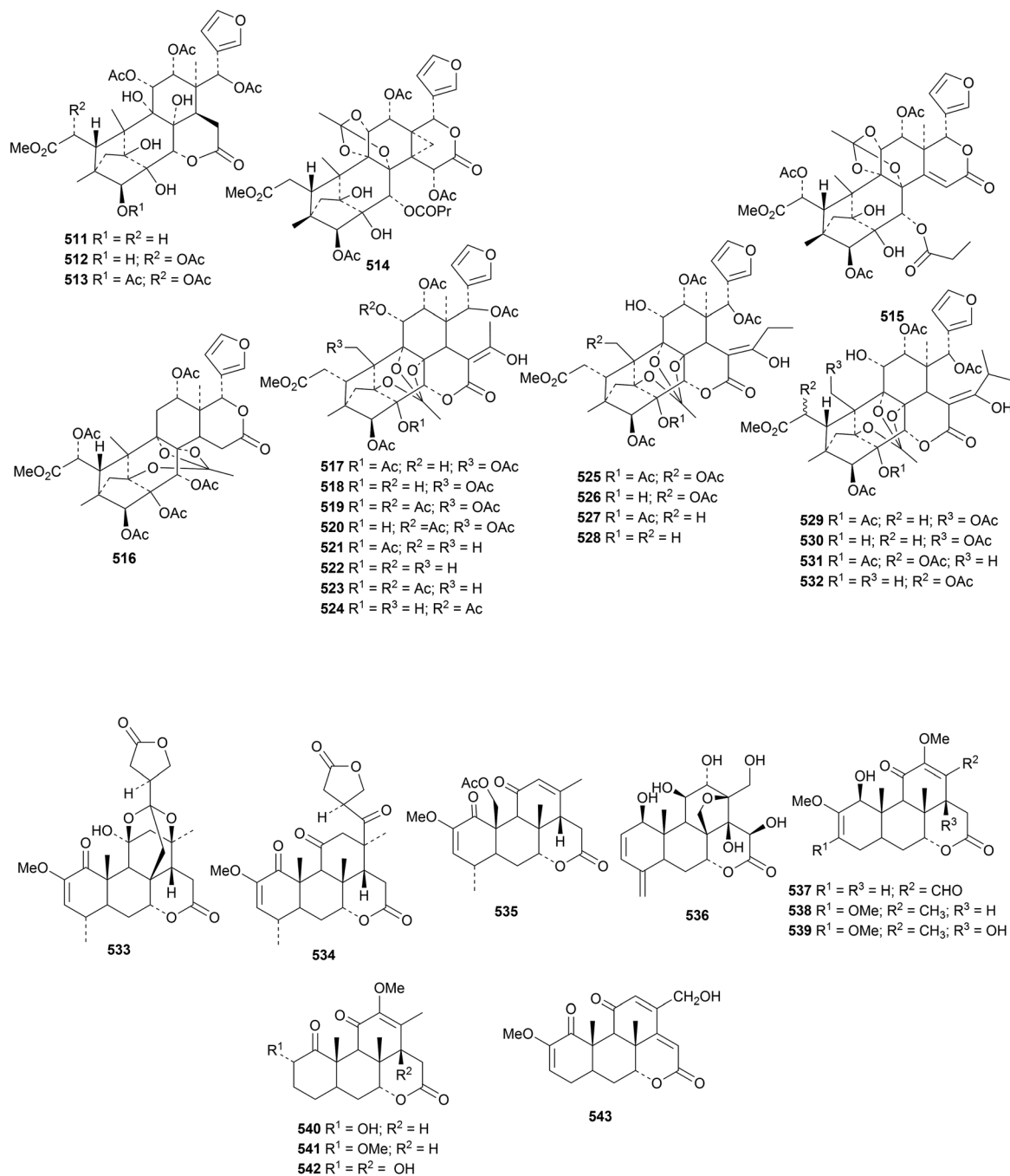


pashia acid 570, from *Pyrus pashia*, is 2 α ,3 β ,27-trihydroxy-12-oleanen-28-oic acid.¹⁸⁴

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 penta-hydroxyoleanenone 578 and the corresponding 3-ketone 579 from *Gueldenstaedtia verna*,¹⁹⁰ the 11-hydroperoxide 580 from *Holarhena curtisii*,¹⁹¹ 3 β ,6 β ,29-trihydroxy-12-oleanen-28-oic acid 581 from *Spermacoce latifolia*,¹⁹² 2 α ,3 β ,29-trihydroxy-12-





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-oxosaresinolic acid **587** and $2\alpha,3\alpha$ -dihydroxy-11,13(18)-oleanadien-28,19 β -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 $18\alpha H$. 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 -amyryn from *Dichrocephala benthamii*,²⁶¹ the caffeoyl esters **609** and **610** from *Waltheria indica*²⁶² and the coumaroyl ester **611** from *Astilbe rivularis*.²⁶³

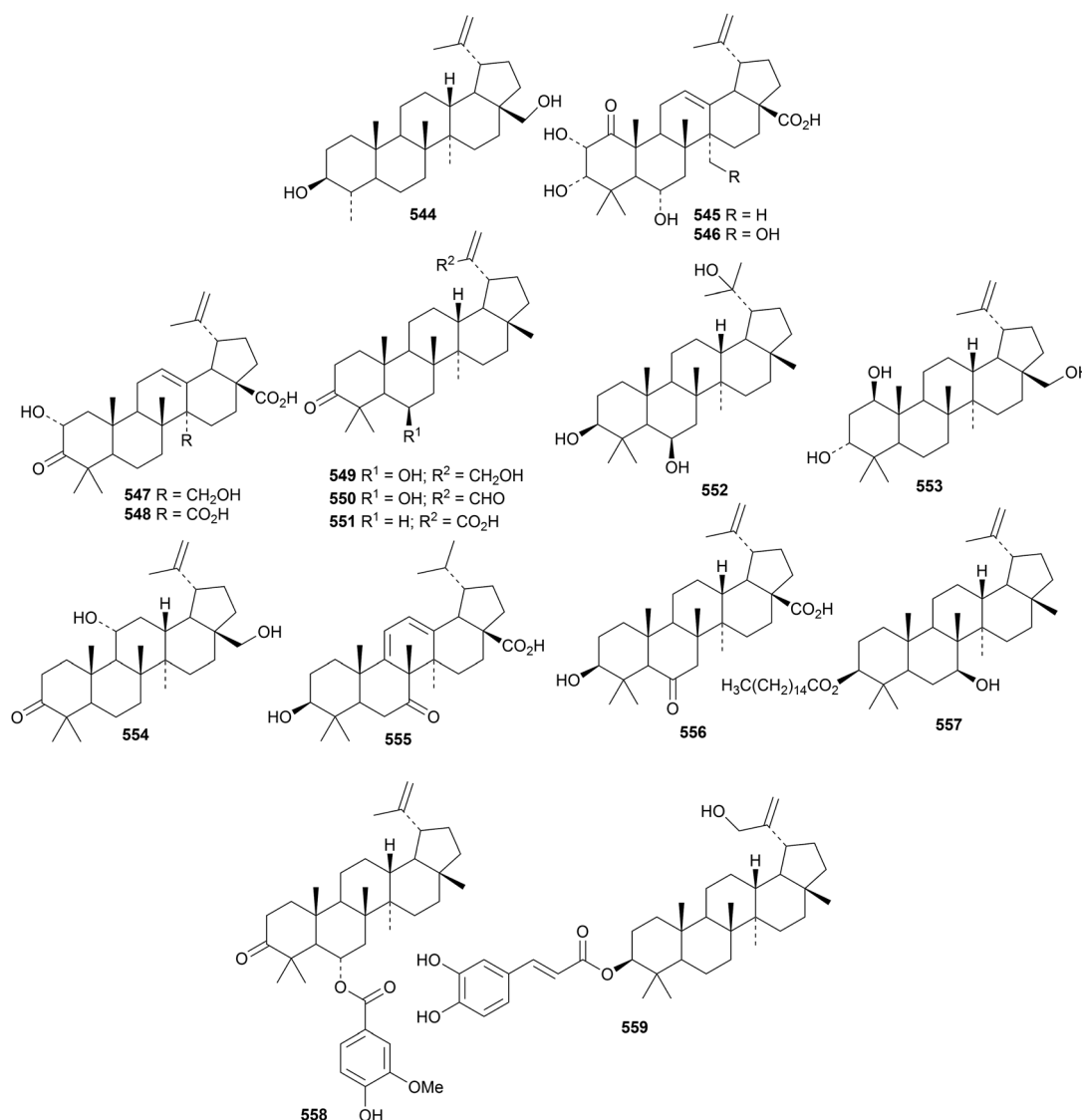
There have been many reports of the biological activities of oleanane triterpenoids and their saponins including the anti-tumour activity²⁶⁴ and stem cell differentiation activity²⁶⁵ of oleanolic acid and the antitumour activity of ardisiposilloside,²⁶⁶ boswellic acids,²⁶⁷ β -escin²⁶⁸ and raddeanin A.²⁶⁹ The biological properties of glycyrrhizic acid²⁷⁰ and other triterpenoids²⁷¹ 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	<i>Erythrina abyssinica</i>	205
Aesculosides S1, S2	<i>Aesculus sylvatica</i>	206
Akeqintoside E	<i>Akebia quinata</i>	207
Amphipaniculosides A	<i>Amphilophium paniculatum</i>	83
Aquaticasaponins A, B	<i>Gleditsia aquatica</i>	208
Ardinuloside	<i>Ardisia insularis</i>	209
Bigelovii C	<i>Salicornia bigelovii</i>	210
Bigelovii D	<i>Salicornia bigelovii</i>	211
Boromoenosides A–D	<i>Albizia boromoensis</i>	212
Brachyantherosides A1–A5, B6, B9	<i>Stauntonia brachanthera</i>	183
Catunariosides I, J	<i>Catunaregam spinosa</i>	213
Centellasaponin H	<i>Centella asiatica</i>	214
Clematograpeolenoside A	<i>Clematis graveolens</i>	215
Comastomasaponin I	<i>Comastoma pedunculatum</i>	216
Coriacea saponin A	<i>Holboellia coriacea</i>	217
Crotalariosides C, (E/Z)-D, (E/Z)-E, (E/Z)-F	<i>Polygala crotalarioides</i>	218
Cyrrillin B	<i>Cyrrilla racemiflora</i>	185
Enterolacaciamine	<i>Enterolobium cyclocarpum</i>	219
Floraassamsaponins I–VIII	<i>Camellia sinensis</i> var. <i>assamica</i>	220
Ginsenoside Ro sulfate	<i>Silphium laciniatum</i>	16
Glomerulosides A–H	<i>Glochidion glomerulatum</i>	221
Glomerulosides I, II	<i>Glochidion glomerulatum</i>	222
Hemslosides Ma4, Ma5	<i>Hemsleya chinensis</i>	223
Hippophosides E, F	<i>Hippophae rhamnoides</i>	224
Lebbeckosides A, B	<i>Albizia lebbek</i>	225
Leptocarposides B, C, D	<i>Ludwigia leptocarpa</i>	226
Lobatoside O	<i>Actinostemma lobatum</i>	113
Lonicerosides K, L, M	<i>Weigela subsessilis</i>	227
Macedonoside E	<i>Glycyrrhiza uralensis</i>	198
Meliomosides A–G	<i>Meliosma henryi</i>	228
Oleiferasaponins C1, C2, C3	<i>Camellia oleifera</i>	229
Oleiferosides I–M	<i>Camellia oleifera</i>	230
Oleiferosides N, O	<i>Camellia oleifera</i>	231
Oleiferosides P–T	<i>Camellia oleifera</i>	232
Pachystelanoside A	<i>Pachystela msolo</i>	195
Perennisosides XIII–XIX	<i>Bellis perennis</i>	233
Poliusaposides A, B, C	<i>Teucrium polium</i>	234
Rotundinoside A	<i>Ilex rotunda</i>	235
Serjanioside D	<i>Serjania marginata</i>	236
Schefflerasides A, B	<i>Schefflera sessiliflora</i>	237
Schekwangsiensides Ia, Ib, IIa, IIb, III–VI, VIIa, VIIb, VIII	<i>Schefflera kwangsiensis</i>	238
Schisusaponins A–F	<i>Schima superba</i>	201
Securiosides C, D, E	<i>Securidaca inappendiculata</i>	239
Stauntosides G, H	<i>Stauntonia obovatifoliola</i>	240
Vulgaside I	<i>Prunella vulgaris</i>	241
Zanhasaponins D–H	<i>Zanha golungensis</i>	242





has been found in *Clerodendrum philippinum* var. *simplex*.²⁷³ 3 β -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 \rightarrow 18)-abeotaraxerane derivative **618**, from *Pittosporum illicioides*, is related to isoaleuritic acid.²⁷⁶ Two taraxerane saponins with known gens have been reported from *Euphorbia dracunculoides*.²⁷⁷ 9 β ,26-Epoxy-7-multiforen-3 β -ol **619** has been isolated from *Trichosanthes baviensis*.²⁷⁸ Hainanenone A **620**, from *Drypetes hainanensis*, is 23-nor-3-friedelanone²⁷⁹ and the 24-norfriedelane **621** has been found in *Celastrus stylosus*.¹⁷⁴ *Drypetes congestiflora* is the source of 3 α ,16 β -friedelanediol **622**.²⁸⁰

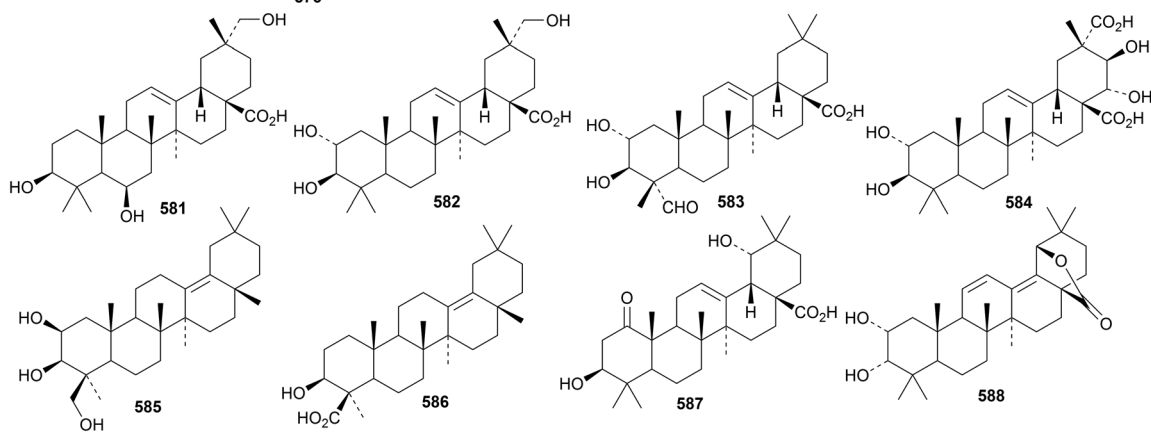
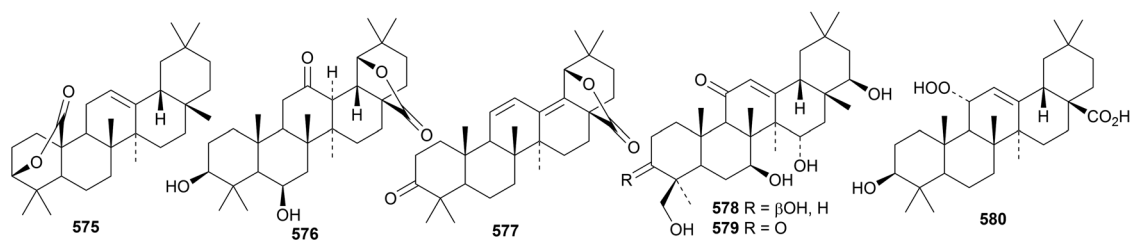
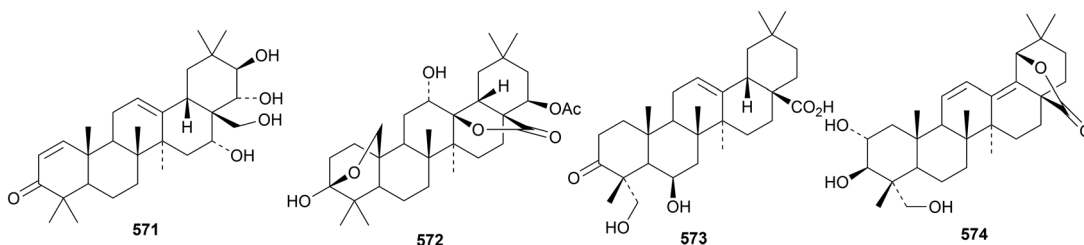
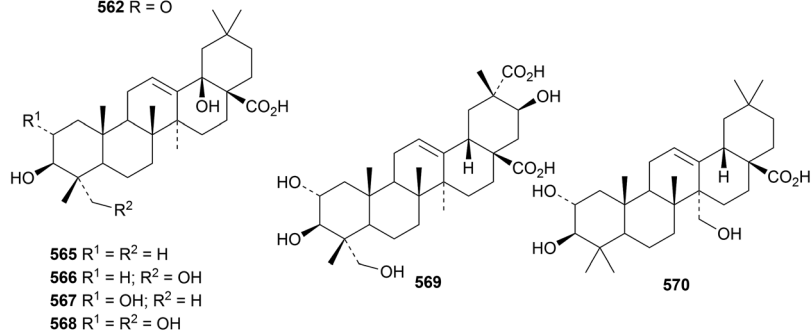
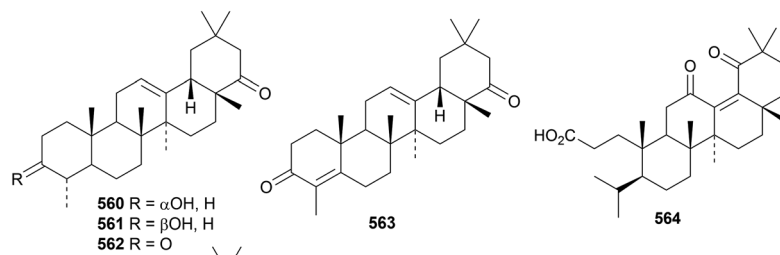
7. The ursane group

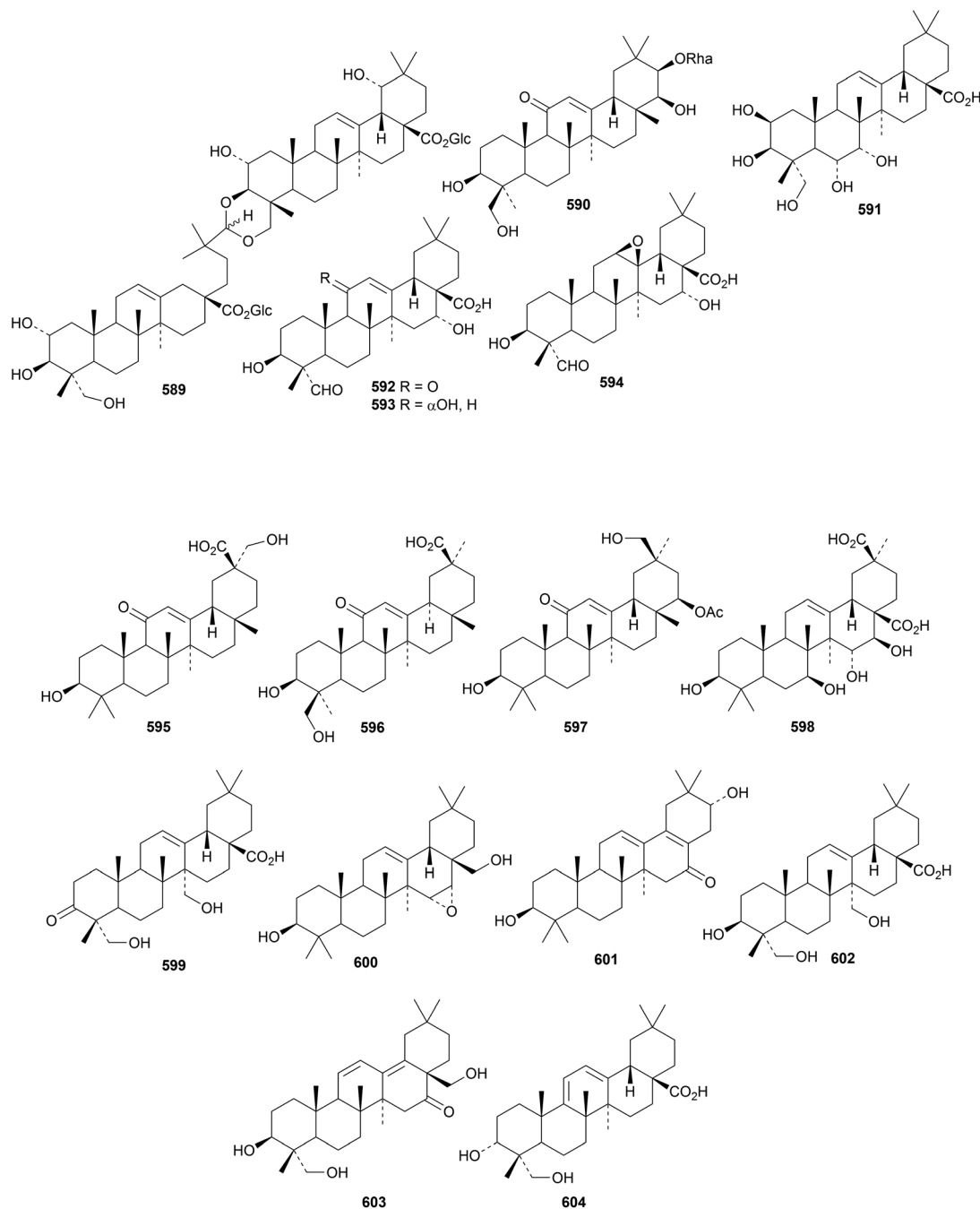
The antitumour properties of ursolic acid have been well studied.^{281–283} Urmiensolide B **623** and urmiensic acid **624**, from *Salvia urmiensis*, are 17,22-secoursane derivatives that showed significant antiproliferative activity.²⁸⁴ Further 17,22-

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

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





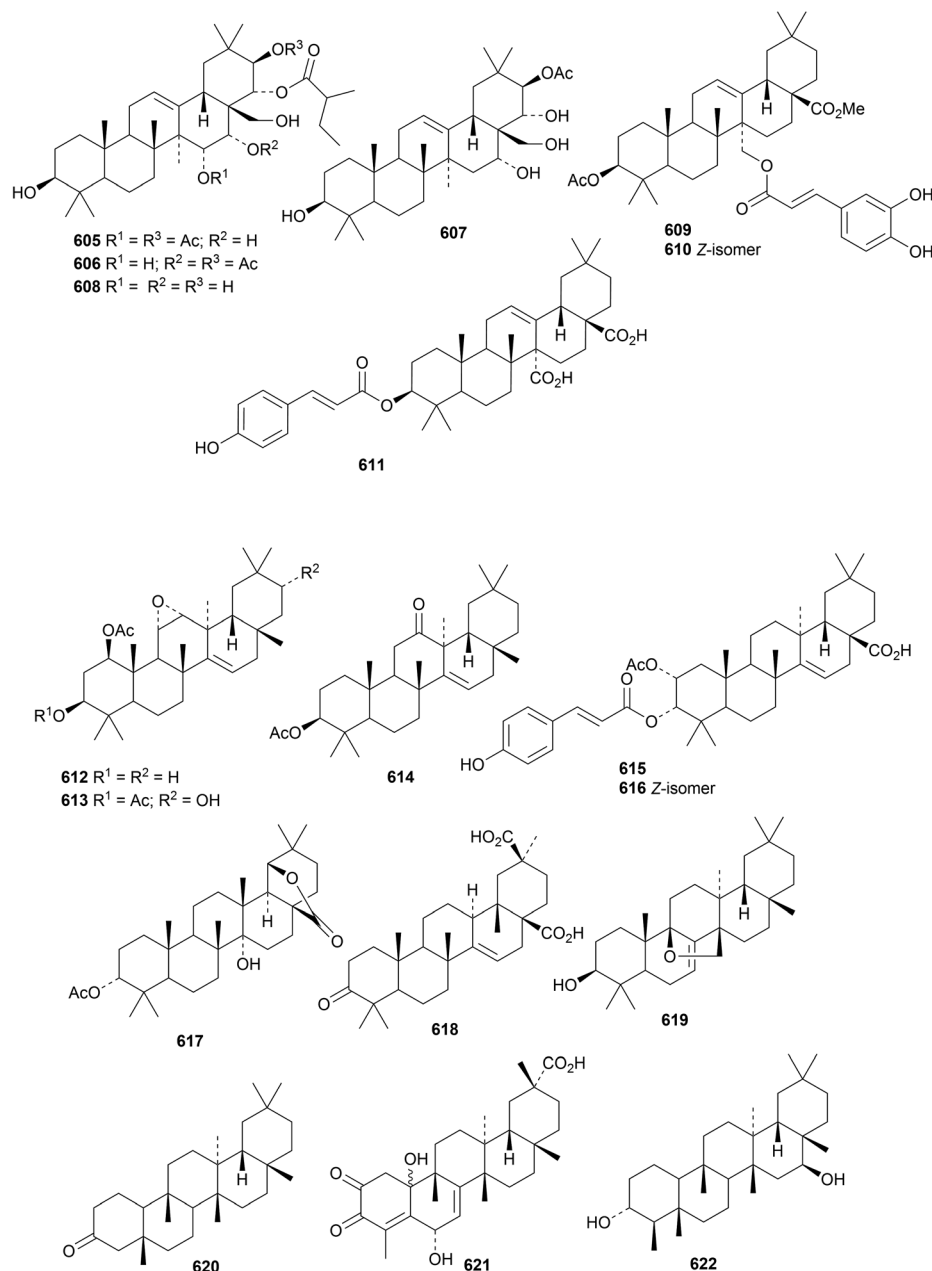


secoursanes include the apoptosis-inducing **625** from *Salvia urmiensis*²⁸⁵ and **626** and **627** from *Salvia syriaca*.²⁸⁶ *Rubus lambertianus* is the source of the 18,19-secoursanes **628** and **629** together with the glucopyranosyl esters **630**, **631** and **632**.²⁸⁷ The related 18,19-secoursane **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**,





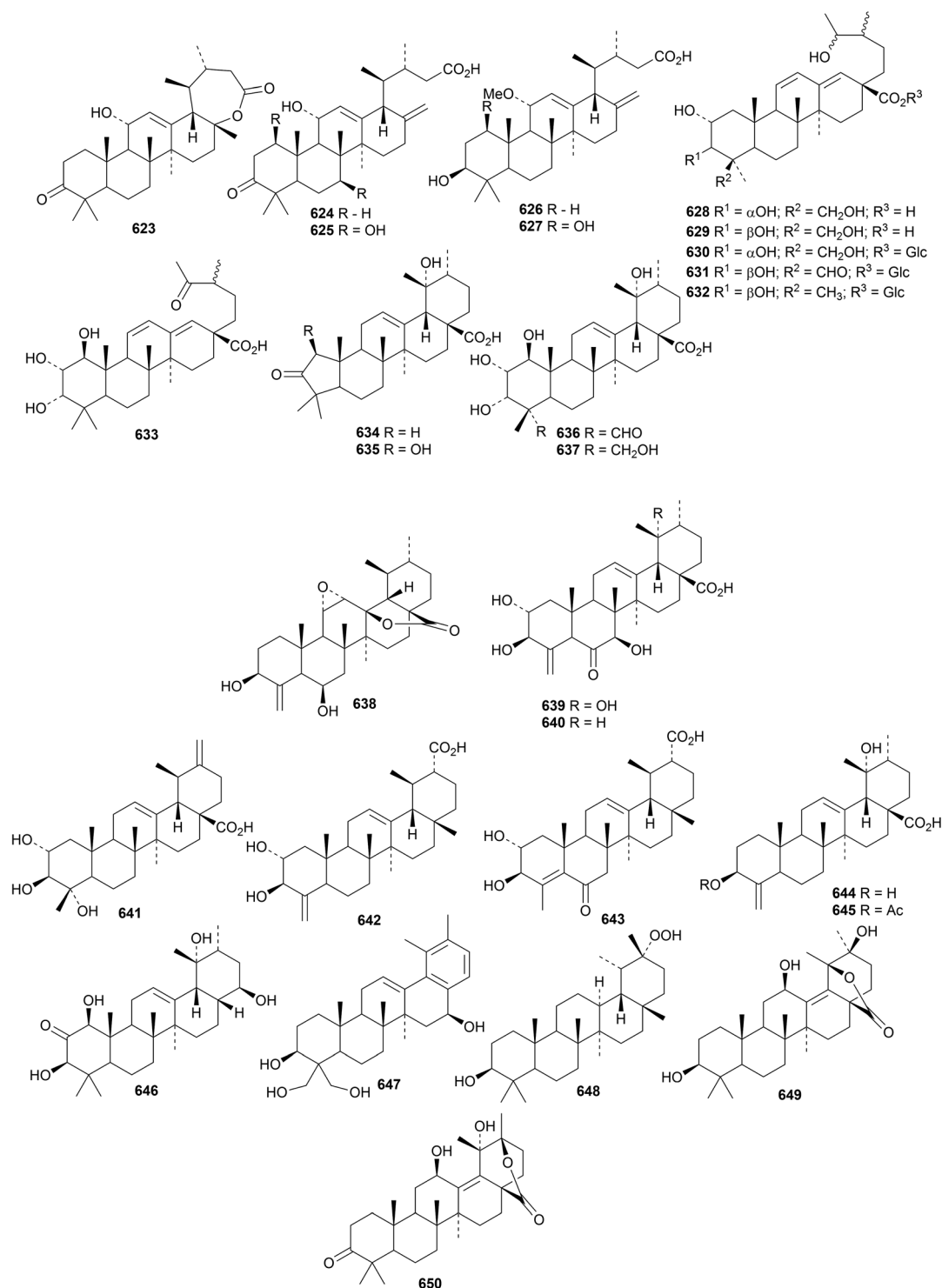
with an aromatic ring E, is present in *Gardenia jasminoides* var. *radicans*.²⁹² Ixeritriterpenol **648** has been reported from *Ixeris chinensis* with unusual stereochemistry at C13 and C19.²⁹³ The structure of 3 β ,12 β ,20 β -trihydroxy-13(18)-ursen-28,19 β -olide **649**, from *Ilex latifolia*, 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 3 β ,6 β ,23-trihydroxy-12,20(30)-ursadien-28-oic acid **655** from *Spermacoce latifolia*,¹⁹² 1 α ,2 β ,3 β ,19 α -tetrahydroxy-12-ursen-28-oic acid **656**

from *Vitellaria paradoxa*,²⁹⁵ the enone **657** from *Codium dwarf-kense*,²⁹⁶ 2 β ,3 β ,19 α ,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 20 β configuration, from *Ilex pubescens*,³⁰¹ pittangretosides C₁ and L with the genins **671** and **672**, respectively, from



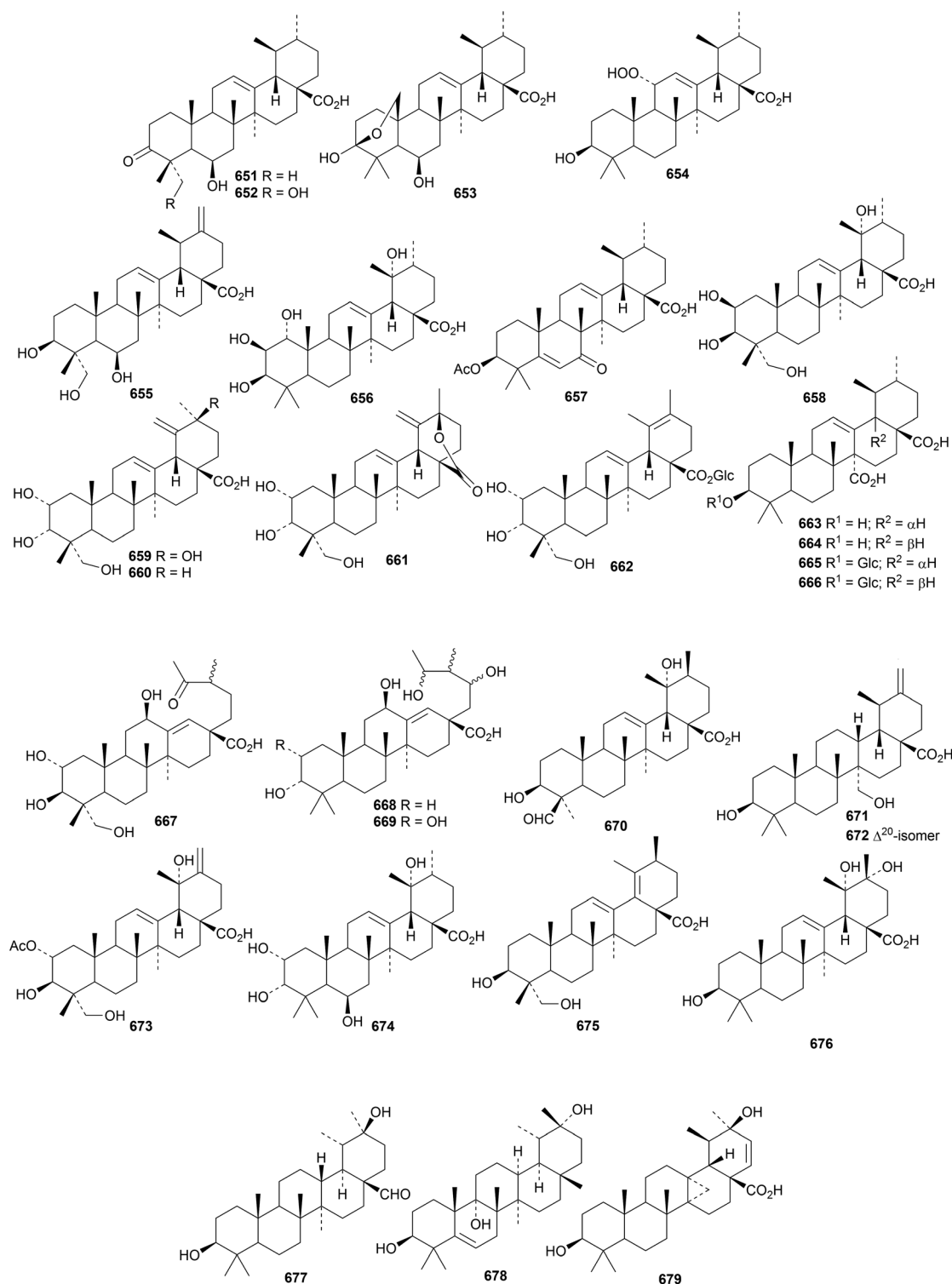


*Pittosporum angustifolium*³⁰² and vulgaside II with genin 673 from *Prunella vulgaris*²⁴¹ and saponins from *Callicarpa kwangtungensis* with genin 674,²⁴⁶ *Ilex cornuta* with genin 675 (ref. 303) and *Ilex kudingcha* with genin 676.³⁰⁴

Named ursane saponins with known genins include amphipaniculoside B from *Amphilophium paniculatum*,⁸³ catunariosides 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

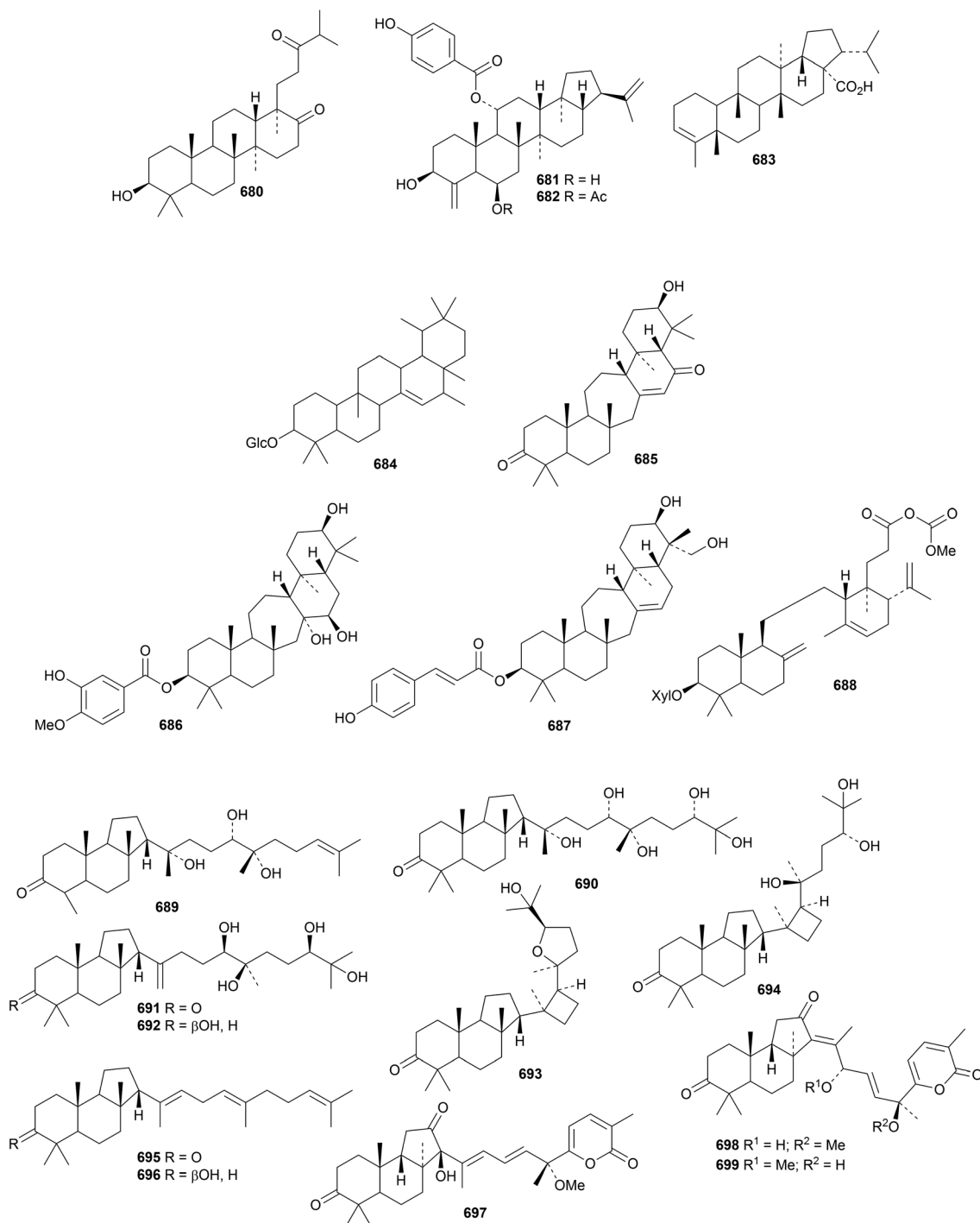




Fagonicin **677**, from *Fagonia indica*, is 3 β ,20 β -dihydroxytaraxastan-28-al with an unusual stereochemistry at C13 (ref. 200) and genicunolide C **678**, from *Euphorbia geniculata*, is 5-taraxastene-3 β ,9 α ,20 α -triol.²⁷² Ilexpublenin T, from *Ilex*

pubescens is a taraxastane saponin with a known genin³⁰¹ 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





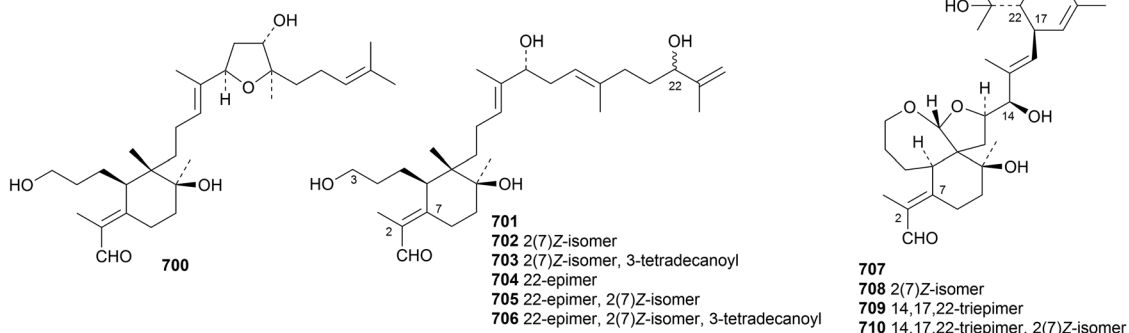
8. The hopane group

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 21 β -Hydroxy-14-serratene-3,16-dione **685** has been isolated from *Lycopodiella cernua* together with the serratene 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 stelletins 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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