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Triterpenoids

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This review covers the isolation and structure determination of triterpenoids reported during 2012 including squalene derivatives, lanostanes, holostanes, cycloartanes, cucurbitanes, dammaranes, euphanes, tirucallanes, tetranortriterpenoids, quassinoids, lupanes, oleananes, friedelanes, ursanes, hopanes, serratanes, isomalabaricanes and saponins; 348 references are cited.

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1. Introduction

There is continued interest in the anticancer activities of triterpenoids^{1–3} and their potential for treatment or prevention of diabetes and Alzheimer's disease.⁴ The oral absorption and metabolism of triterpenoid saponins has been reviewed.⁵ Surveys of triterpenoids from *Ceriops*,⁶ and *Ilex*⁷ species and *Sapindus mukorossi*,⁸ have appeared.

2. The squalene group

Sapelenins G 1–J 4 are further anti-inflammatory squalene derivatives from the bark of Cameroonian *Entandrophragma cylindricum*.⁹ The highly oxidised squalene derivative 5 has been isolated from Peruvian *Protium subserratum*.¹⁰ The structures of saiyacenols A 6 and B 7, from the red alga *Laurencia viridis*, support the accepted pathway for the formation of the aplysiols.¹¹ The mechanism of triterpene biosynthesis in *Botryococcus braunii* has been reviewed.¹²

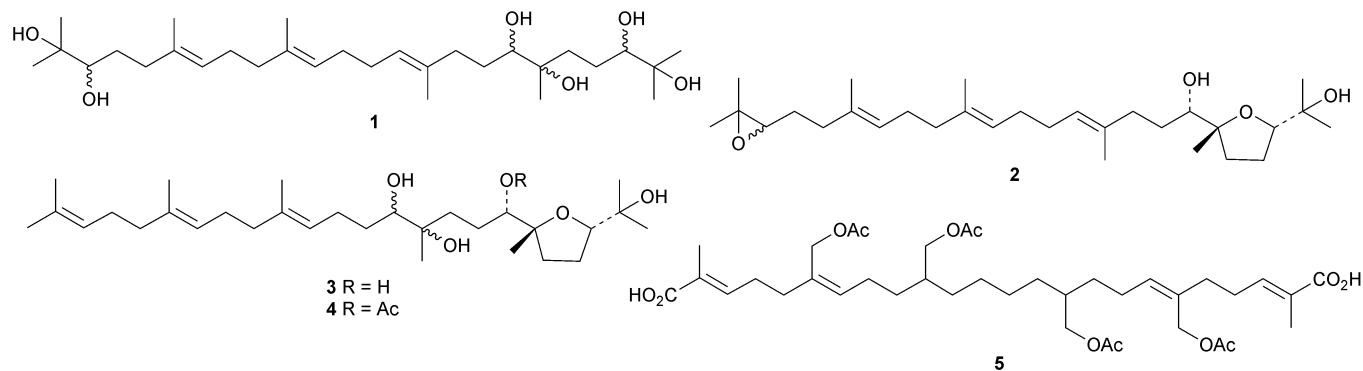
3. The lanostane group

New protostanes include alisol Q acetate 8 (ref. 13) and alisol X 9 (ref. 14) from *Alisma orientale* and the epoxy-ketone 10 from the leaves of *Aglaia odorata*.¹⁵ The tetraterpenes abiesteranes A 11 and B 12, from *Abies fabri*,¹⁶ and abibalsamins A 13 and B 14, from the oleoresin of *Abies balsamea*,¹⁷ appear to have arisen by Diels–alder cycloadditions of rearranged lanostanes with the monoterpene β -myrcene. The structure of 13 was confirmed by X-ray analysis. A series of rearranged lanostanes, neoabiesteranes A 15–F 20, has been reported from *Abies recurvata*.¹⁸ The structures of neoabiesterane A 15 were confirmed by X-ray analysis. The compounds showed some cytotoxic activity. The mariesane lactone 21 has been obtained from *Abies sibirica*.¹⁹ The tetranor derivative 22 and the 3,4-secolanostane 23 have been found in *Abies holophylla*.²⁰

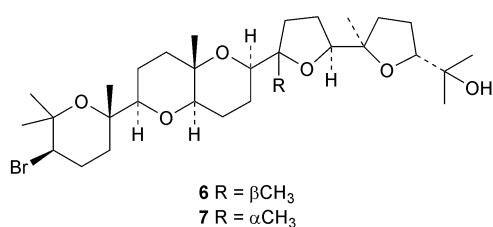
Pseudoferic acids A 24, B 25 and C 26 are interesting new 16,24-cyclised lanostanes from *Pseudolarix kaempferi*.²¹ The stems of *Schisandra glaucescens* contain the ring A-cleaved lanostanes schiglausins A 27–H 34, together with the intact derivatives schiglausins I 35 and J 36.²² The structure of schiglausin A 27 was confirmed by X-ray analysis. Schiglausin H 34 is the methyl ester of micranic acid A. An impressive array of rearranged, ring A-cleaved and intact lanostanes, kadpolysperins A 37–N 50, has been isolated from *Kadsura polysperma*.²³ Kadcoctones A 51 and B 52 are unusual rearranged lanostane derivatives from *Kadsura coccinea* where they occur with kadcoctone C 53, whose structure was confirmed by X-ray analysis.²⁴ Secococcinic acids G 54–K 58 are further constituents of *Kadsura coccinea*.²⁵ Three esters 59–61 of 3-epidehydrotumulolic acid have been obtained from *Wolfiporia extensa*.²⁶ Other new lanostanes include lanosta-5,15-dien-3 α -ol 62 from *Arctium lappa*²⁷ and inonotsuoxodiols B 63 and C 64, epoxyinonotsudiol 65 and methoxyinonotsutriol 66 from *Inonotus obliquus*.²⁸

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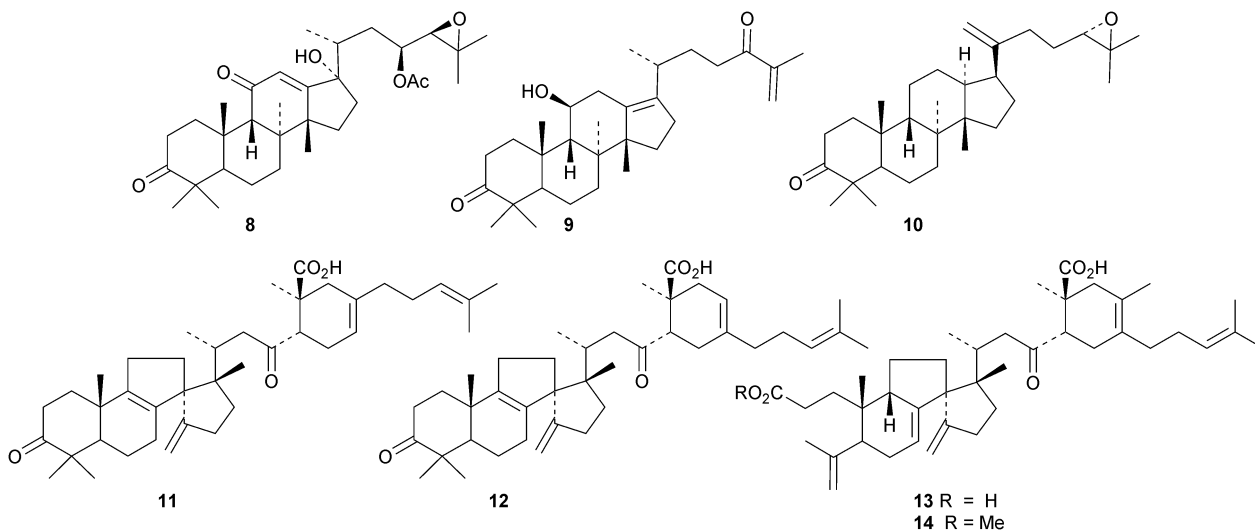


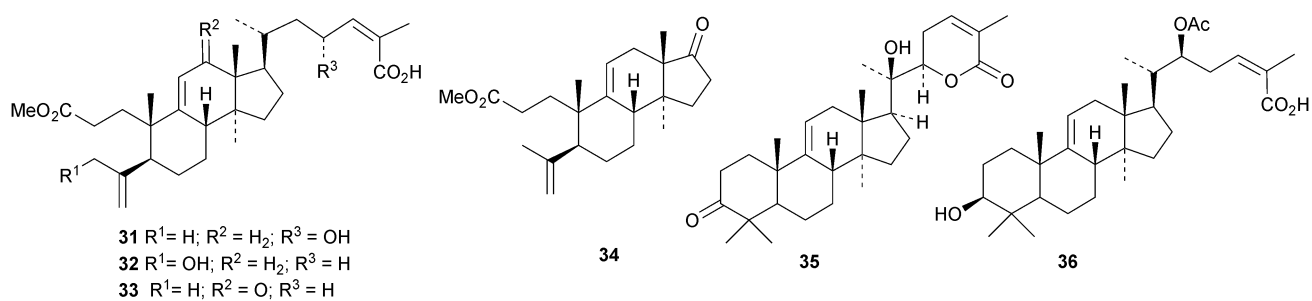
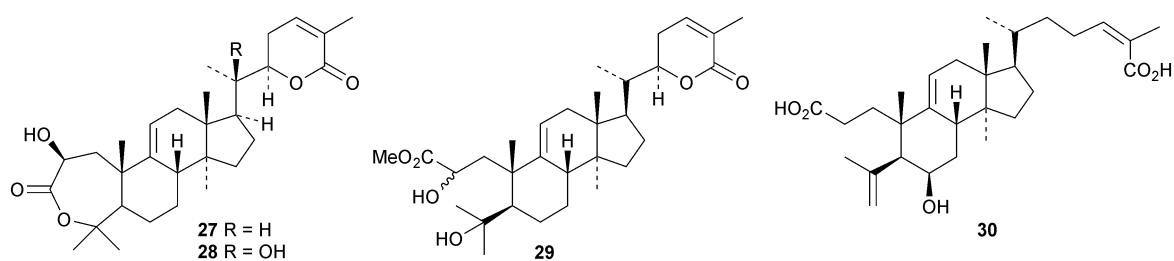
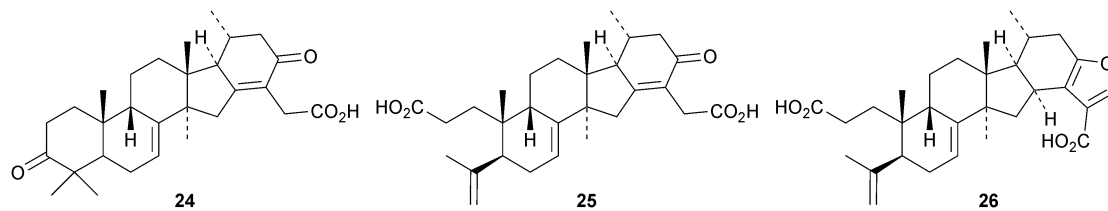
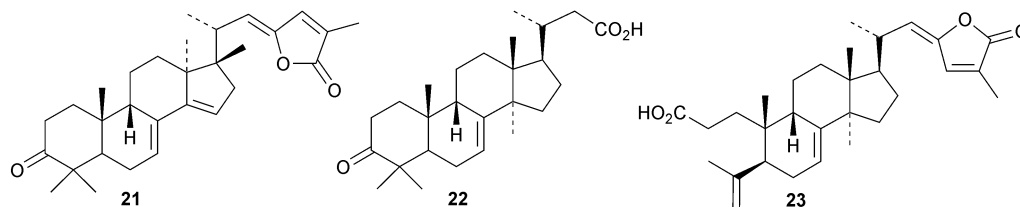
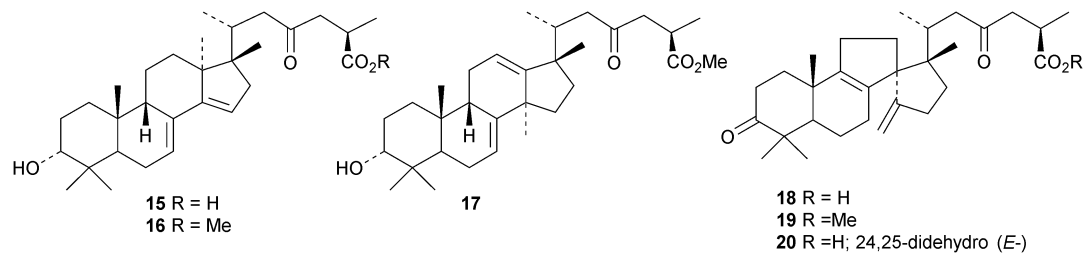
Sarasinosides N–R are 30-norlanostane glycosides from the sponge *Lypastrotethya* sp. with the new genins **67**, **68**, **69** and the 30-nor-18(13 → 14)-abeo-derivative **70**.²⁹ Scillanostaside F, with the new genin **71**, and scillanostaside G, with a known tetra-norlanostane genin, have been isolated from the bulbs of *Scilla scilloides*.³⁰

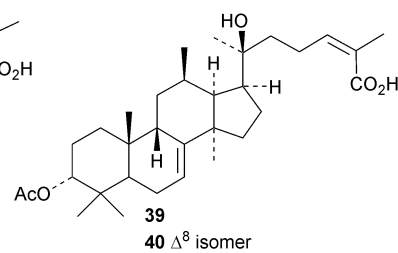
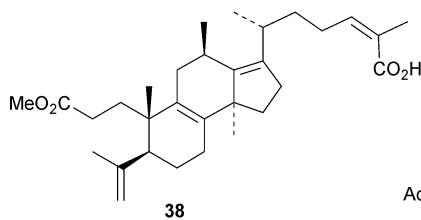
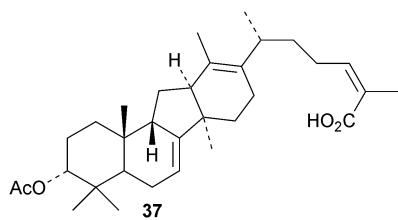
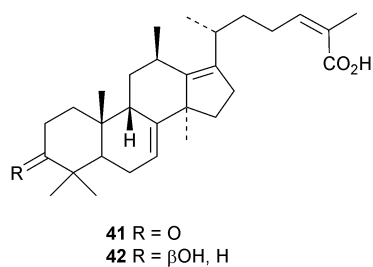
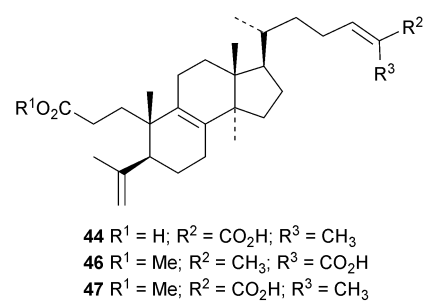
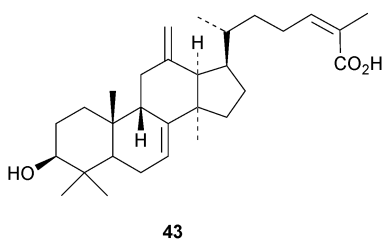
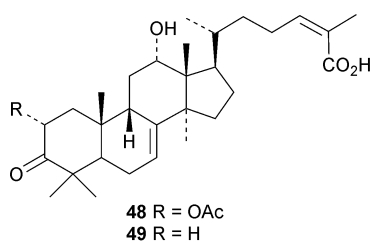
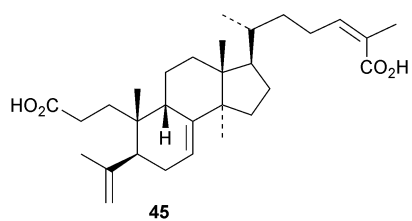


New compounds from *Ganoderma sinense* include the pentanor derivative ganosineniol A **72**, ganoderic acids J_c **73** and J_d **74**, ganodermatetraol **75**, the glucosyl ester ganosinoside A **76** with a known genin, ganolucidic acid γ_a **77**, ganolucidate F **78**, ganoderiol J **79** and methyl lucidenate H_a **80**.³¹ Ganodermacetal **81** is an acetonide from *Ganoderma amboinense*³² and lucialdehyde E **82** is a further compound from *Ganoderma lucidum*.³³ Reviews have appeared on the triterpenoids of *Ganoderma lucidum*^{34,35} and lanostanes from fungi.³⁶

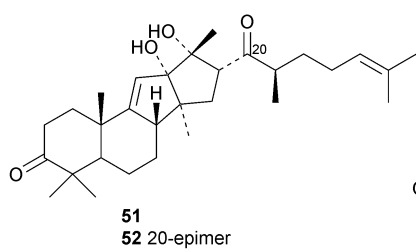
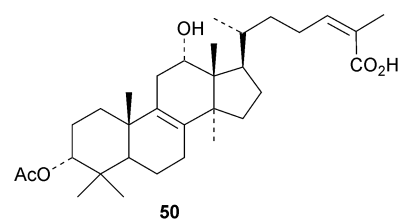
Astraodoric acids A **83**–D **86** are metabolites of the mushroom *Astraeus odoratus*.²⁹ The structure of astraodoric acid B **84** was confirmed by X-ray analysis. The structure of astrakurkulol **87**, from the Indian edible mushroom *Astraeus hygrometricus*, was also confirmed by X-ray analysis.³⁷ The corresponding lactone, astrakurkuronone **88**, was also obtained. Two highly acetylated lanostanes, coprinacins A **89** and B **90**, have been



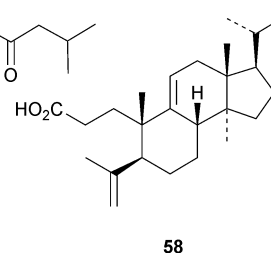
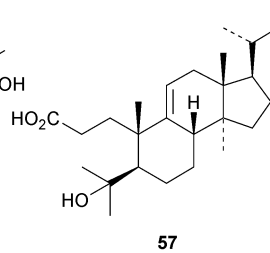
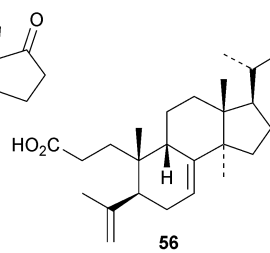
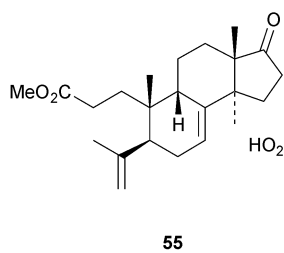
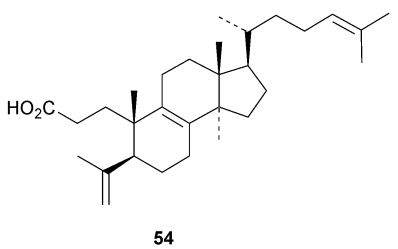
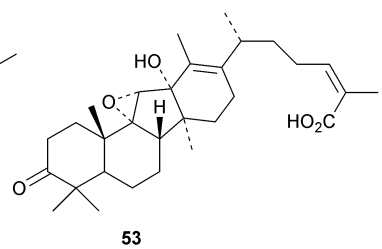


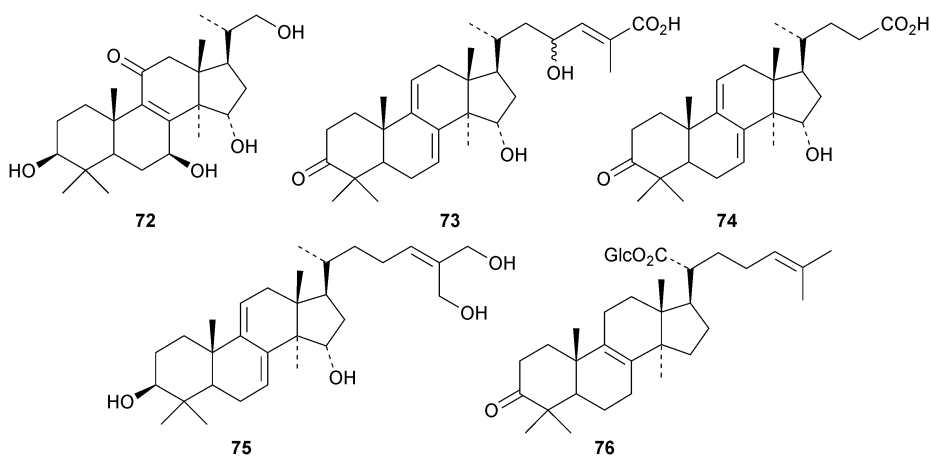
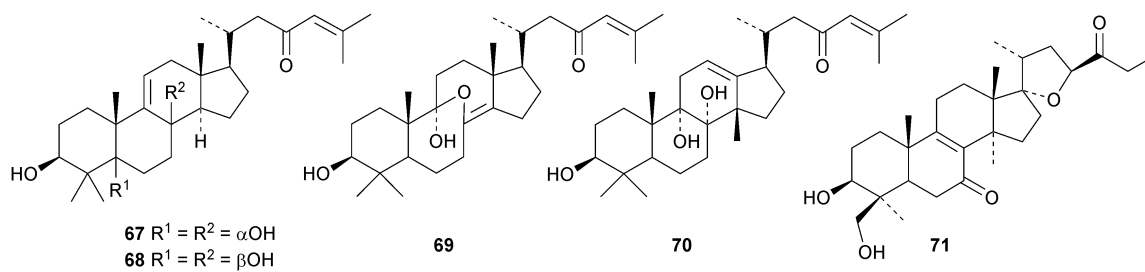
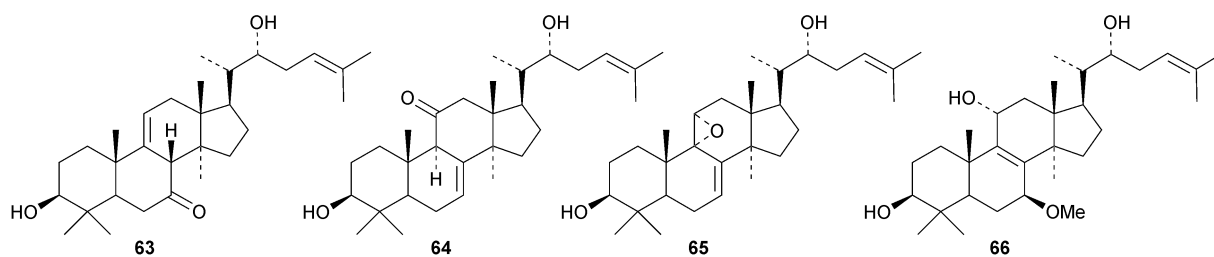
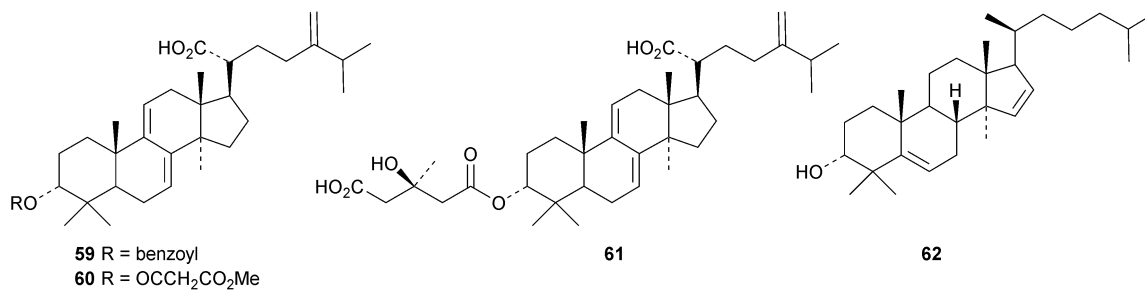
40 Δ^8 isomer42 R = β OH, H46 R¹ = Me; R² = CH₃; R³ = CO₂H47 R¹ = Me; R² = CO₂H; R³ = CH₃

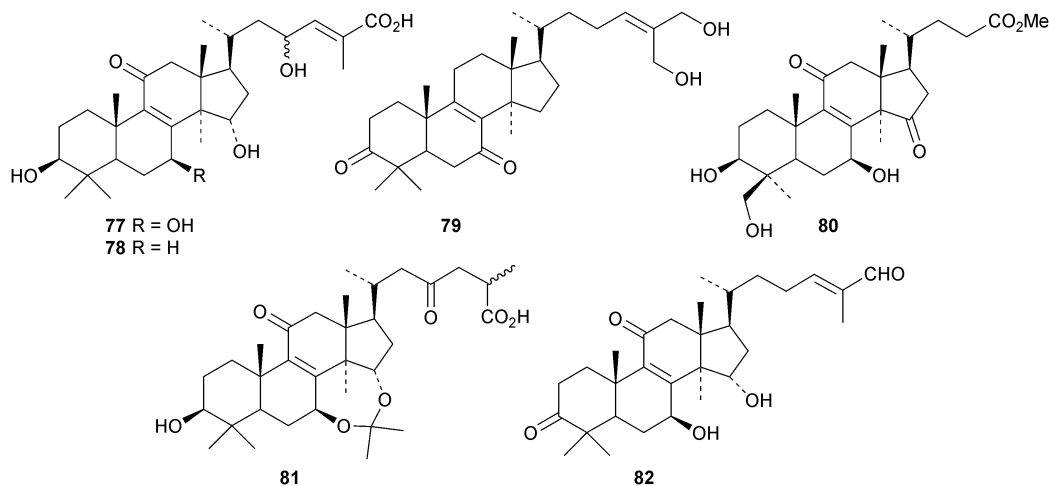
49 R = H



52 20-epimer





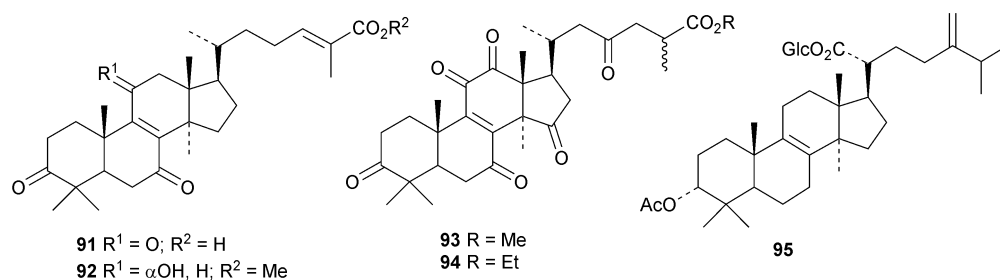
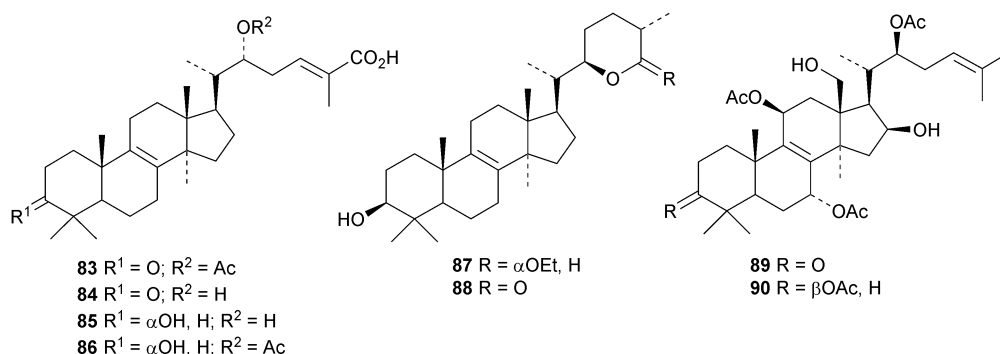


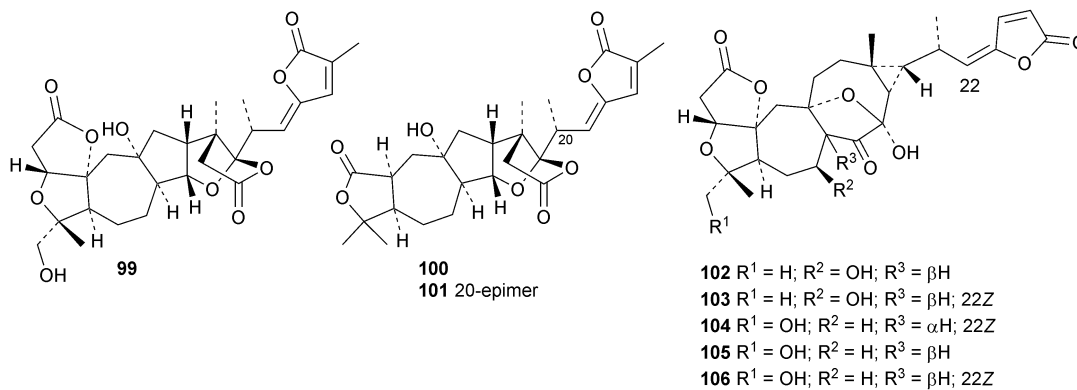
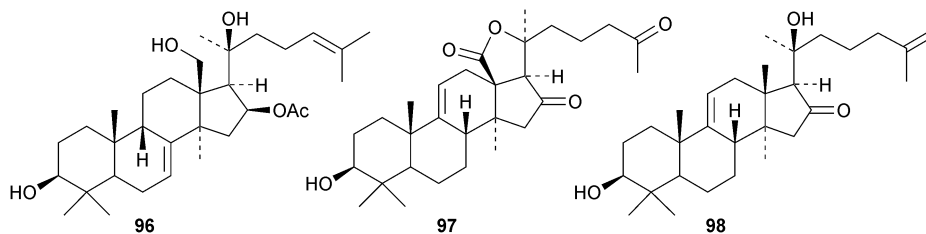
reported from *Coprinus cinereus*.³⁸ Other fungal metabolites include **91–94** from *Antrodia camphorate*³⁹ and formitoside K **95**, a glucoside with a new genin, from *Fomitopsis nigra*.⁴⁰

Cucumarioside A8 is a lanostane saponin with the new genin **96** from the sea cucumber *Eupentacta fraudatrix*.⁴¹ The sea cucumber *Apostichopus japonicus* is the source of several saponins, 26-*nor*-25-oxoholotoxin A₁ with the new genin **97** and

holototoxins D–G.⁴² Holototoxins F and G have the new genin **98** while the genins of D and E are known. Cucumariosides B₁ and B₂⁴³ and cucumariosides H₂, H₃ and H₄,⁴⁴ from *Eupentacta fraudatrix*, all have known genins. Holostane saponins and their biological activity have been reviewed.⁴⁵

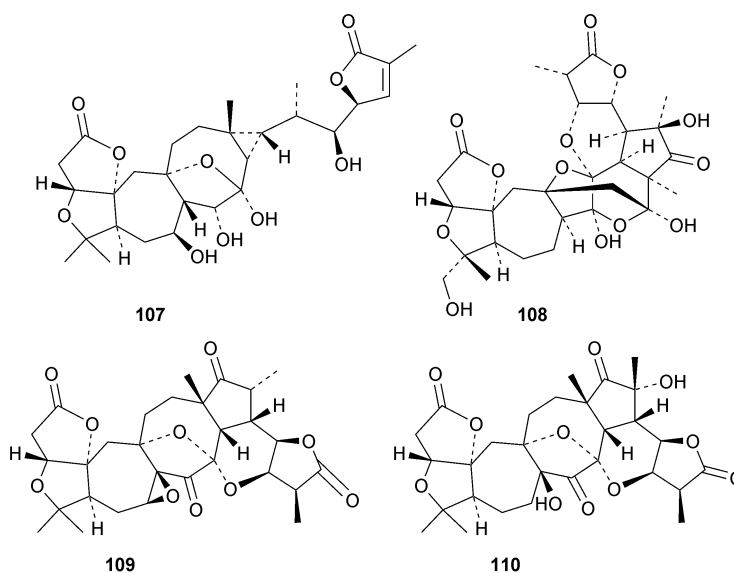
Interesting new structures continue to appear from *Schisandra* species. Schilancitrilactones A **99**, B **100** and C **101**

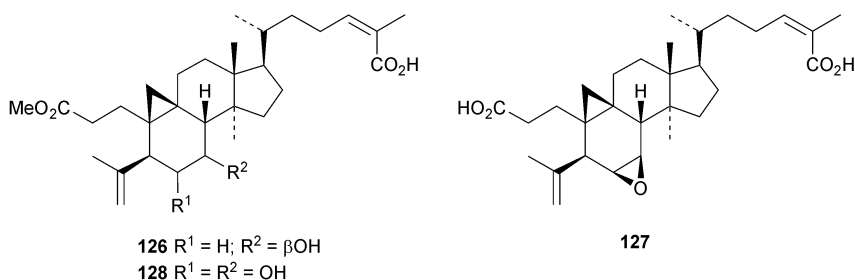
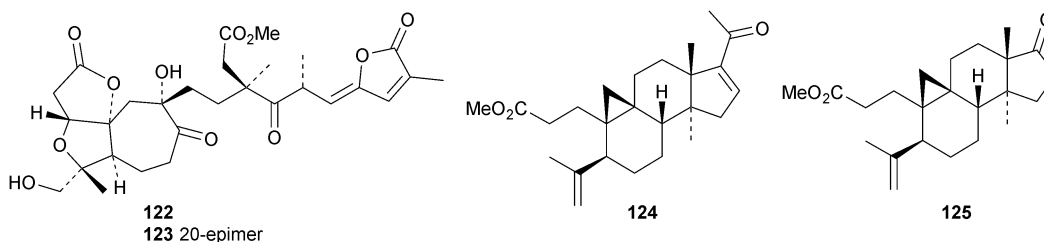
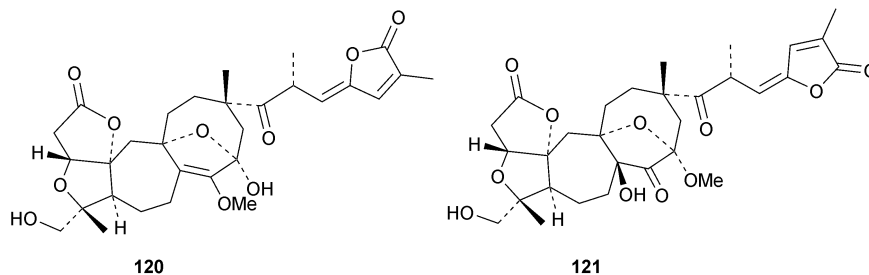
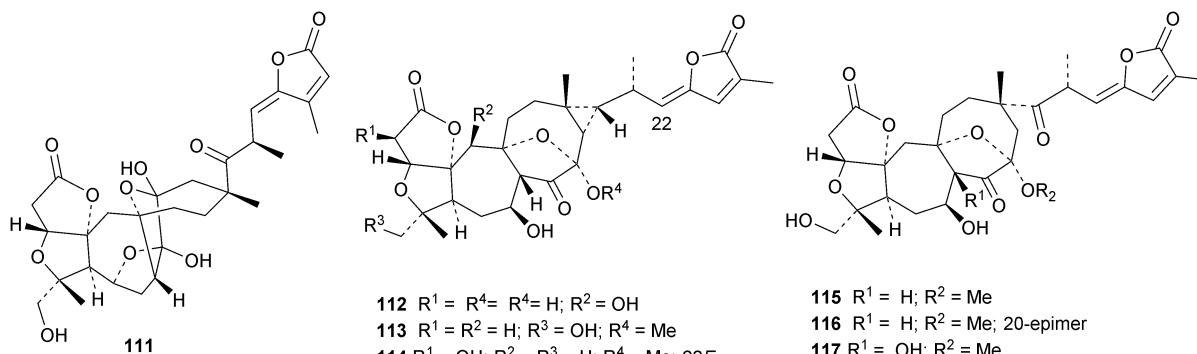




have been reported from *Schisandra lancifolia*.⁴⁶ The structures of all the schilancitrilactones were confirmed by X-ray analyses. New structures from *Schisandra sphenanthera* include preschisanartanins E **102**–J **107** and sphenadilactones D **108**–F **110**.⁴⁷ Isoschicagenin C **111**, preschisanartanins K **112**–M **114**,

schisdilactones A **115**–G **121** and schinesdilactones A **122** and B **123** constitute an impressive array of new derivatives from *Schisandra chinensis*.⁴⁸ Schiglausins K **124**–O **128** are simple ring A-cleaved cycloartanes from *Schisandra glaucescens*.⁴⁹

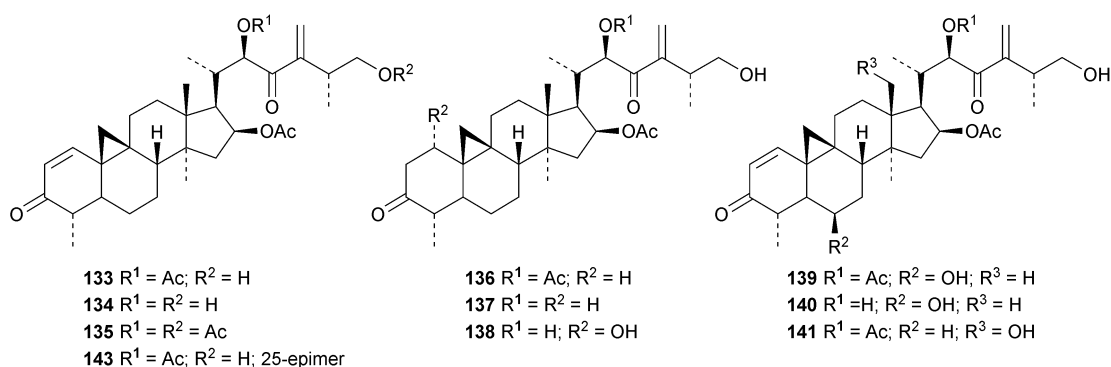
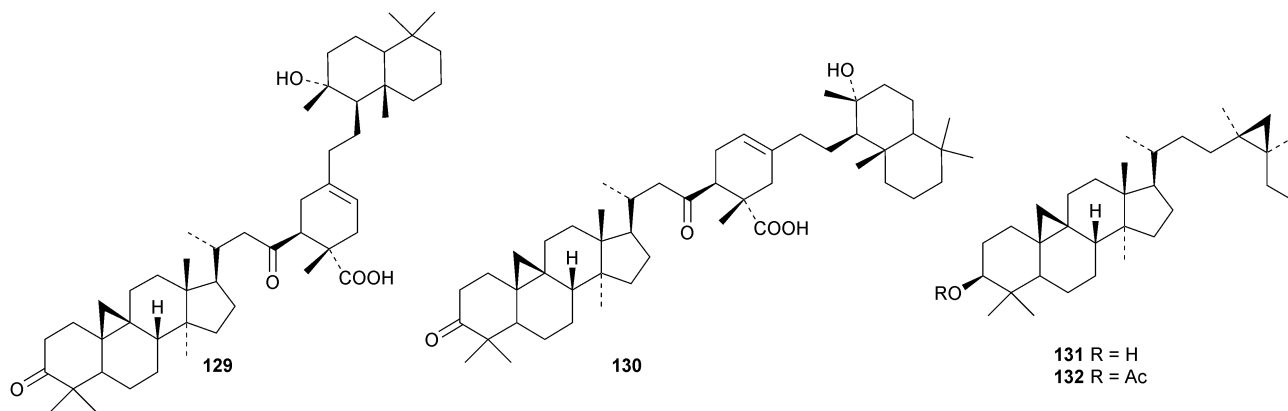




An interesting approach to the “dereplication, residual complexity and rational naming” of the *Actea* triterpenoids has the potential to be applied to other groups of natural products with the same inherent problems.⁵⁰ Pseudolaridimers A **129** and

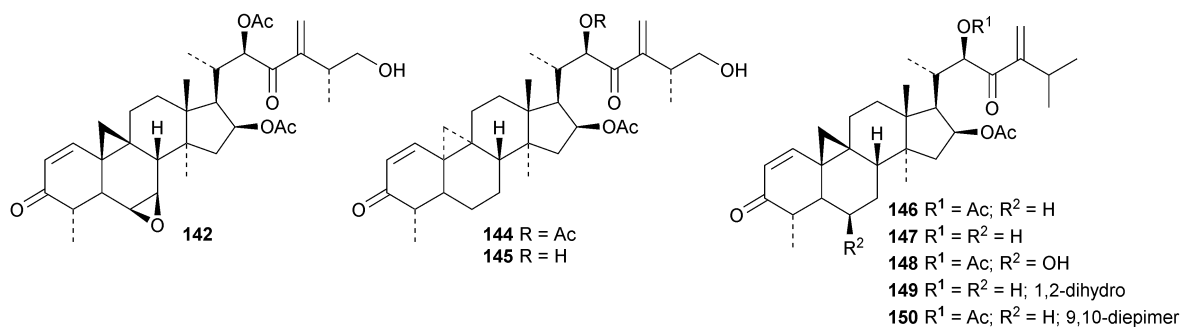
B **130**, from *Pseudolarix amabilis*, appear to have arisen by a Diels–Alder reaction involving a cycloartane and a labdane.⁵¹ The structure of **129** was confirmed by an X-ray analysis of the corresponding methyl ester. The cycloartanes lygodipenoids A

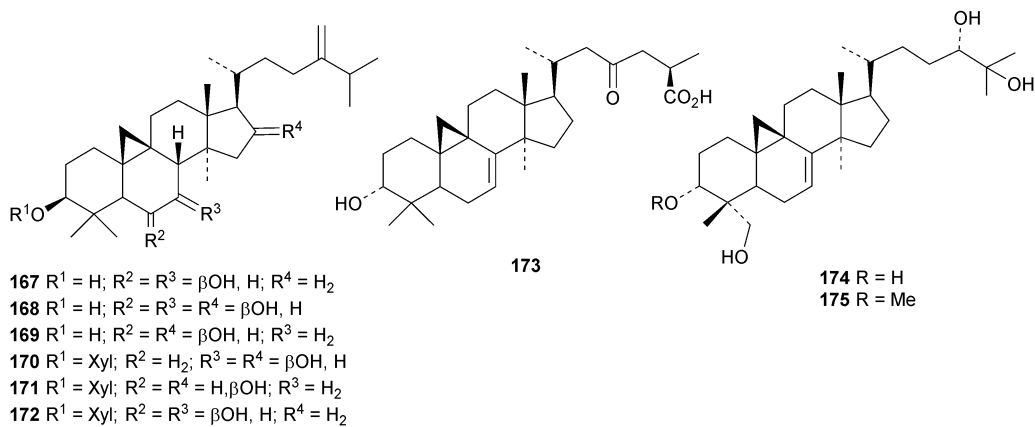
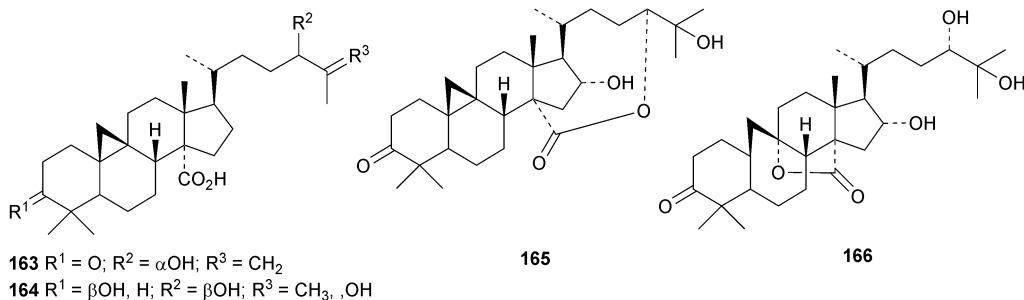
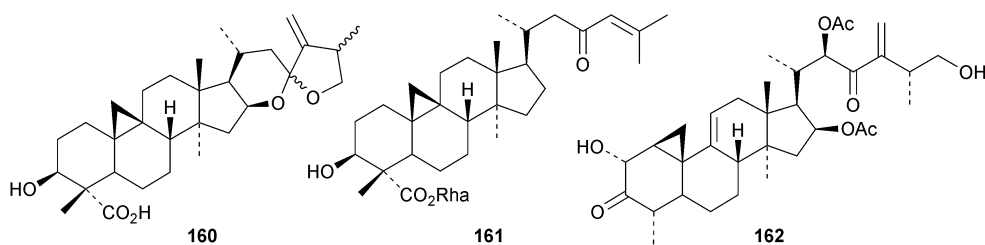
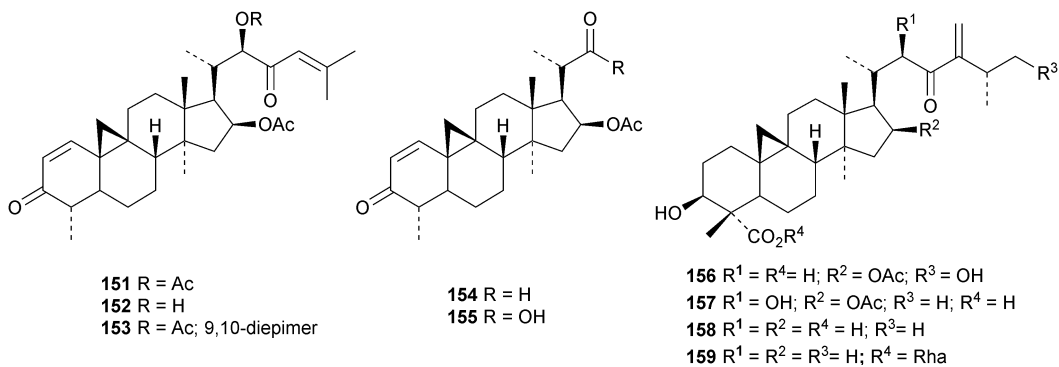


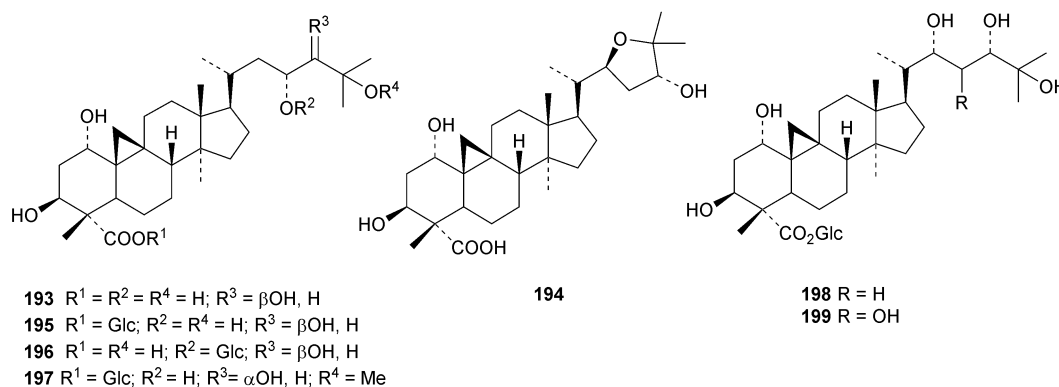
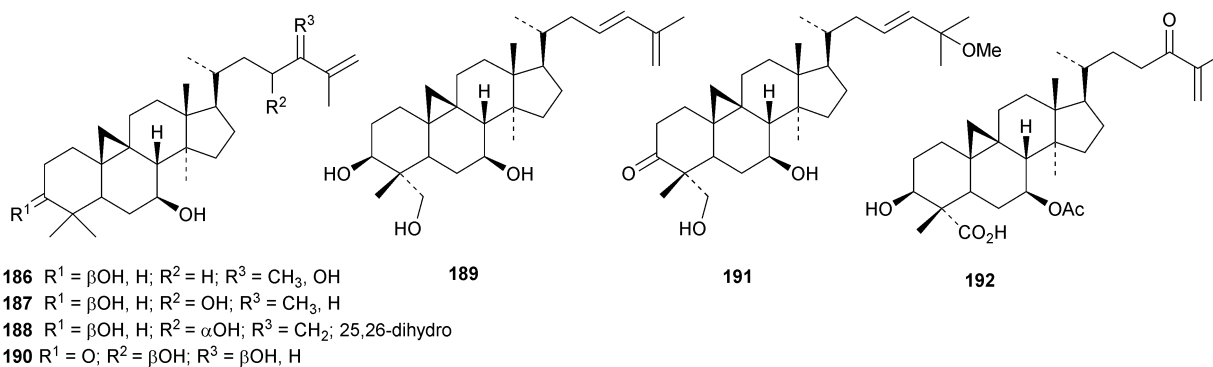
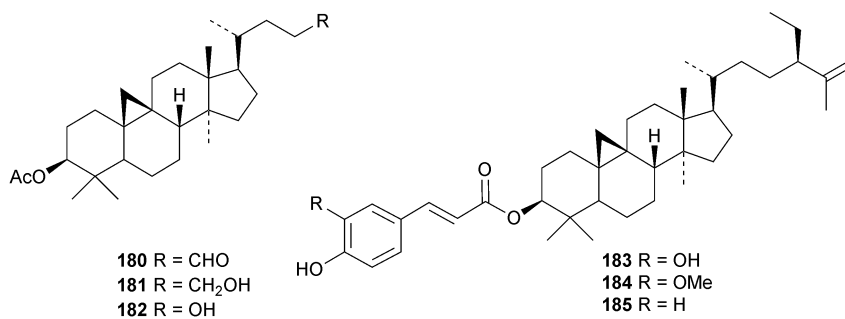
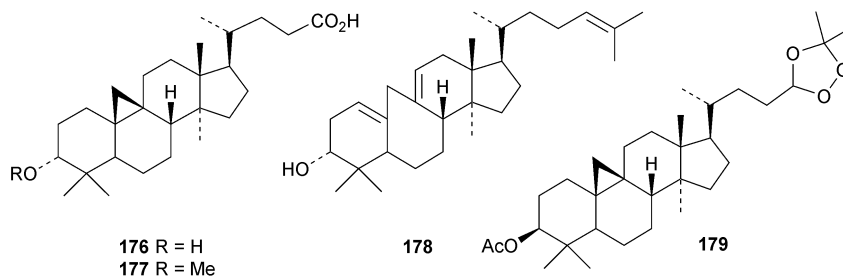


131 and B 132, from *Lygodium japonicum*, have an additional cyclopropane in their side chains.⁵² Thirty new cycloartane proteasome inhibitors 133–162 have been reported from *Neoboutonia melleri*.⁵³ An interesting UV light-induced inversion of the configurations at C-9 and C-10 was observed in this series. Caloncobic acids A 163 and B 164 and caloncobalactones A 165 and B 166 are constituents of the leaves of *Caloncoba glauca*.⁵⁴ Compounds 167–172 are new cycloartanes from the leaves of *Homonoia riparia*.⁵⁵ Neoabiestrines G 173–I 175 have been

reported from *Abies recurvata*.¹⁸ The structure of neoabiestrine H 174 was confirmed by X-ray analysis. Other new cycloartanes include the trinor derivatives 176 and 177 from *Abies holophylla*,²⁰ rotundusolide C 178 from the rhizomes of *Cyperus rotundus*,⁵⁶ 179–182 from the aerial parts of *Atemisia lagocephala*,⁵⁷ three esters 183–185 of cyclomargenol from *Krameria pauciflora*,⁵⁸ euphonerins A 186–G 192 from the leaves of *Euphorbia nerifolia*,⁵⁹ cycloccidentalacids A 193 and B 194 and the related saponins cycloccidalisides I 195–V 199 from



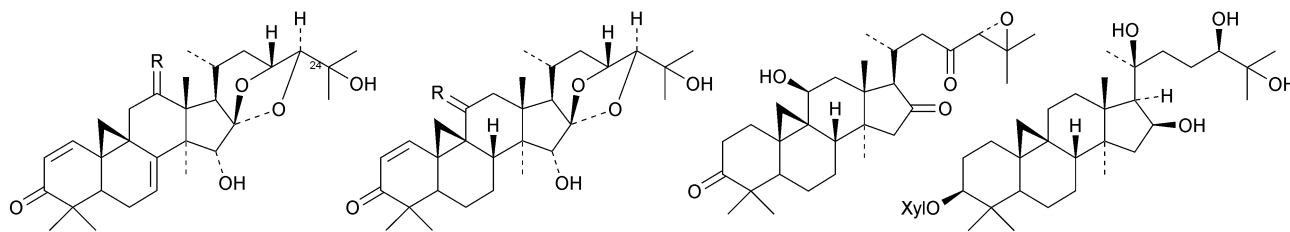
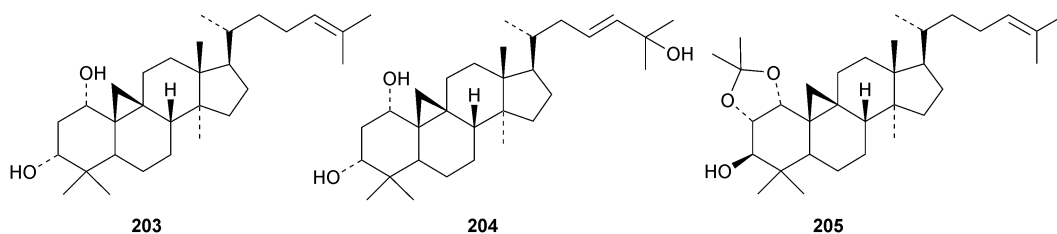
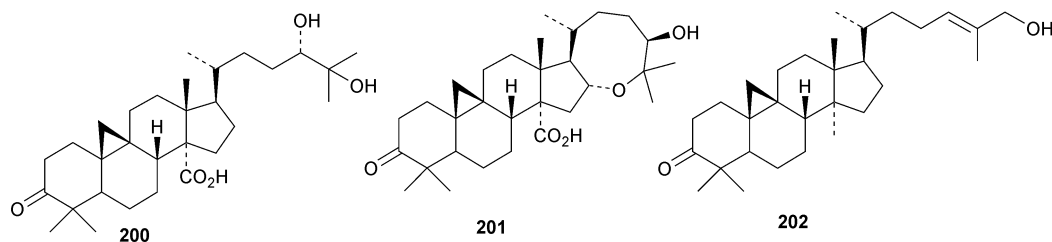




Cassia occidentalis,⁶⁰ glaucartanoic acids **200** and **201** from the fruit of *Caloncoba glauca*⁶¹ and **202** from the leaves of *Aglaia exima*.⁶² Compounds **203**, **204** and the acetone **205**, a likely artefact, have been obtained from the resin of *Commiphora opobalsamum*.⁶³ The structures of **203** and **205** were confirmed by X-ray analyses.

New cycloartanes continue to be isolated from *Cimicifuga* species. *Cimicifuga foetida* is the source of compounds **206–209**

(ref. 70) and of 24-*epi*-cimigenol-3-one **210** and the xyloside foetinoside **211**.⁶⁴ The ring A-cleaved derivative **212**, the cimigenol arabinosides **213–215**, the 25-dehydrocimigenol arabinoside **216**, compounds **217–219** and the shengmanol arabinoside **220** have all been isolated from the roots of *Cimicifuga heracleifolia*.⁶⁵ Other new compounds include the galactopyranosides **221–223**, all with new genins, from the roots



206 R = O

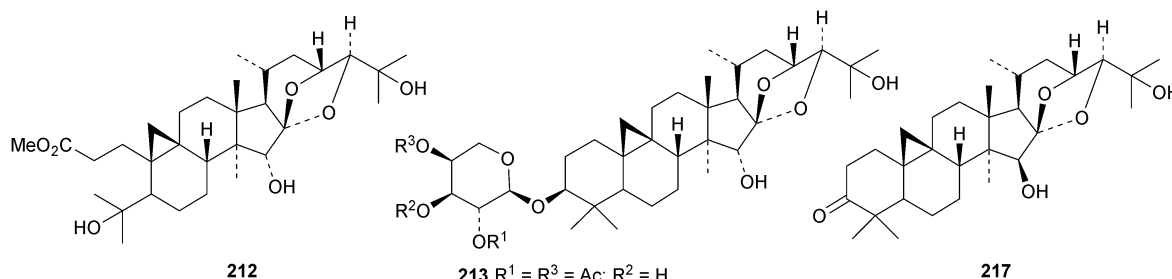
210 R = H₂; 7,8β-dihydro; 24-*epi*

207 R = O

208 R = βOH, H; 7,8-didehydro; 1,2-dihydro

209

211



212

213 R¹ = R³ = Ac; R² = H

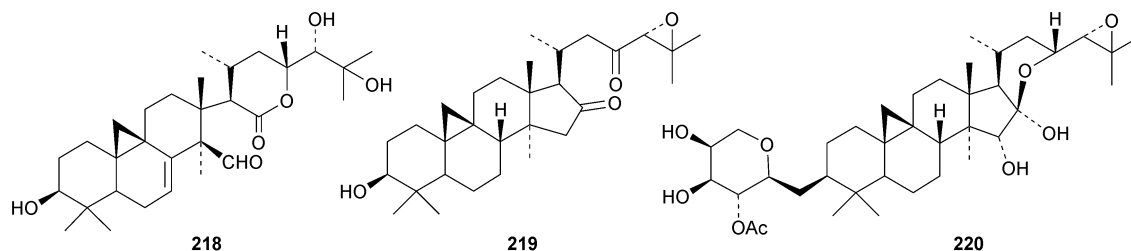
214 R¹ = H; R² = R³ = Ac

215 R¹ = R² = H; R³ = Ac

216 R¹ = R³ = H; R² = Ac; 25,26-anhydro

217



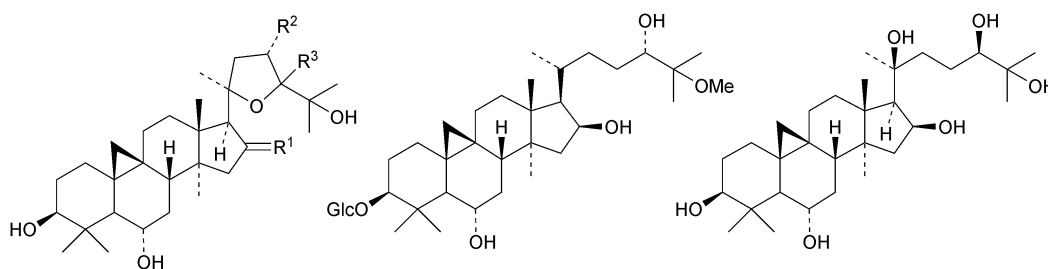
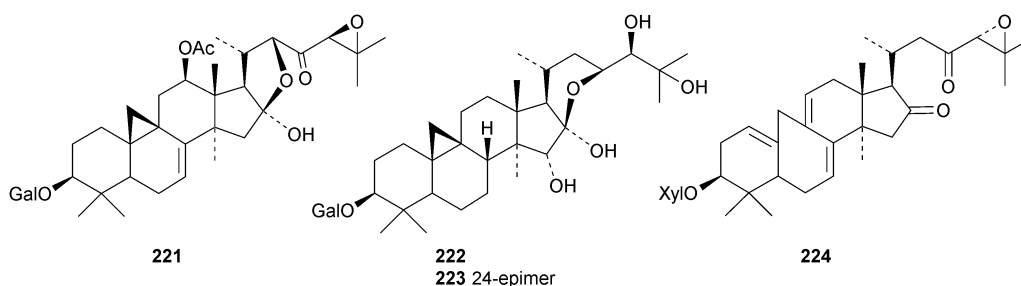


of *Cimicifuga simplex*⁶⁶ and isocimipodocarpaside **224** from *Cimicifuga racemosa*.⁶⁷

Six cycloartane saponins with the new genins **225**–**228** have been obtained from *Astragalus angustifolius*.⁶⁸ Cycloquivinoside **A 229** is a new saponin from *Astragalus chivensis*.⁶⁹ The new genin cycloartane-3 β ,6 α ,16 β ,20 S ,24 R ,25-hexol **230** has been identified in the saponins of *Astragalus stereocalyx*⁷⁰ and in saponins from *Astragalus schottianus*.⁷¹ Nervisides **A 231**–**C 233**, from *Nervilia fordii*, all have new genins.⁷² Other cycloartane saponins with new genins include curculigosaponins **N** and **O** from *Curculigo orchoides* with the genin **234** (ref. 73) and two saponins from *Thalictrum fortune* with the genins **235** and **236**.⁷⁴ The ring-A cleaved cycloartanes sootependial **237** and sootepenoic acid **238** have been isolated from the exudates of *Gardenia sootepensis*.⁷⁵ Novel cycloartane saponins with known genins include cycloascidoside from *Astragalus mucidus*,⁷⁶ cyclogaleginoside **C** from *Astragalus galegiformis* and cycloascauloside **D** from *Astragalus caucasicus*,⁷⁷ hareftosides **A**–**D** from

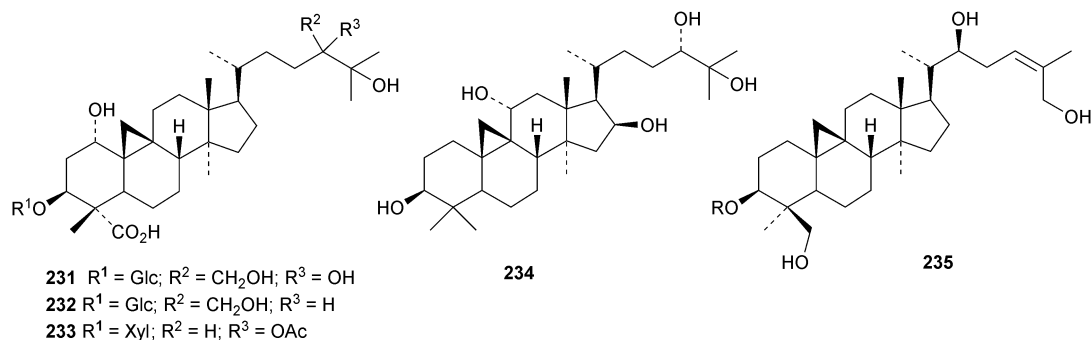
Astragalus hareftae,⁷⁸ neoastragaloside **I** from *Astragalus membranaceus*⁷⁹ and unnamed saponins from *Astragalus erinaceus*.⁸⁰

A new nitrogen-containing cucurbitane, endecaphyllacin **C 239**, has been reported from the tubers of *Hemsleya endecaphylla*.⁸¹ Eleoacarpucins **A 240**–**H 247** are 16,23-epoxy derivatives from *Eleoacarpus chinensis*.⁸² The new cucurbitanes jinfushanencins **A 248** and **B 249** occur in the tubers of *Hemsleya penxianensis*, together with the glycosides jinfushanosides **E**–**K**.⁸³ Jinfushanoside **K** has the new genin **250**. Other new cucurbitanes include **251**–**253** from the fruit of *Momordica charantia*,⁸⁴ 10 β -hydroxybryodulcosigenin **254** from *Saniculi-phyllum guangxiense*,⁸⁵ six new compounds **255**–**260** from the leaves of *Momordica charantia*⁸⁶ and isoarvenin **III 261** from the fruit of *Trichosanthes kirilowii*.⁸⁷ The 3,4-*seco*-cucurbitane **262** is a constituent of *Russula lepida* and *Russula amarissima*.⁸⁸ The unlikely 10 α -methyl lanostane structure **263** has been proposed for a compound from *Momordica charantia*.⁸⁹ Perhaps the compound is a cucurbitane! Reviews have appeared on



- 225** R¹ = β O₂CCH₂OH, H; R² = H; R³ = α H
226 R¹ = β O₂CCH₂OH, H; R² = OH; R³ = α H
227 R¹ = O; R² = H; R³ = α H
228 R¹ = β OH, H; R² = H; R³ = β H



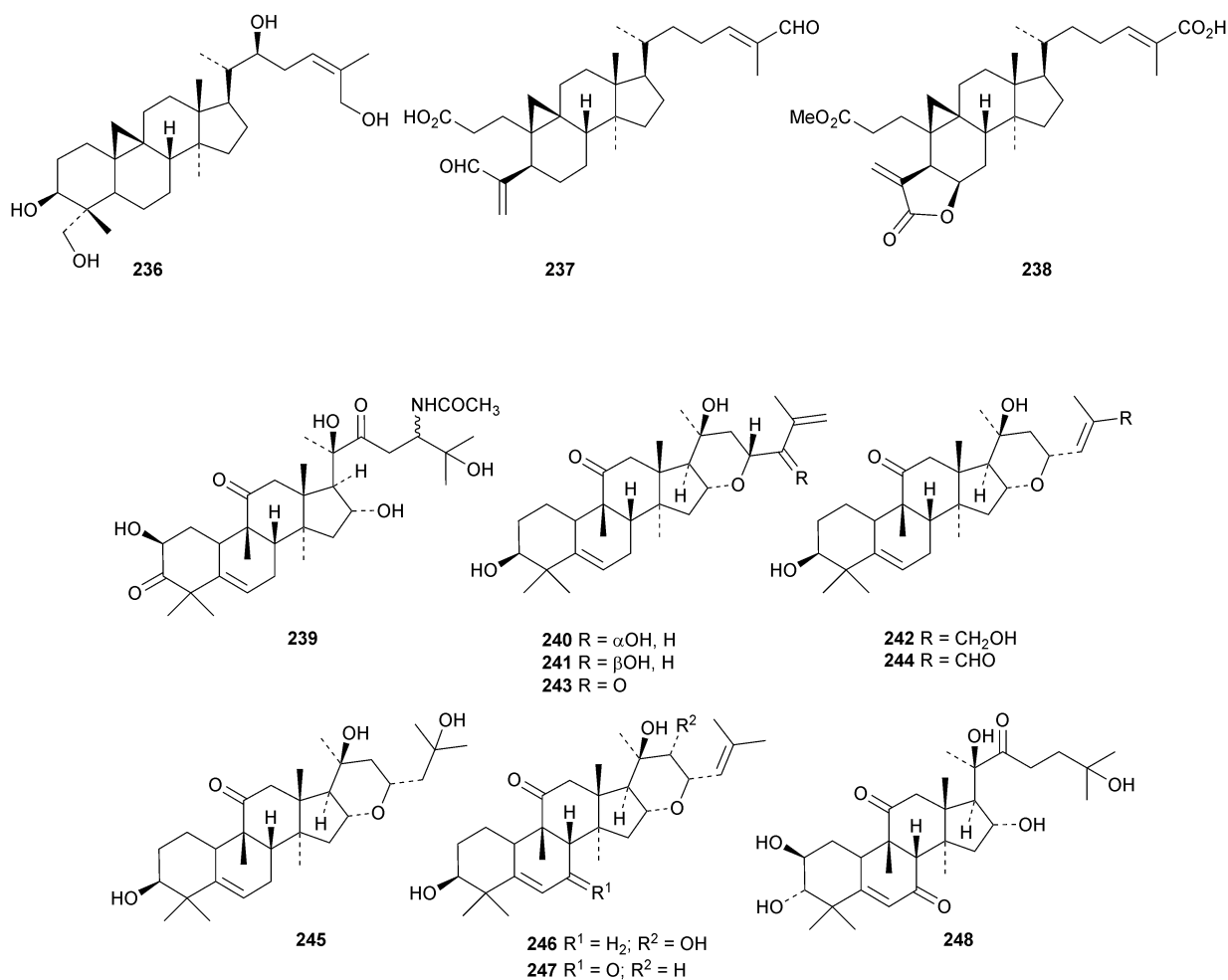


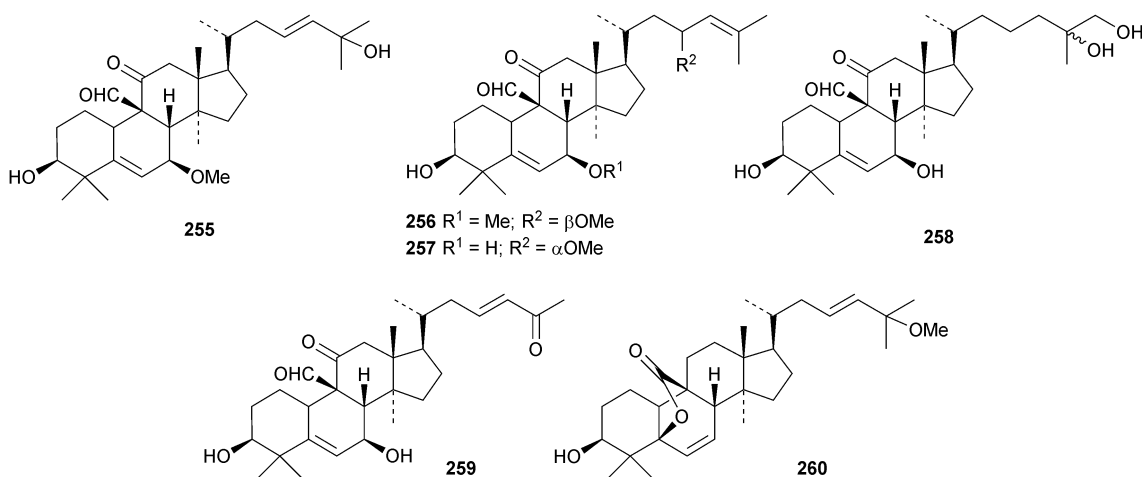
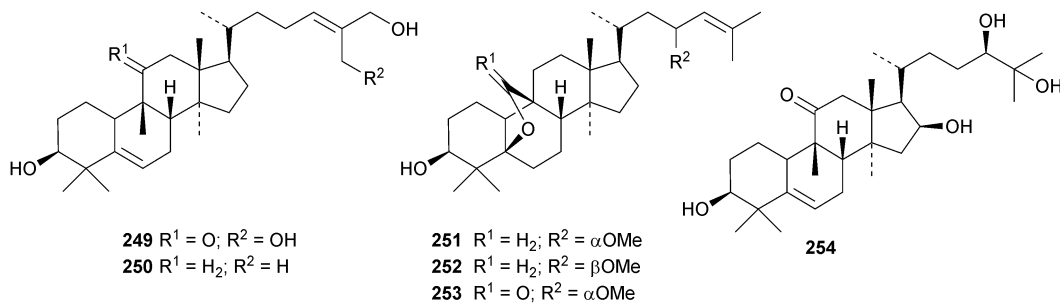
cucurbitacins and bottle gourd toxicity,⁹⁰ medicinally important plants of the Cucurbitaceae⁹¹ and the anticancer activity of the cucurbitacins.^{92,93}

4. The dammarane group

A review of ginsenoside derivatives and their antitumour activity has been published.⁹⁴ New saponins from the stems and leaves of *Panax ginseng* include ginsenosides Rh₁₄–Rh₁₇ with the new

genins **264** (Rh₁₅) and **265** (Rh₁₇)⁹⁵ and ginsenosides Rh₁₈–Rh₂₀.⁹⁶ The new genin **266** of ginsenoside Rh₁₈ was also isolated together with the dammarane **267**.⁹⁶ Two new saponins of 20S-protopanaxatriol have also been found in *Panax ginseng* together with the dammarane **268**.⁹⁷ The biological activity of an artefact **269** from the acid hydrolysate of *Panax ginseng* has been investigated.⁹⁸ The hexanordammarane saponin, ginsenoside R₁₀ **270**, has been isolated from the stems and leaves of *Panax quinquefolium*.⁹⁹

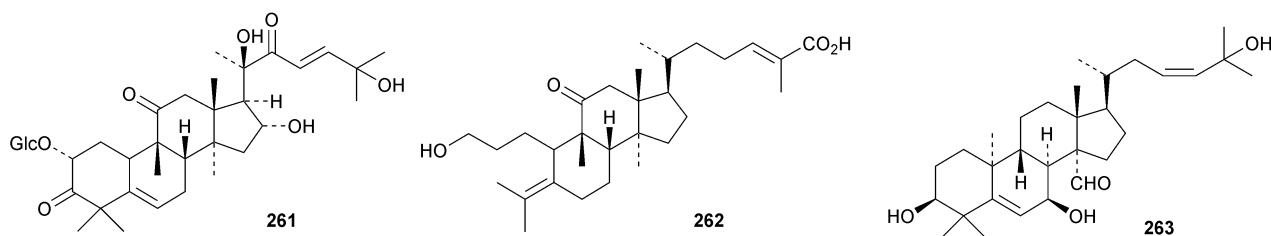


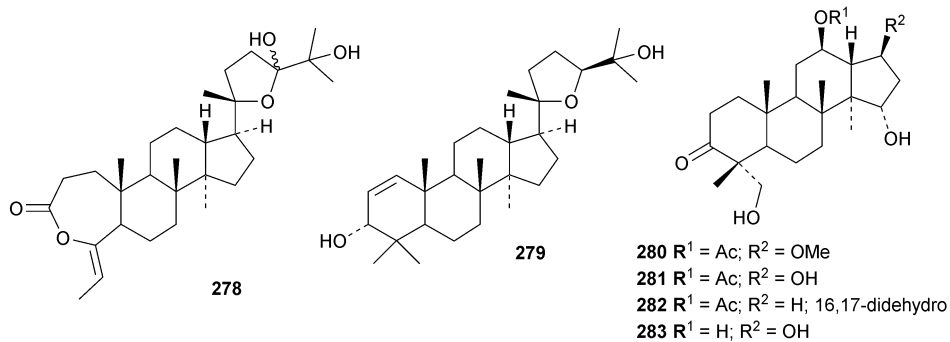
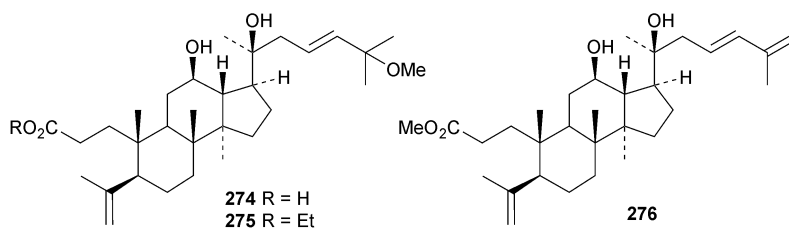
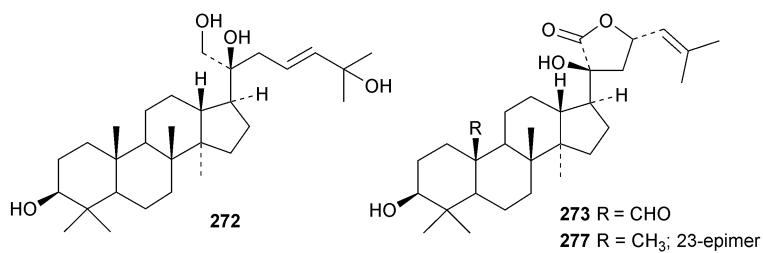
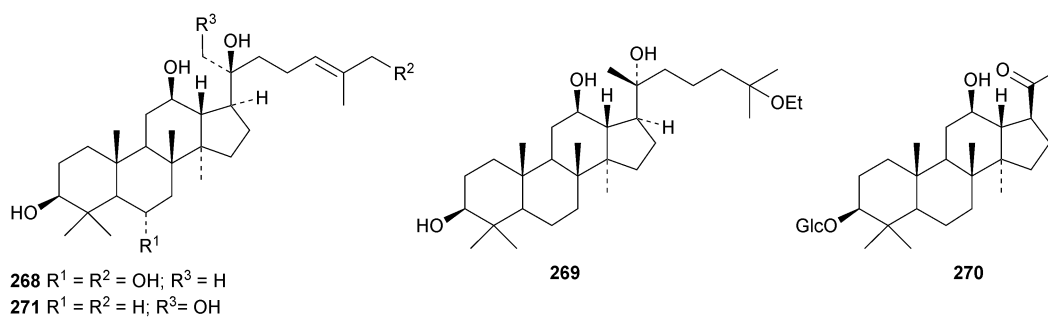
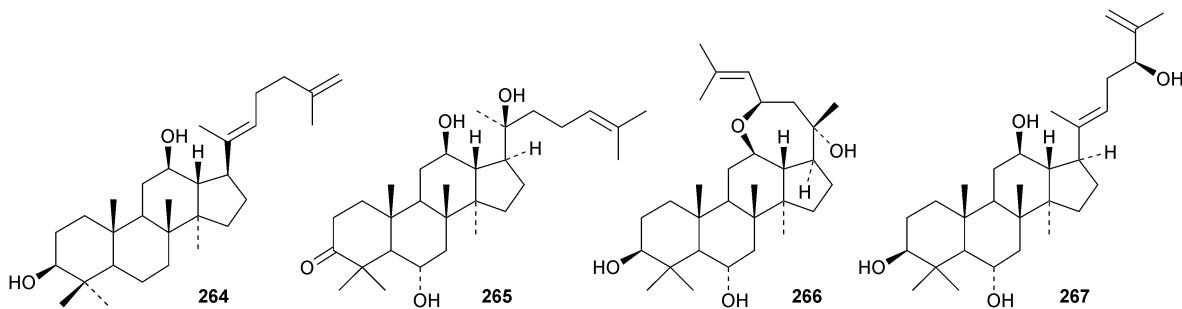


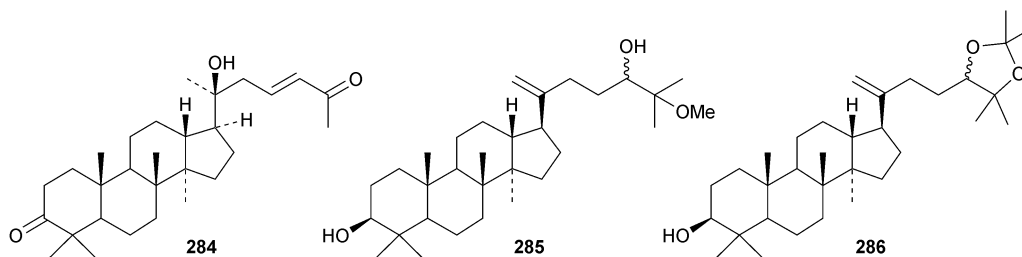
Saponins with the new genins **271** and **272** (ref. 100) and **273** (ref. 101) have been isolated from *Gynostemma pentaphyllum*. Cyclocariosides D–G, with the new genins **274** and **275**, cyclocarioside H, with a known genin, and the dammarane cyclocarin A **276** are constituents of the leaves of *Cyclocarya paliurus*.¹⁰² Dammarane saponins with known genins have been

isolated from the roots of *Machilus yaoshansis*.¹⁰³ This paper also reports a revision the C-23 configuration of *Gynostemma pentaphylla* saponins as in **277**.

New dammaranes include the rearranged aglinone **278** and aglinin E **279** from the bark of *Aglaia smithii*,¹⁰⁴ the nor-derivatives **280–283** from *Dysoxylum hainanense*,¹⁰⁵ the

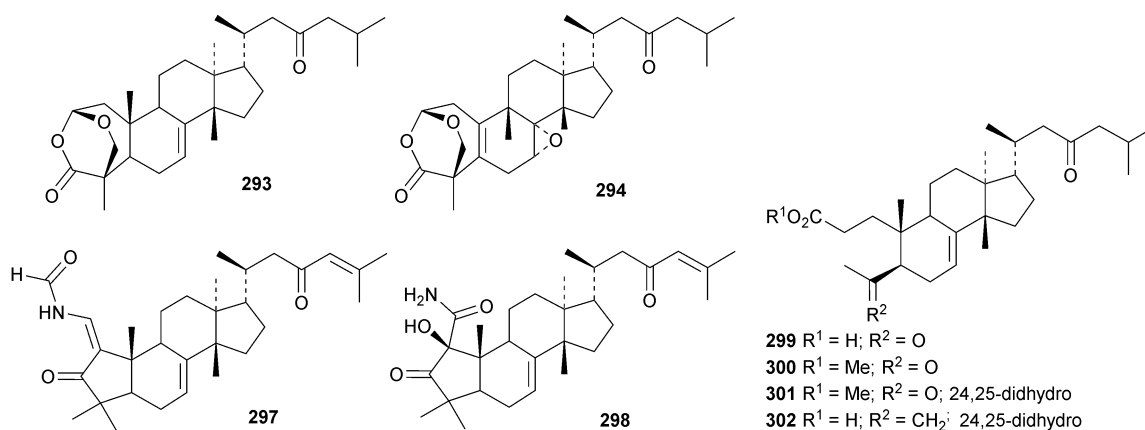
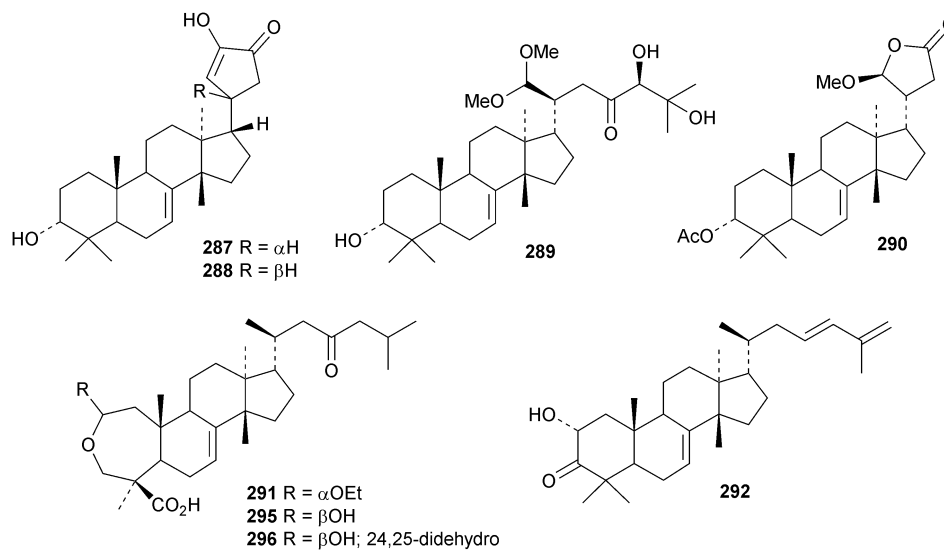


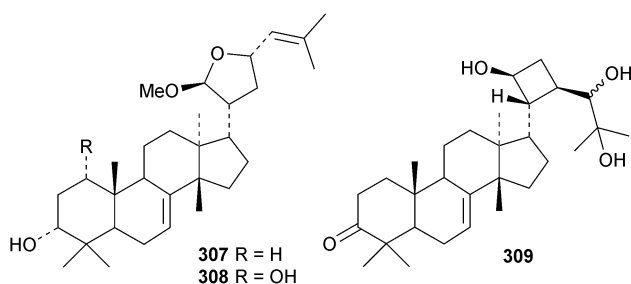
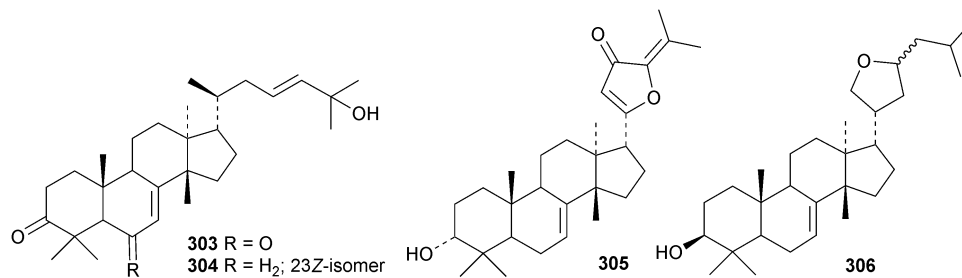




27-nor-derivative **284** from *Dipterocarpus obtusifolius*¹⁰⁶ and the two probable artefacts **285** and **286** from the leaves of *Aglaia odorata*.¹⁵

Novel dammarane saponins with known genins include acerbosides A and B from *Hovenia acerba*,¹⁰⁷ chikusetsusaponins FK₁–FK₇, FH₁, FH₂, FM and FT₁–FT₄ from *Panax japonicus*,^{108,109} gypenbiosides A and B from *Gynostemma*

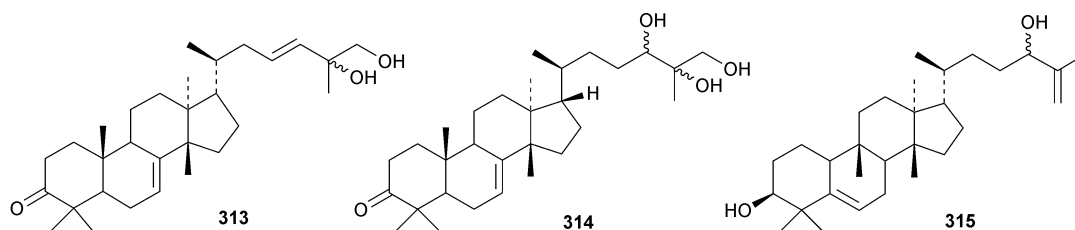
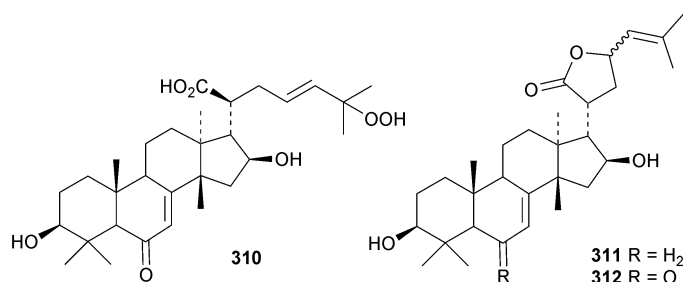


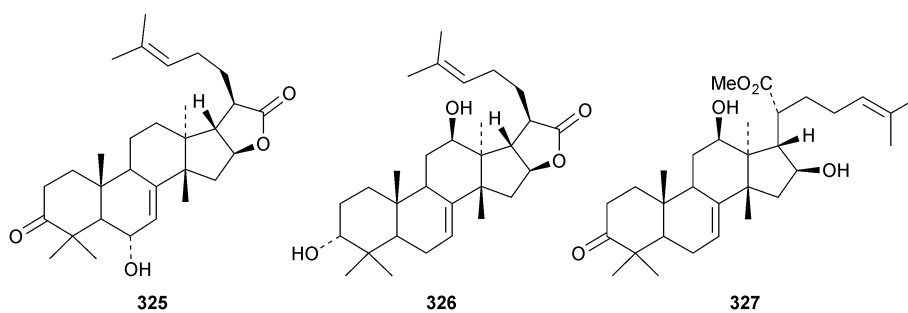
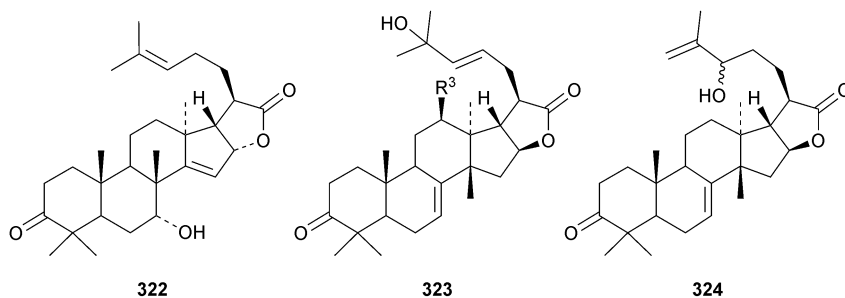
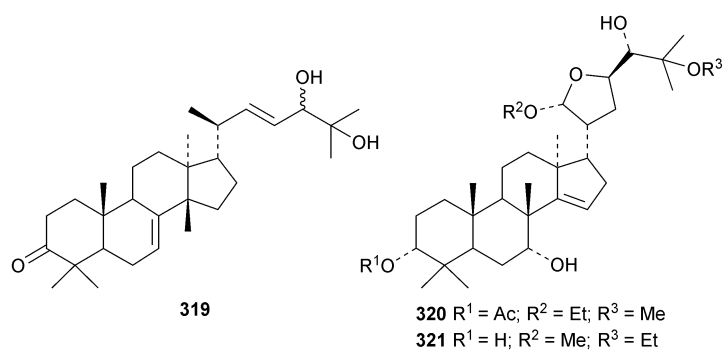
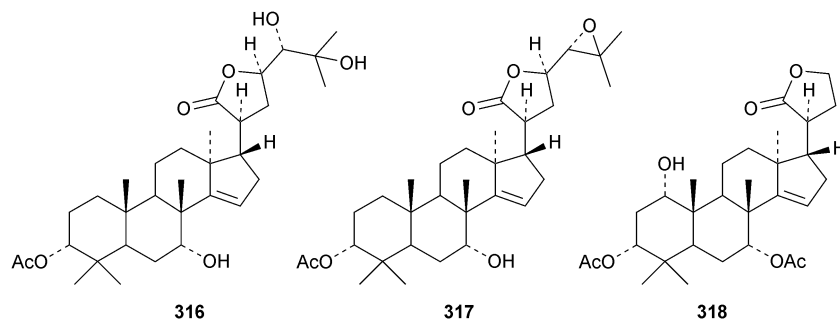


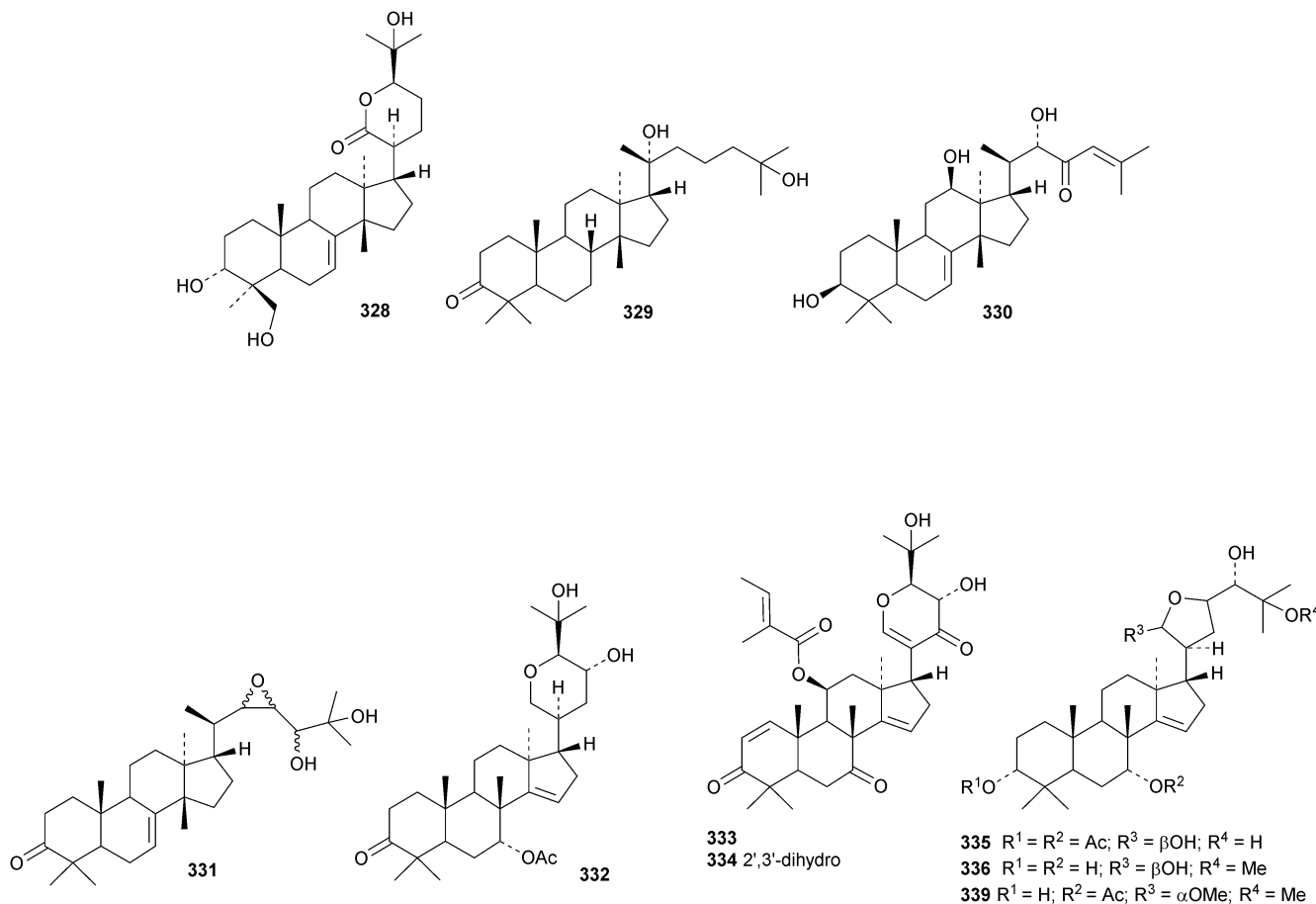
pentaphyllum,¹¹⁰ 20*R*-pseudoginsenoside F₁₁ (ref. 111) and quinquenosides Ja and Jb¹¹² from *Panax quinquefolium*.

New compounds from the stem bark of *Aphanamixis grandifolia* include the tautomeric tirucallane

cyclopentenones **287** and **288** (ref. 113) and the tirucallanes **289** and **290**.¹¹⁴ Compounds **287** and **288** were originally named aphafranins A and B, names used by the authors for previous compounds. Their names have been changed to aphafraones A and B.¹¹⁵ Two further derivatives **291** and **292** were obtained from the leaves and twigs of *Aphanamixis grandifolia*.¹¹⁶ Some of these compounds clearly incorporate the extraction solvent. Aphanamgrandins A **293**–**302** constitute a series of 2,3-*seco*- and 3,4-*seco*-tirucallanes from the stems of *Aphanamixis grandifolia*.¹¹⁷ They were accompanied by the ring-A intact derivatives aphanamgrandin J **303** and the dienone **304**. The structures of aphanamgramins A **293** and B **294** were confirmed by X-ray analyses. Other new tirucallanes include the 21-*nor*-derivative dysoxylentin A **305** from *Dysoxylum lenticellatum*,¹¹⁸ ixoroid **306** from the flowers of *Ixora coccinea*,¹¹⁹ **307** and **308** from the stem bark of *Araliopsis synopsis*,¹²⁰ capulin **309** from *Capuronianthus mahafalensis*,¹²¹ **310**–**312** from the stem bark of *Melia toosendan*,¹²² dysohainanin F **313** from *Dysoxylum hainanense*¹²³ and







24,25,26-trihydroxytirucall-7-en-3-one **314** from *Salacia hainanensis*.¹²⁴ The 19(10 → 9)-abeotirucallane **315** has been reported from *Euphorbia mellifera*.¹²⁵

Chisiamols G **316** and H **317** (ref. 126) and chisopanins L **318**–O **321** (ref. 108 and 127) are new apotirucallanes from *Chisocheton paniculatus*. A series of compounds from the leaves and twigs of *Melia toosendan* includes the apoeuphane mesendanin K **322**, the euphanes mesendanins L **323**–P **327**, the tirucallanes mesendanins Q **328**–T **331** and the apotirucallane mesendanin U **332**.¹²⁸ The apotirucallane **332** was also isolated from *Dysoxylum hainanense* and named dysohainanin E.¹²³ Other new apotirucallanes include piscidinones A **333** and B **334** from *Walsura trifoliata*,¹²⁹ agladorals A **335**–E **339** from *Aglaia odorata* var. *microphyllina*¹³⁰ and trichostemonate **340** from the roots of *Walsura trichostemon*.¹³¹ The structure of **340** was confirmed by X-ray analysis. Toonaciliatavarins A **341**–H **348** are constituents of *Toona ciliata*.¹³²

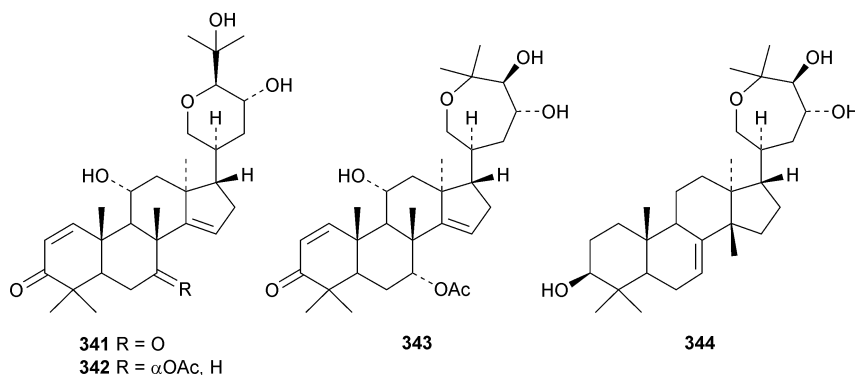
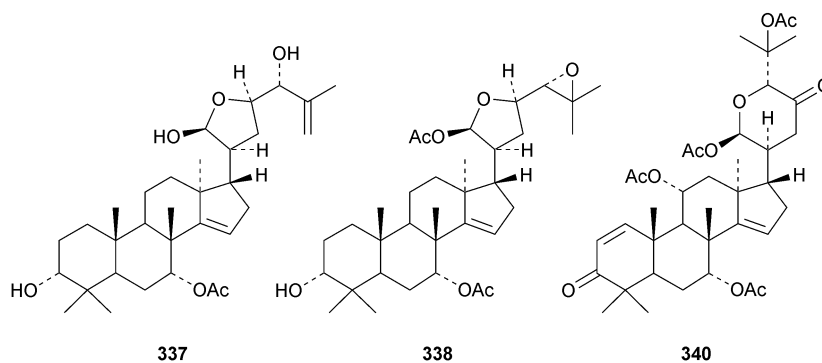
4.1 Tetranortriterpenoids

A review of the structures and biological activities of limonoids from *Cipadessa* species has been published.¹³³ Walsucochinoids

A **349** and B **350** are rearranged limonoids, with an aromatic ring D, from *Walsura cochinchinensis*.¹³⁴ Andhraxylocarpins A **351**, B **352**, C **353** and E **354** are new skeletal types from *Xylocarpus granatum*.¹³⁵ The structures of **349**, **351** and **353** were confirmed by X-ray analyses. Andhraxylocarpin D **355** is the same as chisomicin A, published in 2011. *Hortia oreadica* is the source of the interesting rearranged limonoids **356**–**363**, related to the known hortiolide A.¹³⁶ The structure of hortiolide C **358** was confirmed by X-ray analysis. The configurations at C-5 and C-10 of hortiolide E **362** and 12-hydroxyhortiolide E **363** are wrongly drawn in the paper. Carapanolides A **364** and B **365** are 9,10-*seco* mexicanolide derivatives from the seeds of *Carapa guianensis*.¹³⁷ Other new structural types include citriolide A **366** from the seeds of *Citrus reticulata*,¹³⁸ aphanamixoid A **367** from *Aphanamixis polystachya*¹³⁹ and chukrasones A **368** and B **369** from *Chukrasia tabularis*.¹⁴⁰ The structure of aphanamixoid A **367** was confirmed by X-ray analysis. It was accompanied in the extract by aphanamixoid B **370**.

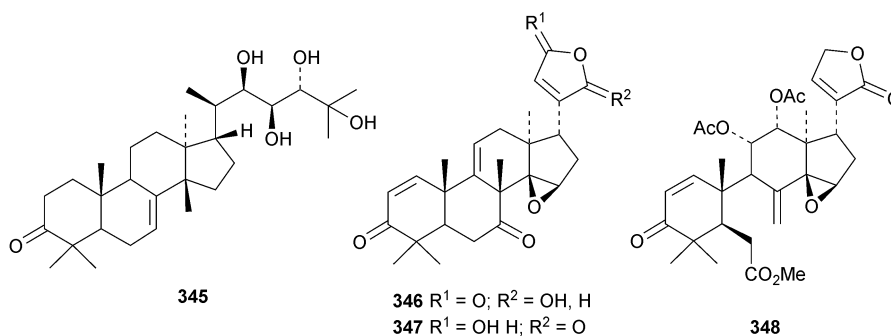
Toonayunnanins A **371**–L **382** constitute a group of assorted limonoids from the leaves of *Toona ciliata* var. *yunnanensis*.¹⁴¹ Toonayunnanin I **378** is the same as toonaciliatin P, published in 2011. Another group of compounds, toonaciliatones B **383**–F

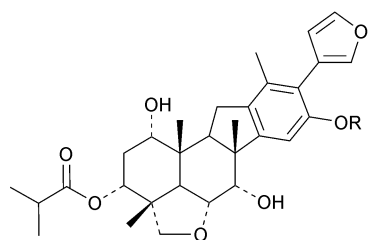




387, has been obtained from the seeds of *Toona ciliata*.¹⁴² Meliatoosenins E 388, F 389, I 390, J 391, L 392–N 394 and P 395–S 398 are new compounds from the fruit of *Melia toosendan*.¹⁴³ Meliatoosenins G, H, K and O, claimed as new compounds, have all been published previously. Other new compounds include andirolides H 399–P 407 from *Carapa guianensis* flowers,¹⁴⁴ ceramicines J 408–L 410 from *Chisocheton ceramicus*¹⁴⁵ and walsuranins A 411–C 413 from *Walsura yunnanensis*.¹⁴⁶

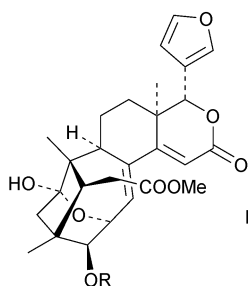
The ring A-cleaved compounds, aphanalides A 414–H 421, have been reported from the fruit of *Aphanamixis polystachya*.¹⁴⁷ The structures of aphanalides A 414 and C 416 were confirmed by X-ray analyses. Aphanagranins A 422–D 425 are constituents of *Aphanamixis grandifolia*.¹⁴⁸ Other species producing multiple new compounds include *Munronia unifoliata* with munronoids A 426–J 435 (ref. 149) and K 436–O 440 (ref. 150) and *Dysoxylum hainanense* with dysohainanins A 441–D 444.¹²³ 6-O-Deacetylseverinolide 445 is a constituent of *Atalantia buxifolia*.¹⁵¹





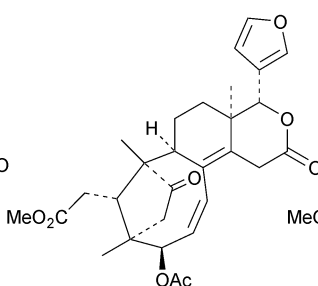
349 R = Me

350 R = H; 3-deacyl; 3-tigloyl

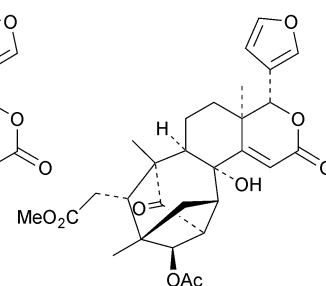


351 R = tigloyl

352 R = Ac

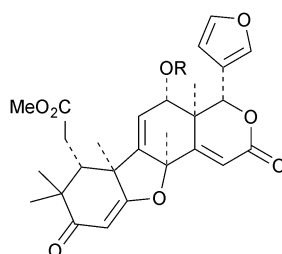


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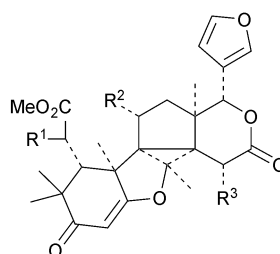
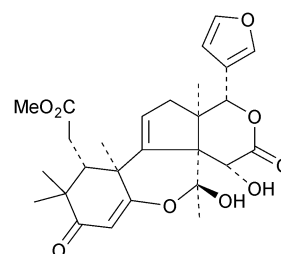
354 R = Ac

355 R = tigloyl

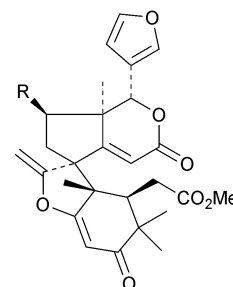


356 R = H

357 R = Ac

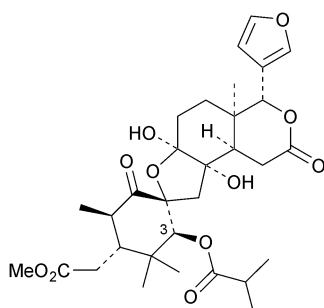
358 R¹ = R² = H; R³ = OH359 R¹ = R³ = OH; R² = H360 R¹ = OH; R² = OAc; R³ = H

361



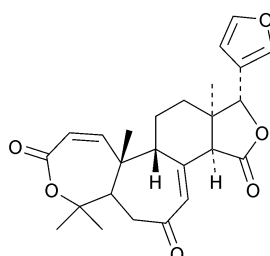
362 R = H

363 R = OH

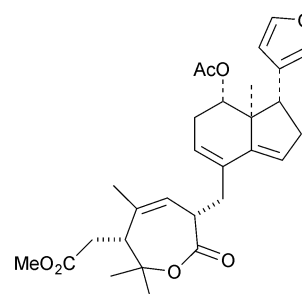


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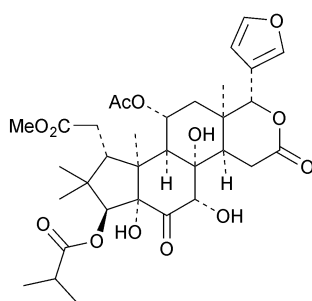
365 3-deacyl; 3-tigloyl



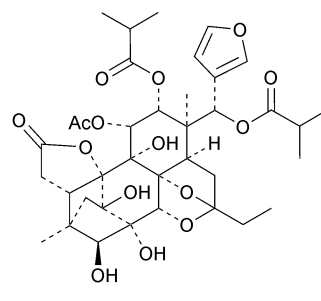
366



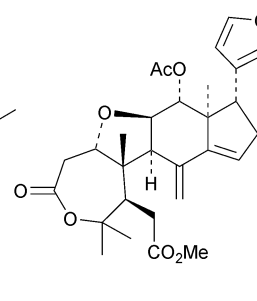
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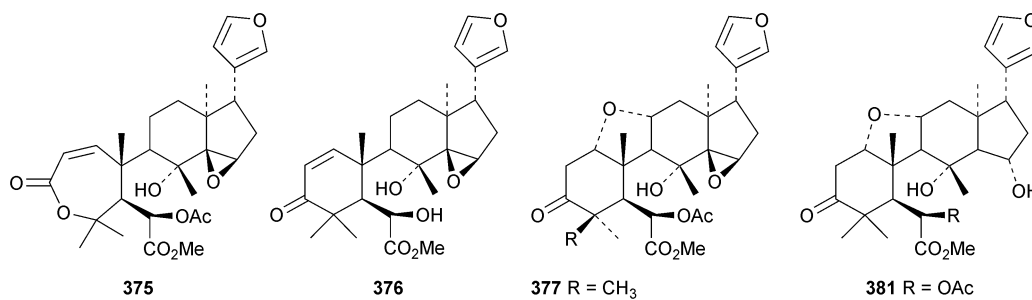
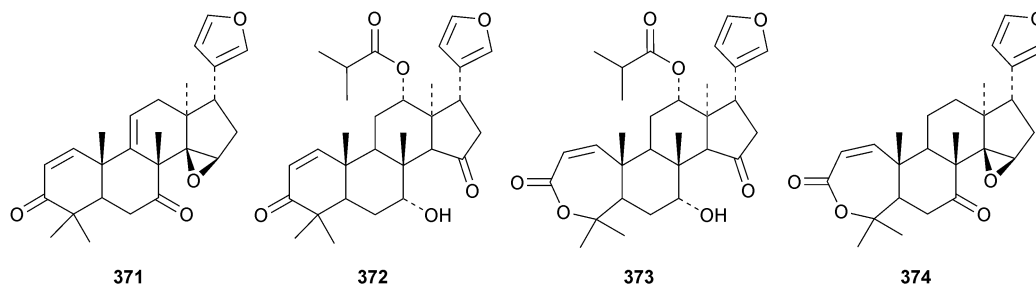


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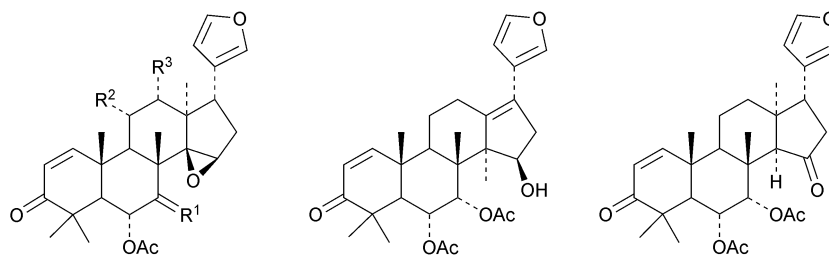
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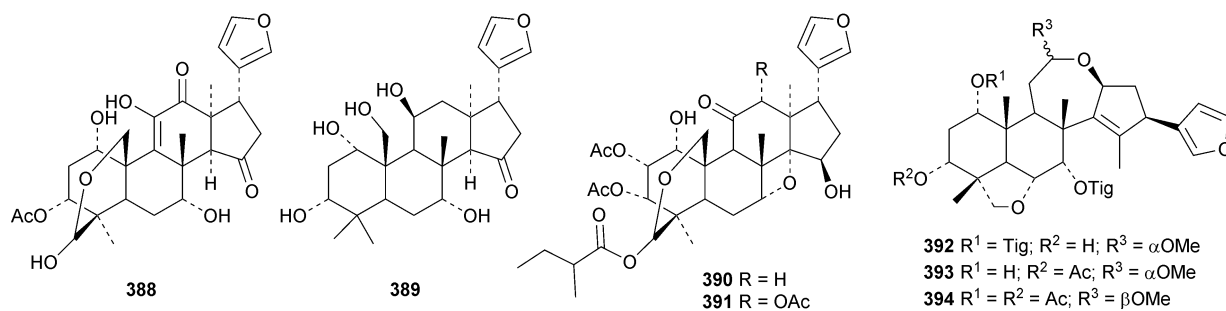


377 R = CH₃
378 R = CH₂OAc
379 R = CH₃; 1,2-didehydro
380 R = CHO; 1,2-didehydro

381 R = OAc
382 R = H

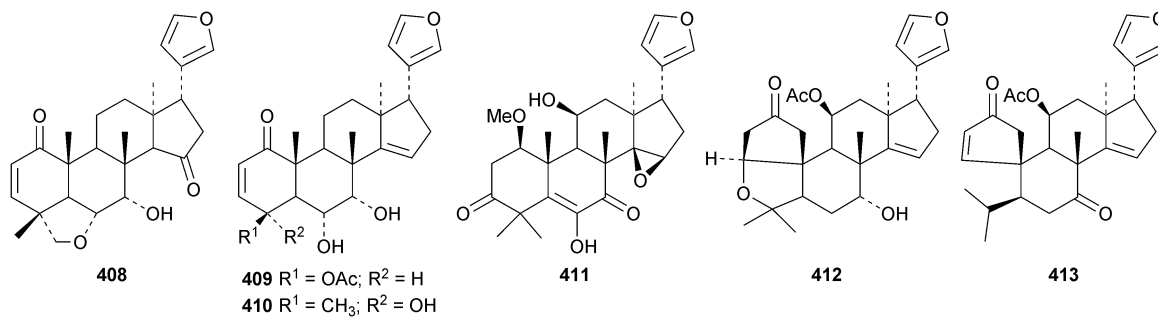
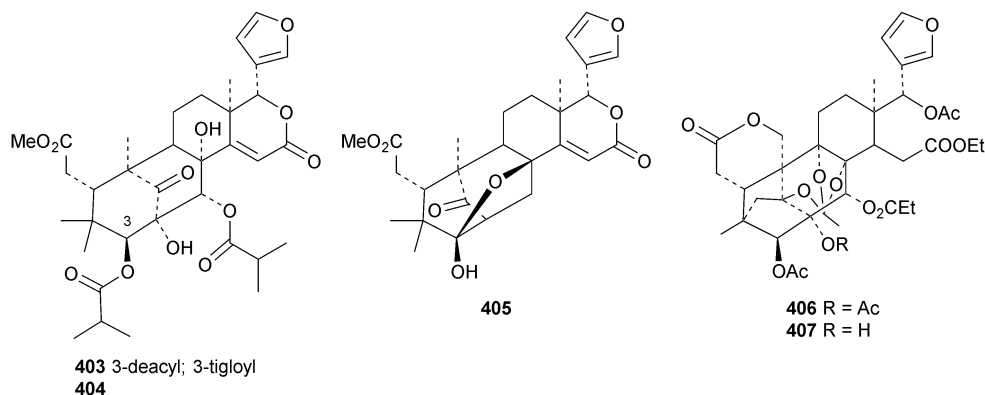
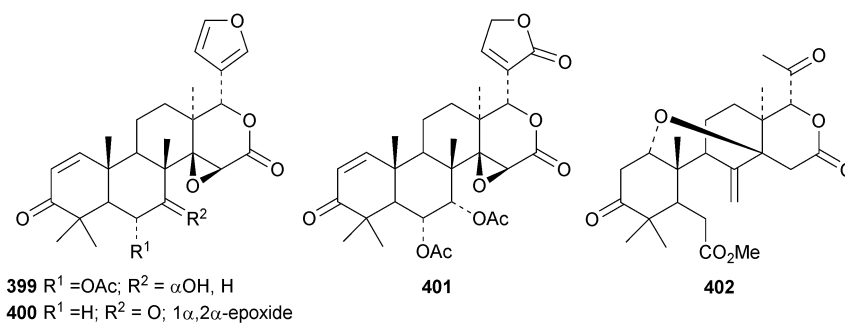
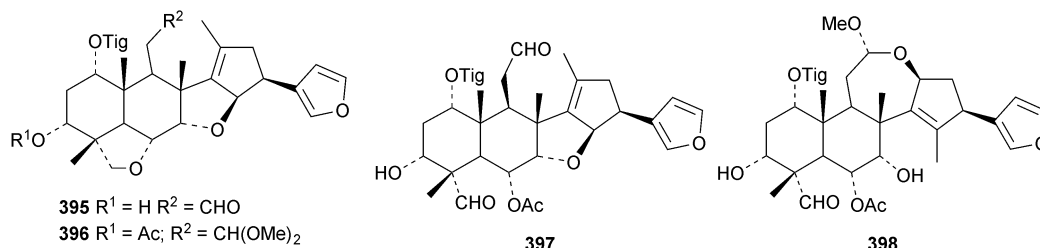


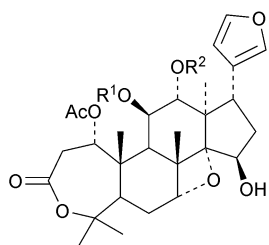
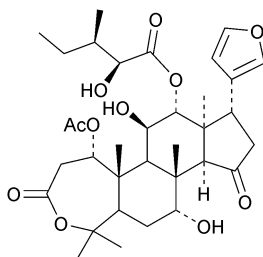
383 R¹ = O; R² = R³ = H
385 R¹ = αOAc, H; R² = OH; R³ = H
386 R¹ = αOAc, H; R² = H; R³ = OH



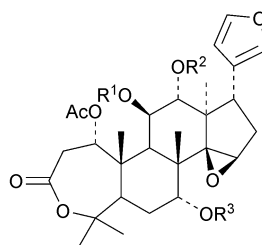
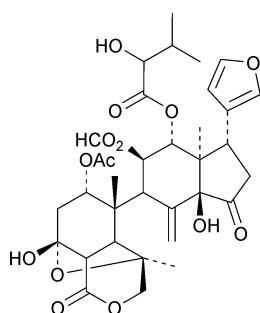
392 R¹ = Tig; R² = H; R³ = αOMe
393 R¹ = H; R² = Ac; R³ = αOMe
394 R¹ = R² = Ac; R³ = βOMe



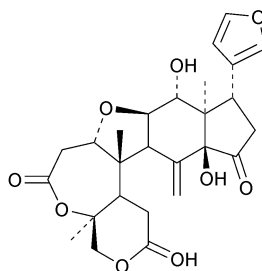


414 R¹ = HCO; R² = Me₂CHCH₂CO415 R¹ = H; R² = Me₂CHCH₂CO416 R¹ = H; R² = Et(Me)CHCH(OH)CO422 R¹ = R² = H

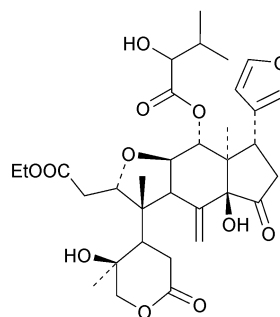
417

418 R¹ = H; R² = Et(Me)CHCH(OH)CO; R³ = H419 R¹ = H; R² = Et(Me)CHCH(OH)CO; R³ = Ac420 R¹ = HCO; R² = Et(Me)CHCH(OH)CO; R³ = H421 R¹ = HCO; R² = Me₂CHCH₂CO; R³ = H

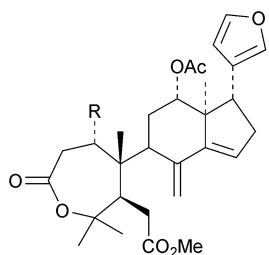
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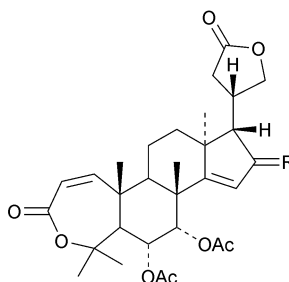


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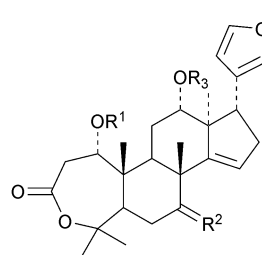
426 R = OAc

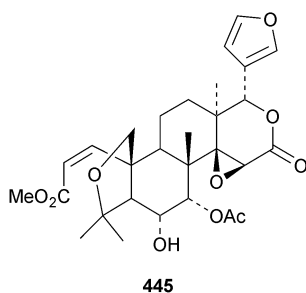
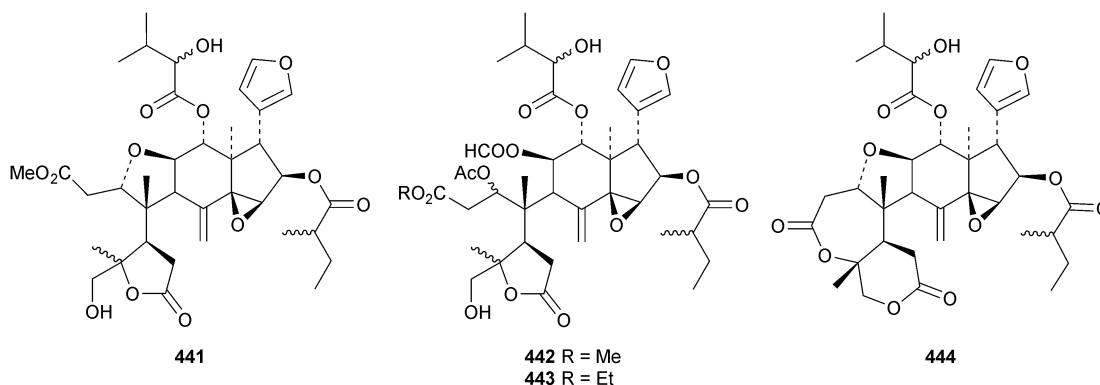
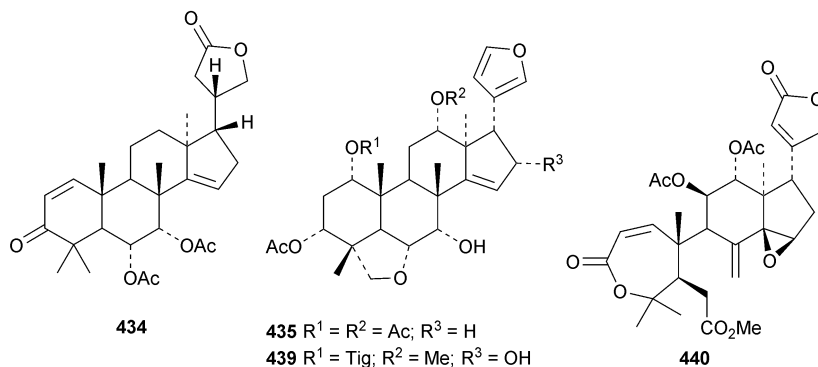
427 R = H; 1,2-didehydro

428 R = H₂; 14β,15β-epoxide429 R = H₂

430 R = O

431 R = βOOH, H

432 R¹ = R³ = Ac; R² = O433 R¹ = R³ = Ac; R² = αOH, H436 R¹ = Ac; R² = αOAc, H; R³ = Et(Me)CHCH(OH)CO437 R¹ = R³ = Ac; R² = αOAc, H438 R¹ = R³ = Ac; R² = αOTig, H



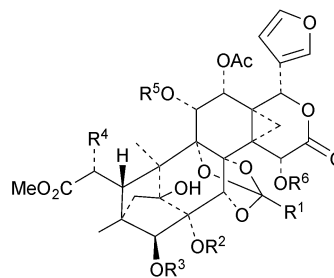
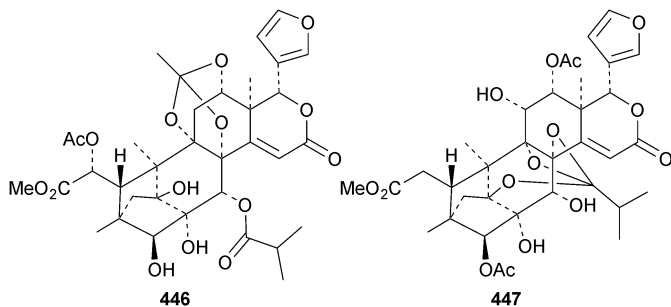
The seemingly unending flow of phragmalin/busein derivatives and variants continues and is matched only by the proliferation of confusing trivial names. These points are well illustrated by *Chukrasia tabularis* and *Chukrasia tabularis* var. *velutina*, the sources of chubularisins A 446–R 463,¹⁵² chuktabrins C 464–J 471 and chuktubararins U 472–X 475,¹⁵³ tabulalins G 476–I 478,¹⁵⁴ chukvelutins D 479–F 481 (ref. 155) and R310B8 482 and velutinalides A 483 and B 484.¹⁵⁶

Chabularisin O 460 is the same as chuktubarin V 474. The structure of chuktabrins C 464 was confirmed by X-ray analysis. Heytrijumalins A 485–I 493 have been isolated from the twigs and leaves of *Heynea trijuga*.¹⁵⁷ Other new compounds in this group include hisomicines D 494 and E 495 from *Chisocheton ceramicus*,¹⁵⁸ malayanines A 496 and B 497 from *Chisocheton erythrocarpus*,¹⁵⁹ senegalensins A 498–C 500 from *Khaya senegalensis*,¹⁶⁰ kotschyins D 501–H 505 from *Pseudocedrela kotschyi*,¹⁶¹ soymidins A 506 and B 507 from *Soymida febrifuga*¹⁶² and swietenin J 508 from *Swietenia macrophylla*.¹⁶³ Five new mexicanolide derivatives, heytrijunolides A 509–E 513, have been obtained from *Heynea trijuga*.¹⁶⁴ Mollucensins R 514–Y 521 are new mexicanolide and phragmalin derivatives from the seeds of *Xylocarpus moluccensis*.¹⁶⁵

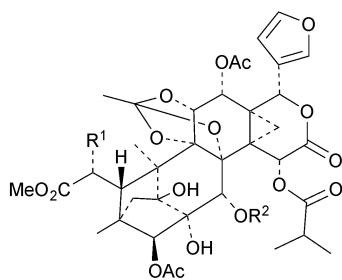
4.2 Quassinoids

The compounds isolated from *Brucea javanica* and their pharmacology have been reviewed.¹⁶⁶ Bruceanic acids E 522 and F 523, buruceanic acid E methyl ester 524, javanic acids A 525 and B 526 and javanicolide H 527 are new compounds from the

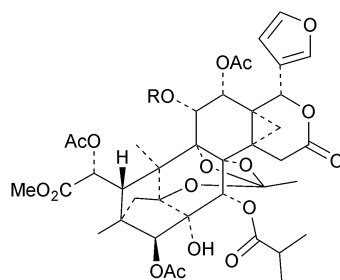




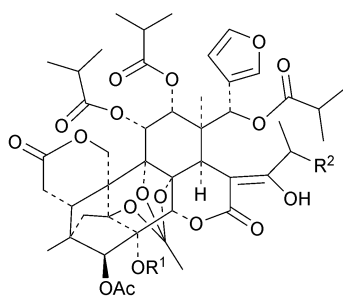
- 448** R¹ = Et; R² = R³ = R⁴ = H; R⁵ = Ac; R⁶ = ⁱPrCO
449 R¹ = Me; R² = EtCO; R³ = Ac; R⁴ = R⁵ = H; R⁶ = ⁱPrCO
450 R¹ = Me; R² = ⁱPrCO; R³ = Ac; R⁴ = R⁵ = H; R⁶ = ⁱPrCO
451 R¹ = ⁱPr; R² = R⁵ = R⁶ = H; R³ = Ac; R⁴ = OAc
452 R¹ = ⁱPr; R² = H; R³ = Ac; R⁴ = OAc; ; R⁵ = R⁶ = Ac



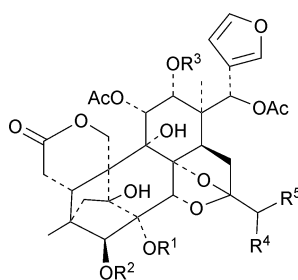
- 453** R¹ = OAc; R² = ⁱPrCO
454 R¹ = H; R² = EtCO



- 455** R = Ac
456 R = H

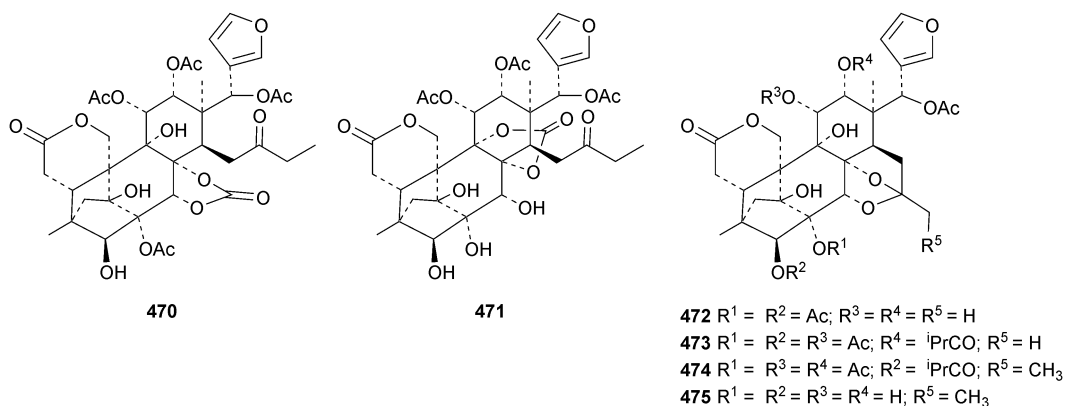
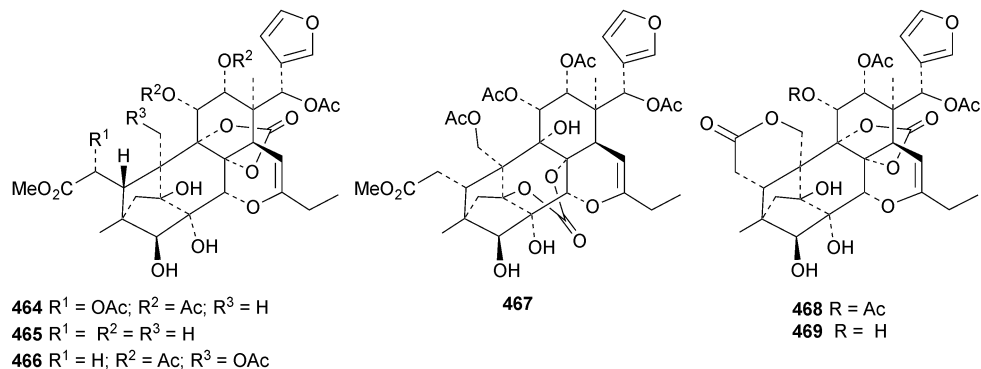


- 457** R¹ = H; R² = CH₃
458 R¹ = Ac; R² = CH₃
459 R¹ = Ac; R² = H



- 460** R¹ = R² = Ac; R³ = ⁱPrCO; R⁴ = R⁵ = H
461 R¹ = H; R² = Ac; R³ = EtCO; R⁴ = Me; R⁵ = H
462 R¹ = Ac; R² = H; R³ = ⁱPrCO; R⁴ = Me; R⁵ = H
463 R¹ = H; R² = Ac; R³ = Ac; R⁴ = Me; R⁵ = Me

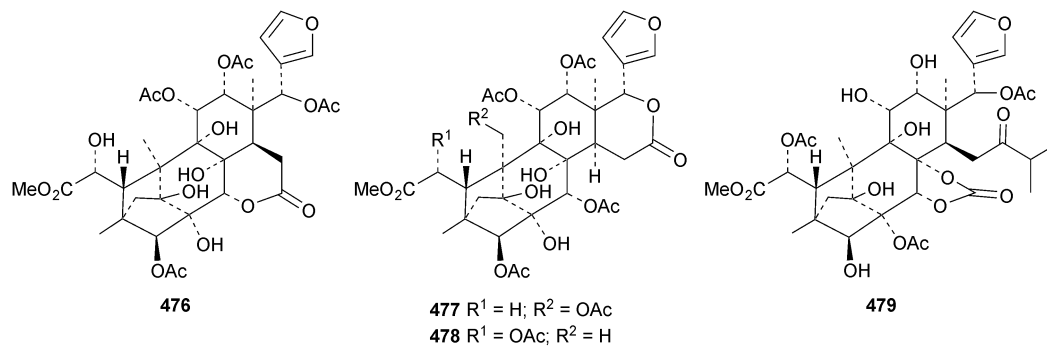


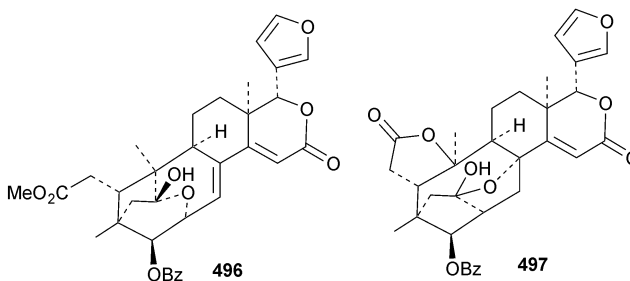
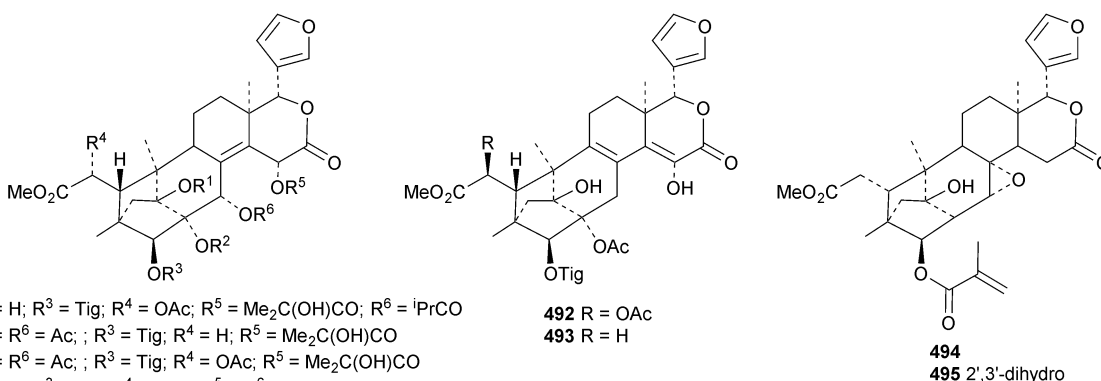
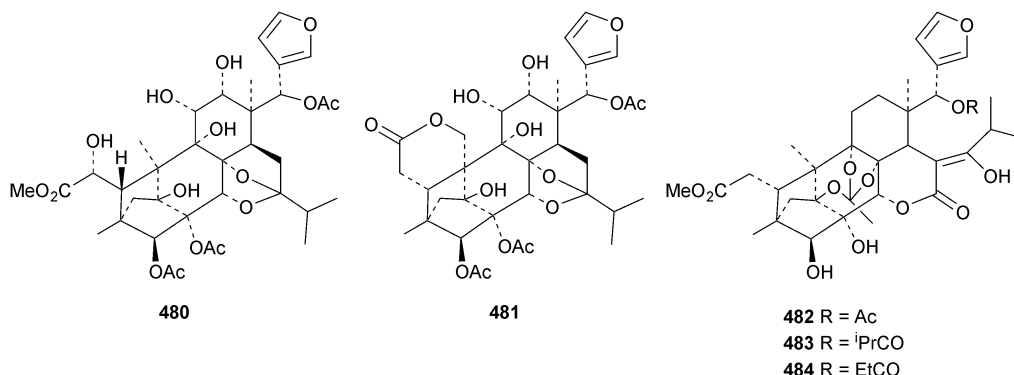


seeds of *Brucea javanica*.¹⁶⁷ Other new quassinoids include picrasin K 528 from *Quassin amara*¹⁶⁸ and odyendanol 529 from the fruit of *Odyendyca gabonensis*.¹⁶⁹

5. The lupane group

Reviews covering the sources and biological properties of betulinic acid¹⁷⁰ and the antineoplastic effects of lupeol¹⁷¹ have



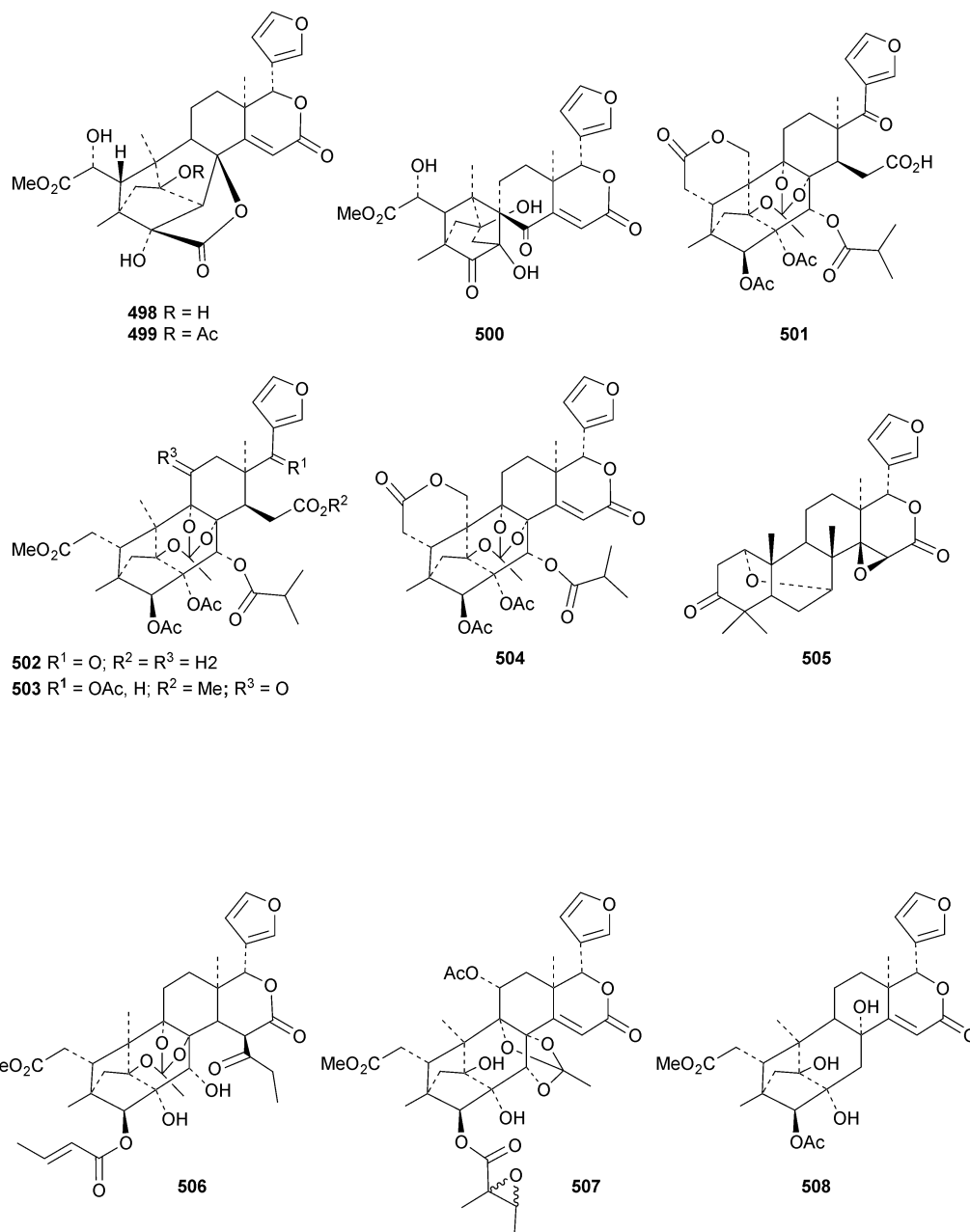


appeared. The 3,4-secolupane derivatives acanthosessiligenins I 530 and II 531 and acanthosessiliosides A 532–F 537 have been isolated from the fruit of *Acanthopanax sessiliflorus*.¹⁷² The 17,18-secolupane 538 has been found in the roots of *Taraxacum platycarpum* together with 3 β -acetoxyilup-18-en-21-one 539, the neolupane derivatives 540–542 and the migrated lupane 543.¹⁷³ Lup-20(29)-ene-2 β ,3 β -diol 544 is a constituent of *Salacia hainanensis*¹²⁴ and the related ketones 545 and 546 have been found in *Fagus hayatae*.¹⁷⁴ Other simple lupane derivatives include glochitriol 547 from *Glochidion lanceolarium*,¹⁷⁵ bengalensinone

548 from *Ficus bengalensis*,¹⁷⁶ 3 β -hydroxylupane-28,29-dioic acid 549 from *Aglaia duperreana*¹⁷⁷ and the norlupane derivatives 550, 551 and 552 from *Dipterocarpus obtusifolius*.¹⁰⁶

Two lupane saponins with the new genin 553 have been isolated from *Schefflera venulosa*.¹⁷⁸ New lupane saponins with known genins include ilekudinichoside E from *Ilex kudincha*,¹⁷⁹ stellatosides C, D and E, the methyl esters of stellatosides B and C and thurberoside A from *Stenocereus eruca*¹⁸⁰ and unnamed saponins from *Liquidambar formosana*¹⁸¹ and *Cichorium intybus*.¹⁸²



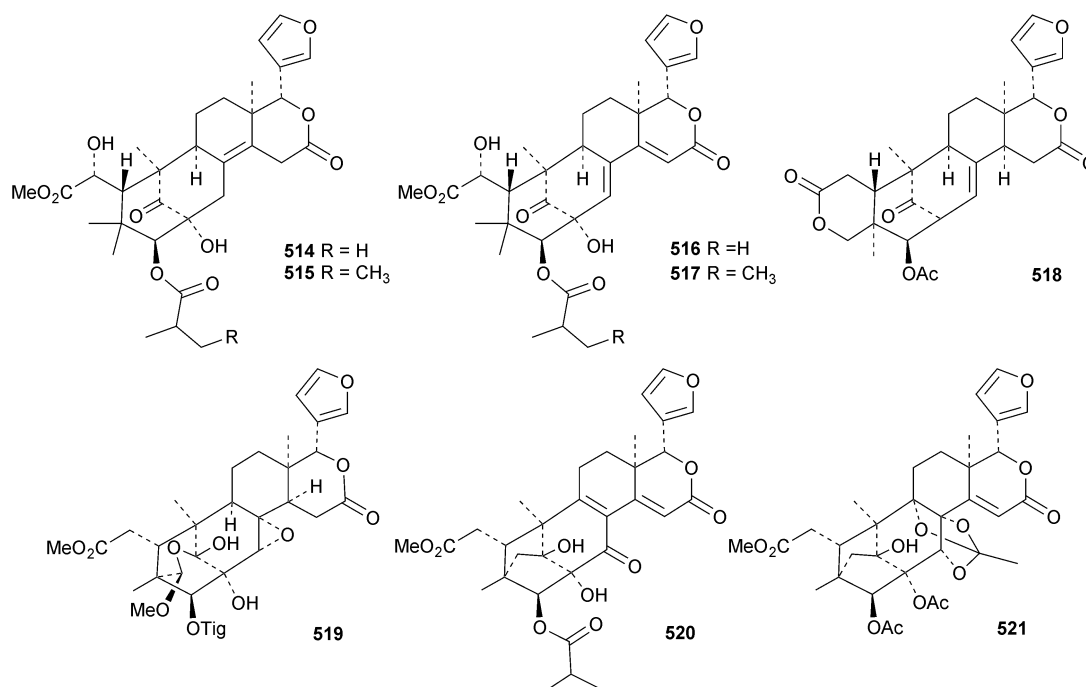
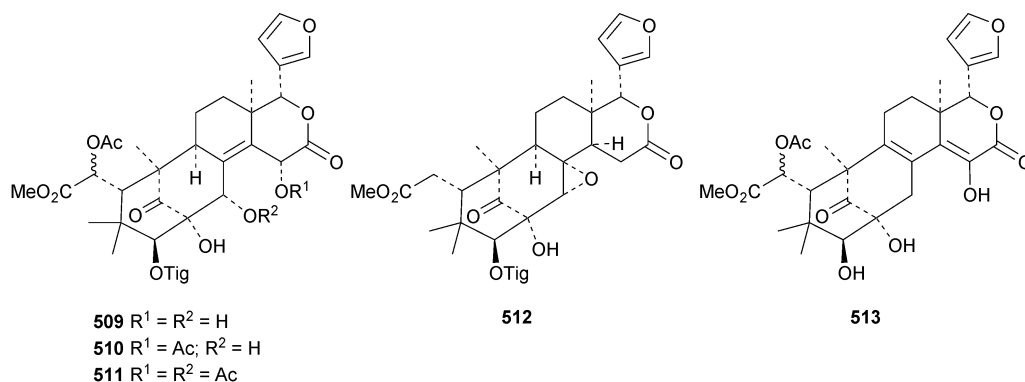


Oleanderocioic acid **554**, a lupane ester with the unusual *cis*-4-acetylcinnamic acid, is claimed to be a constituent of *Nerium oleander*.¹⁸³ Other new lupane esters include the nonanoyl ester of lupeol **555** from *Dorstenia harmsiana*,¹⁸⁴ kurramanoic acid **556** from *Nepeta clarkei*,¹⁸⁵ the myristoyl esters **557** from *Glochidion wrightii*¹⁸⁶ and **558** from *Sinocalamus affinis*,¹⁸⁷ the *cis*-feruloyl ester **559** from *Panax ginseng*,¹⁸⁸ the palmitoyl ester **560** from *Cichorium intybus*¹⁸² and the stearoyl ester **561** from *Ocimum sanctum*.¹⁸⁹

6. The oleanane group

Reviews have appeared on the origins, biosynthesis and biological activity of oleanolic acid¹⁹⁰ and the beneficial effects of arjunolic acid in type 1 diabetes.¹⁹¹ *Fagus hayatae* is the source of the 1,10-secooleanane derivative **562** where it is found with 3 α ,23-dihydroxy-3-oxoolean-12-en-28-oic acid **563** and 3 β ,12 α ,23-trihydroxyoleanan-28,13 β -olide **564**.¹⁷⁴ Sentulic acid from *Sandoricum koetjape* has been identified as 3,4-secooleana-4(23),12-diene-3,27-dioic acid **565**.¹⁹² The 17,22-secooleanenol



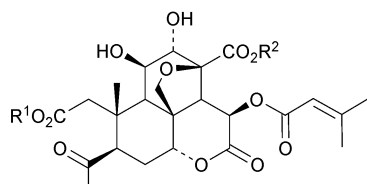
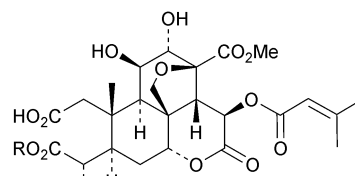


566, from *Pyrenacantha kaurabassana*, has the unusual $18\alpha H$ -configuration.¹⁹³ Zizimauritic acids A 567, B 568 and C 569 are ring-A contracted 20,21-secooleanane derivatives from *Ziziphys mauritiana*.¹⁹⁴ The zizimauritic acids also have the $18\alpha H$ -configuration. A ring-E contracted oleanane derivative 570 has been isolated from the bark of *Diospyros decandra*.¹⁹⁵ Platycodonoids A 571 and B 572 are 28-noroleanane derivatives from the roots of *Platycodon grandiflorum*.¹⁹⁶ The 30-nor derivatives euscaphic acids G 573 and H 574, together with their likely precursor euscaphic acid I 575, are present in *Euscaphis japonica*.¹⁹⁷ Further noroleanane derivatives include

30-noroleanolic acid 576 from *Olea europea*,¹⁹⁸ the 24,30-dinor derivatives 577 and 578 and the 24-nor compounds 579 and 580 from the roots of *Paeonia emodi*¹⁹⁹ and 581 from *Pilea cavaleriei*.²⁰⁰ A 4900 year old oak wood sample found in a freshwater sediment has produced six noroleanane derivatives 582–587 all lacking oxygenation at C-3.²⁰¹

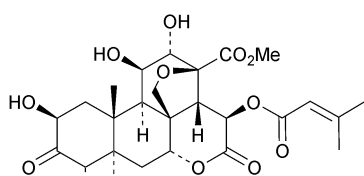
Several olean-18-ene derivatives have been identified including olean-18-ene- $1\beta,2\alpha,3\beta$ -triol 588 from *Salvia atropatana*,²⁰² 589–596 from *Cassine xylocarpa*, 597 from *Maytenus jelskii*,²⁰³ olean-18-ene- $1\alpha,3\beta$ -diol 598 from *Juglans sinensis*²⁰⁴ and $2\alpha,3\alpha,24$ -trihydroxyolean-18-en-28-oic acid 599 from



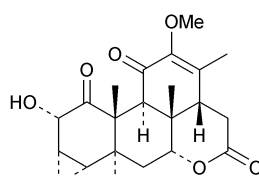
522 R¹ = H; R² = Me523 R¹ = R² = H524 R¹ = R² = Me

525 R = H

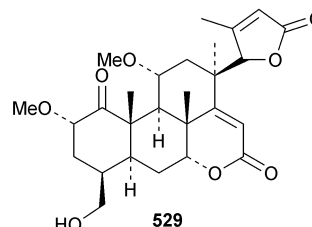
526 R = Me



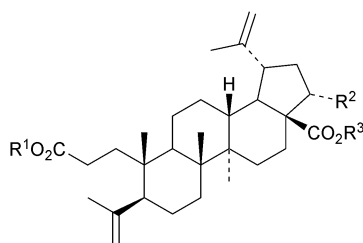
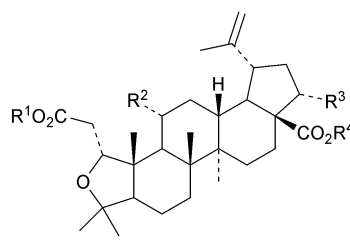
527



528



529

530 R¹ = Me; R² = OH; R³ = H531 R¹ = R² = H; R³ = Glc532 R¹ = Me; R² = OH; R³ = R⁴ = H533 R¹ = Me; R² = OH; R³ = H; R⁴ = Glc534 R¹ = Me; R² = R³ = OH; R⁴ = Glc535 R¹ = Glc; R² = R³ = R⁴ = H536 R¹ = R² = H; R³ = OH; R⁴ = Glc

Eucalyptus exserta.²⁰⁵ The stem bark of *Terminalia arjuna* is the source of oleaterminaloic acids A **600**, B **601** and C **602** together with the 3-glucoside oleaterminalide **603**.²⁰⁶ Other new simple oleanane derivatives include pseuderranic acid **604** from *Pseuderranthemum carruthersii*,²⁰⁷ punicaone **605** from *Punica granatum*,²⁰⁸ turformosinic acid **606** from *Turpinia formosana*,²⁰⁹ 3 β ,23,28-trihydroxyolean-12-en-11-one **607** from *Aster yomena*,²¹⁰ 3 α ,29-dihydroxyolean-12-ene-23,28-dioic acid **608** from *Schefflera farinosa*,²¹¹ oleana-9(11),12-diene-1 β ,3 β -diol **609** from *Salvia xanthocheila*,²¹² 1-*epi*-castanopsol **610** from *Simira glaziovii*,²¹³ the 29,22-olide **611** from *Celastrus orbiculatus*²¹⁴ and the epoxy aldehyde **612** from *Tetraena mongolica*.²¹⁵

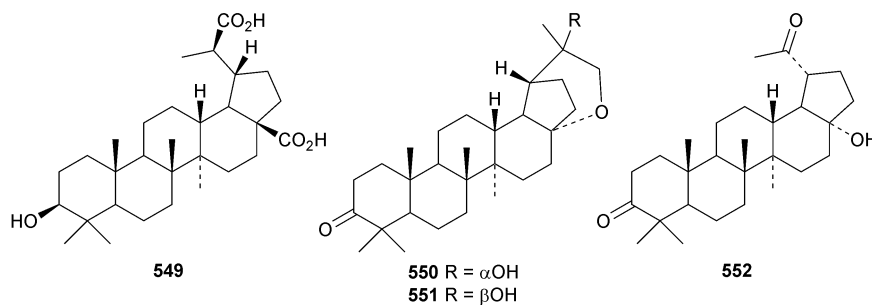
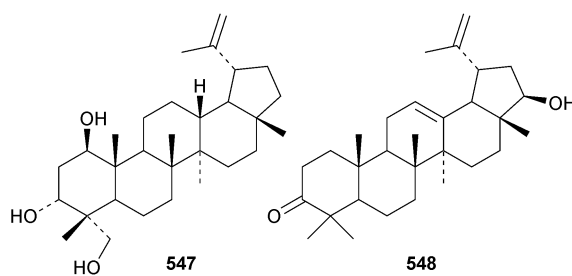
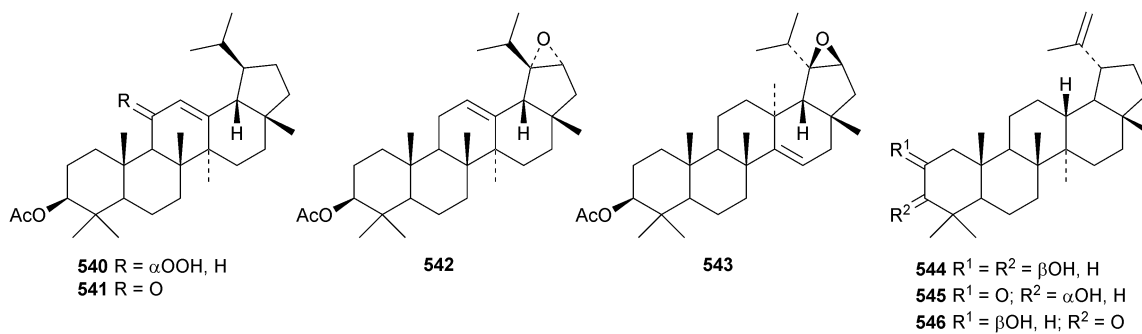
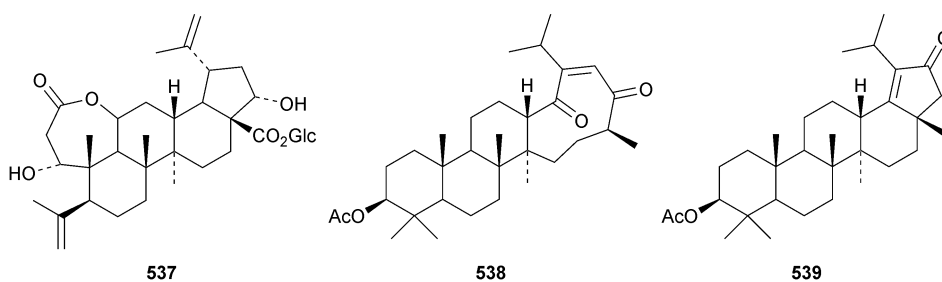
New oleanane esters include the caffeoyl derivatives **613–615**, from *Tetraena mongolica*,²¹⁵ the coumaroyl ester **616** from *Rubia schumanniana*,²¹⁶ the feruloyl ester **617** from *Saniculiphyllum guangxiense*,⁸⁵ the palmitates **618** from *Anemone rivularis*,²¹⁷ **619** from *Barringtonia asiatica*²¹⁸ and **620** from *Lobelia sessilifolia*.²¹⁹ Four esters **621–624** of the 19(18 \rightarrow 17)-*abeo*-28-

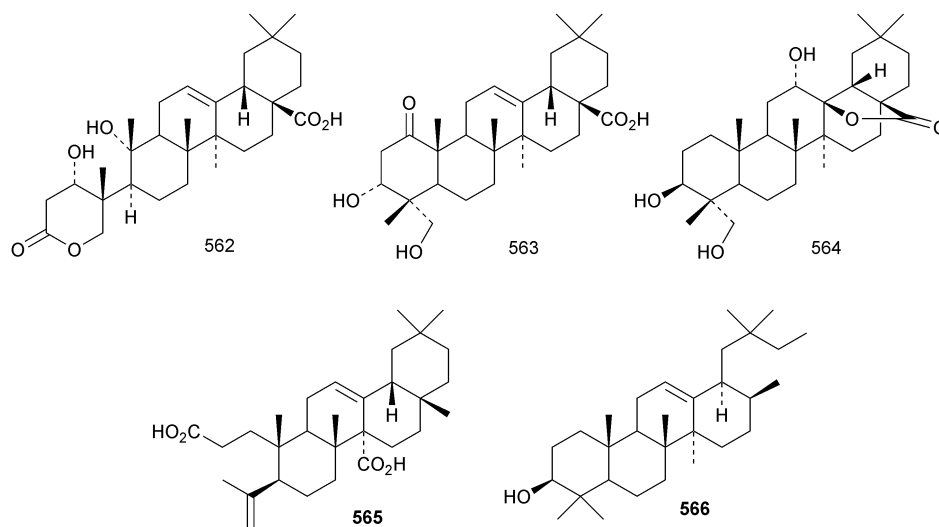
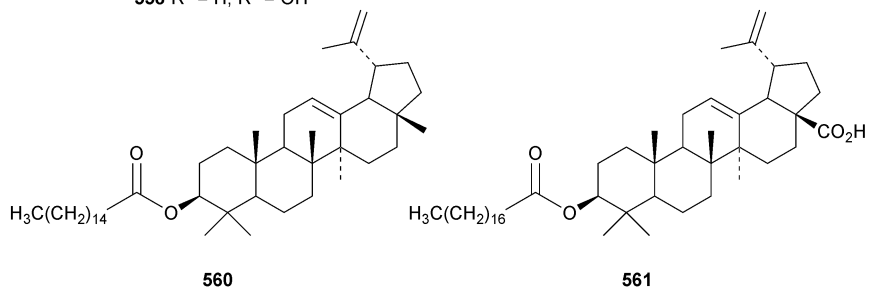
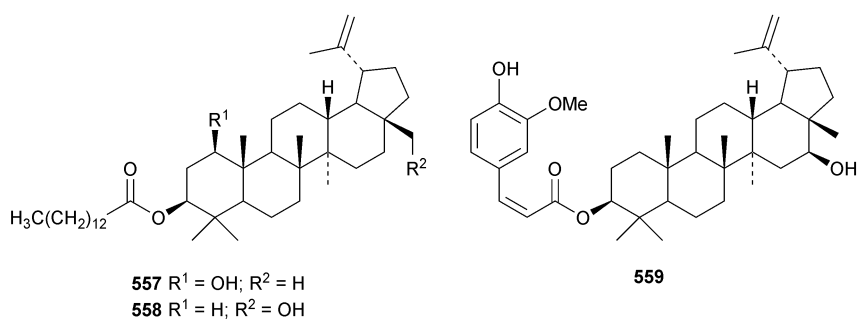
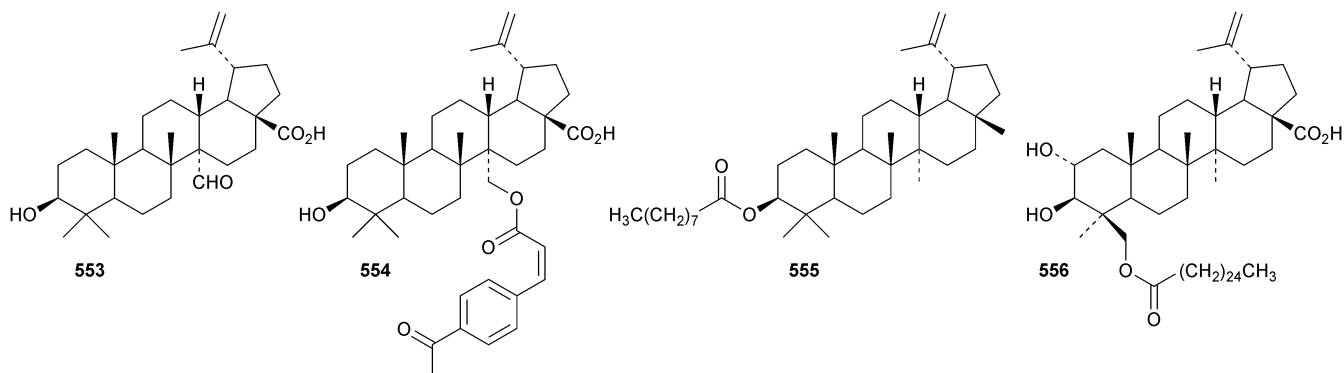
noroleanane phlomstetraol B have been isolated from *Leonurus heterophyllum*.²²⁰

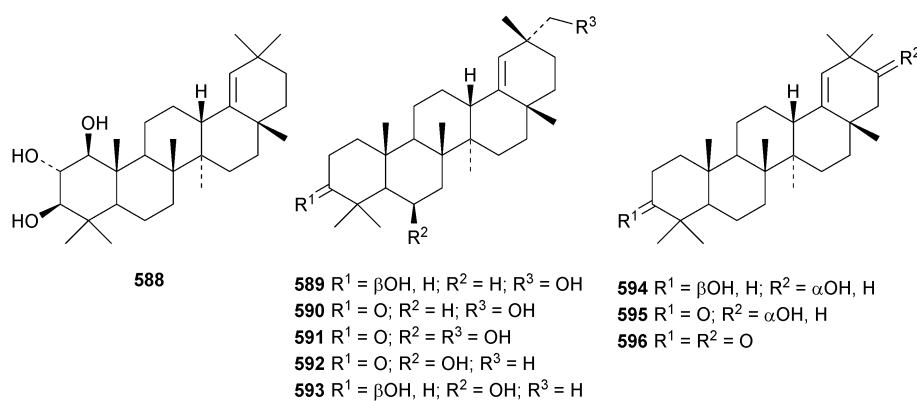
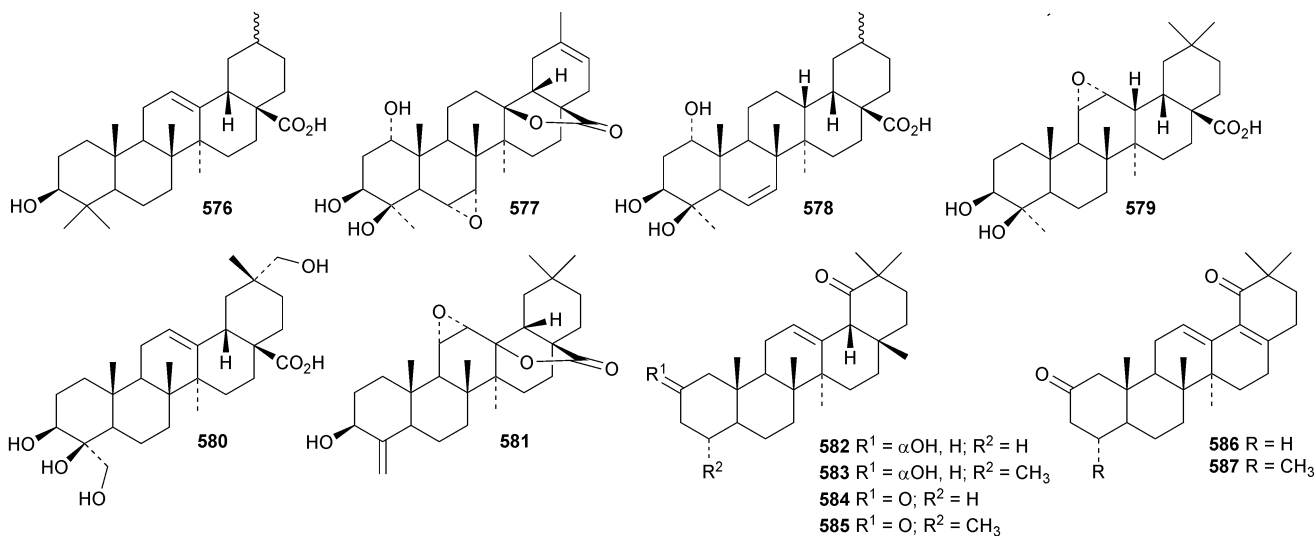
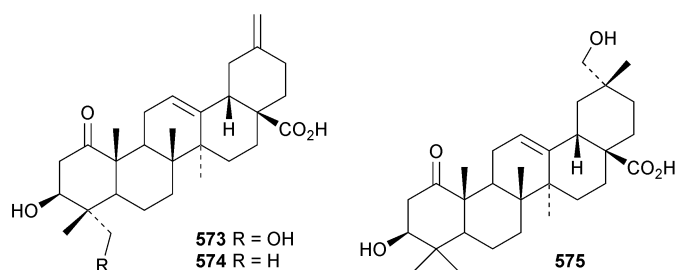
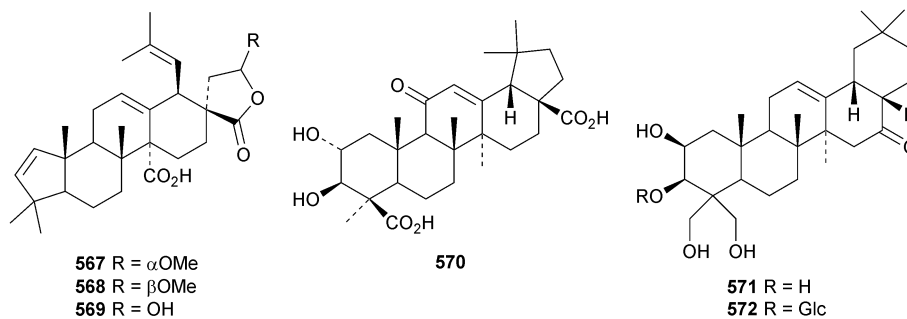
Two oleanane saponins, with the new genin olean-12-ene-2 β ,15 α ,23-triol **625**, have been isolated from *Ammannia auriculata*.²²¹ Antoniosides E–J are oleanane saponins from *Antonia ovata*.²²² Antoniosides E–H have new genins that are esters of olean-12-ene-3 β ,15 α ,16 α ,21 β ,22 α ,23,28-heptol **626**. Sorbifoliasides G–J, from *Xanthoceras sorbifolia*, have known genins and sorbifoliaside K has the new genin oleana-12,15-diene-3 β ,21 β ,22 α ,28-tetrol **627**.²²³ A variety of new 30-noroleanane genins, **628–631**, are included in akemisaponins A–K from *Akebia trifoliata*.²²⁴ Two saponins from *Camellia japonica* have been assigned the names camelliosides E and F that have been used previously.²²⁵ Camellioside E has the new genin 28-norolean-12-ene-3 β ,16 α ,17 β -triol **632**. Four saponins have been isolated from *Astragalus angustifolius* including the new genin olean-12-ene-3 β ,21 β ,22 α ,24,29-pentol **633**.⁶⁸

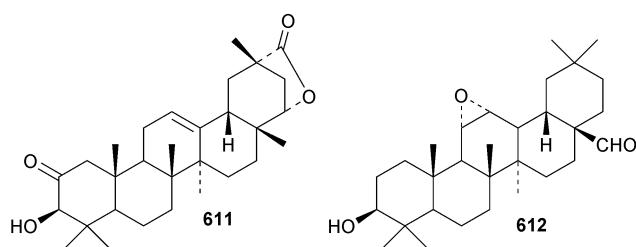
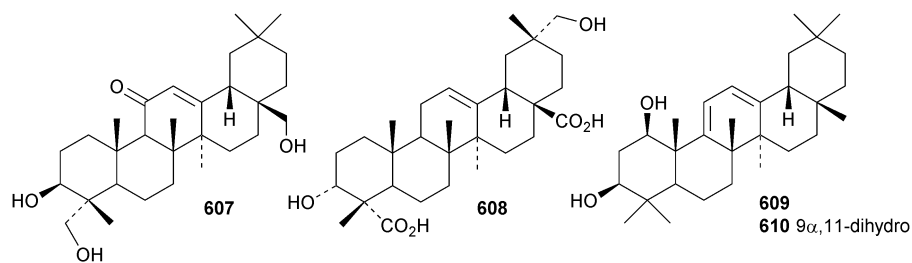
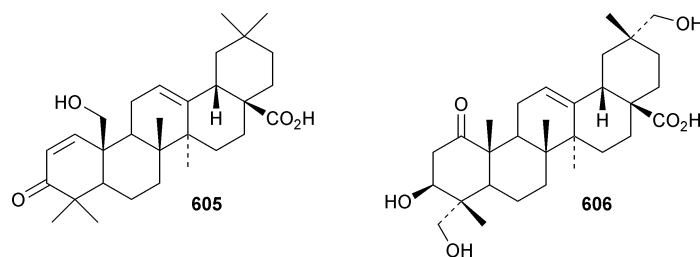
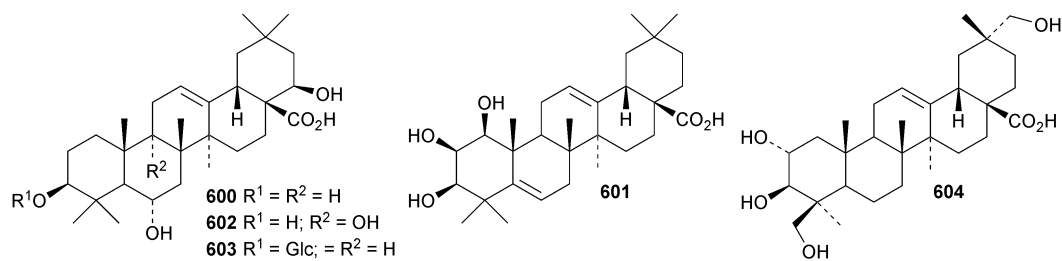
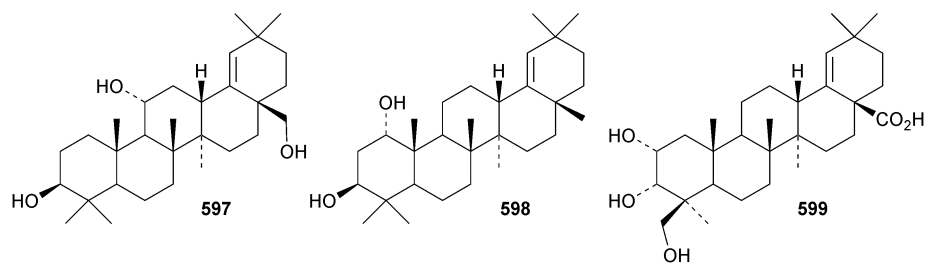
New oleanane saponins with known genins that have been assigned trivial names are listed in Table 1.

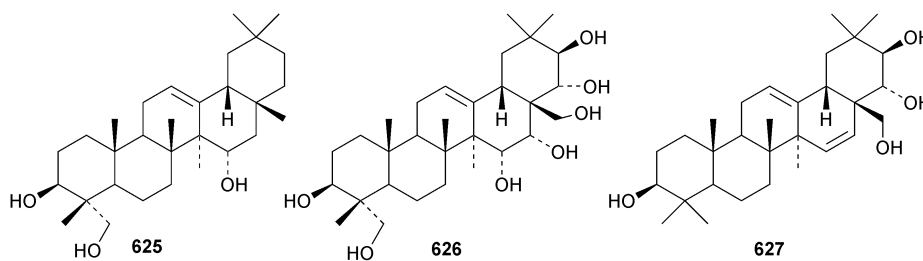
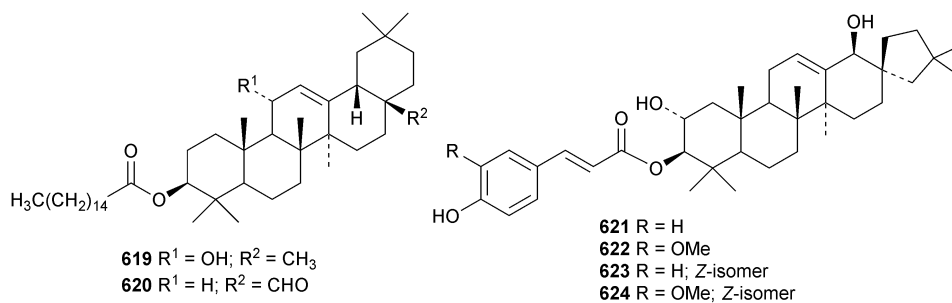
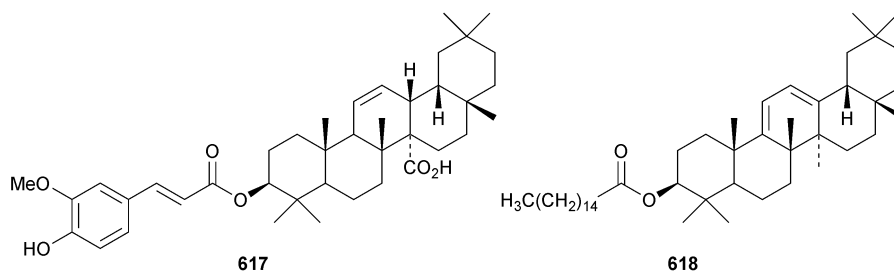
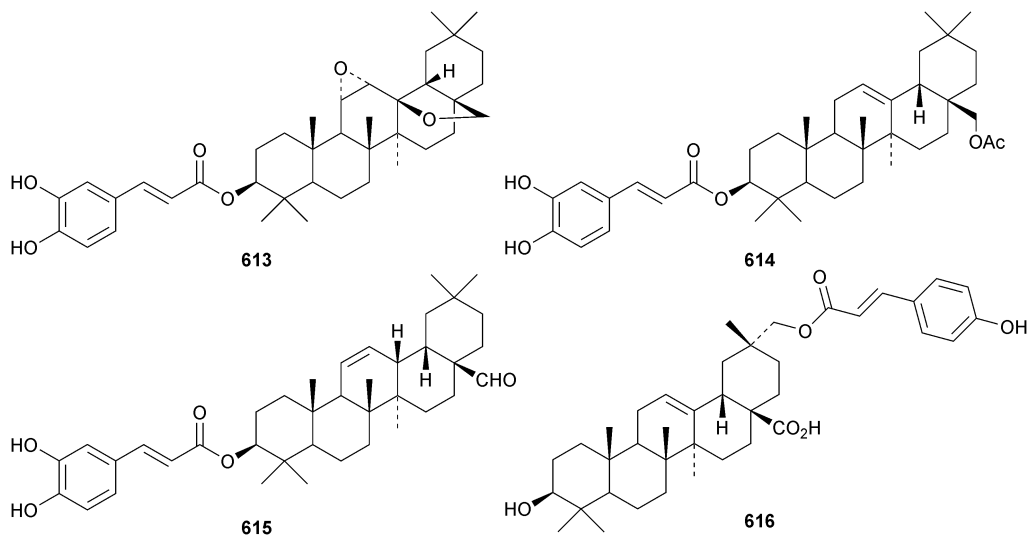












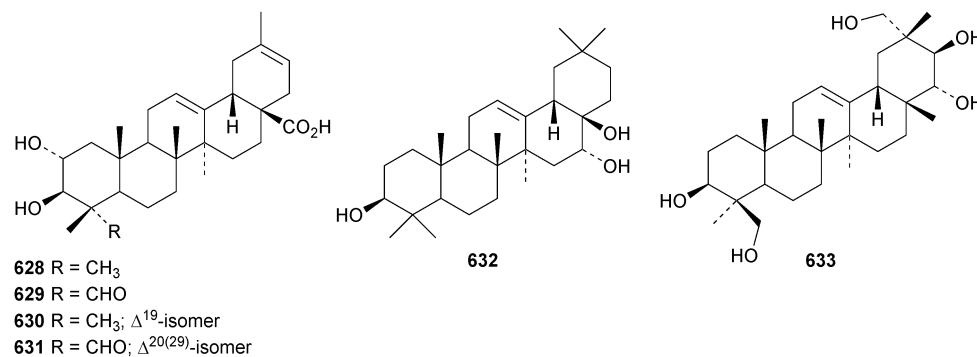


Table 1

Trivial name	Plant species	Ref.
Aesculosides G1–G16	<i>Aesculus glabra</i>	226
Afrocyclamins A and B	<i>Cyclamen africanum</i>	227
Anemonerivulariside A	<i>Anemone rivularis</i>	228
Asperosaponins A–C	<i>Dipsacus Asper</i>	229
Besylvosides I–VI	<i>Aegilops geniculata</i>	230
Bigeloviis A and B	<i>Salicornia bigelovii</i>	231
Bodiniosides C and D	<i>Elsholtzia bodinieri</i>	232
Bonarienosides A–E	<i>Hydrocotyle bonariensis</i>	233
Bunkankasaponin F	<i>Xanthoceras sorbifolia</i>	234
Centelloside D	<i>Centella asiatica</i>	235
Chakasaponin IV	<i>Camellia sinensis</i>	236
Dumortierinoside A methyl ester	<i>Isolatocereus dumortieri</i>	237
Elmalienosides A–C	<i>Cephalaria elmaliensis</i>	238
Entadosides A–D	<i>Entada phaseoloides</i>	239
Gardenisides A–C	<i>Gardenia jasminoides</i>	240
Guaianin P	<i>Guaiacum officinale</i>	241
Gummoside A, gummoside A methyl ester	<i>Stenocereus alamosensis</i>	237
Hareftoside E	<i>Astragalus hareftae</i>	78
Hederifoliosides A–E	<i>Cyclamen hederifolium</i>	242
Ilexsaponins D–F	<i>Ilex pubescens</i>	243
Ilexsaponin D (duplicate name)	<i>Ilex pubescens</i>	244
Kalopanaxsaponins L and M	<i>Kalopanax pictus</i>	245
Lobatosides L and M	<i>Actinostemma lobatum</i>	246
Lonicacanthoides IV and V	<i>Lonicera macranthoides</i>	247
Mimengosides H and I	<i>Buddleja lindleyana</i>	248
Oleiferasaponin A ₁	<i>Camellia oleifera</i>	249
Paviosides A–H	<i>Aesculus pavia</i>	250
Pleurosaponins A–K	<i>Pleurospermum kamschaticum</i>	251
Polygalasaponins LI–LIII	<i>Polygala japonica</i>	252
Raddeanosides R ₂₀ –R ₂₂	<i>Anemone raddeana</i>	253
Sanchakasaponins A–D	<i>Camellia japonica</i>	254
Sanchakasaponins E–H	<i>Camellia japonica</i>	255
Sandrosaponin XI	<i>Ferula hermonis</i>	256
Seneciapittosides A and B	<i>Pittosporum senacia</i>	257
Silenoviscoside F	<i>Silene viscidula</i>	258
Sorbifoliasides A–F	<i>Xanthoceras sorbifolia</i>	234
Teaseedsaponins A–L	<i>Camellia sinensis</i>	259
Treleaseside A	<i>Stenocereus eruca</i>	180

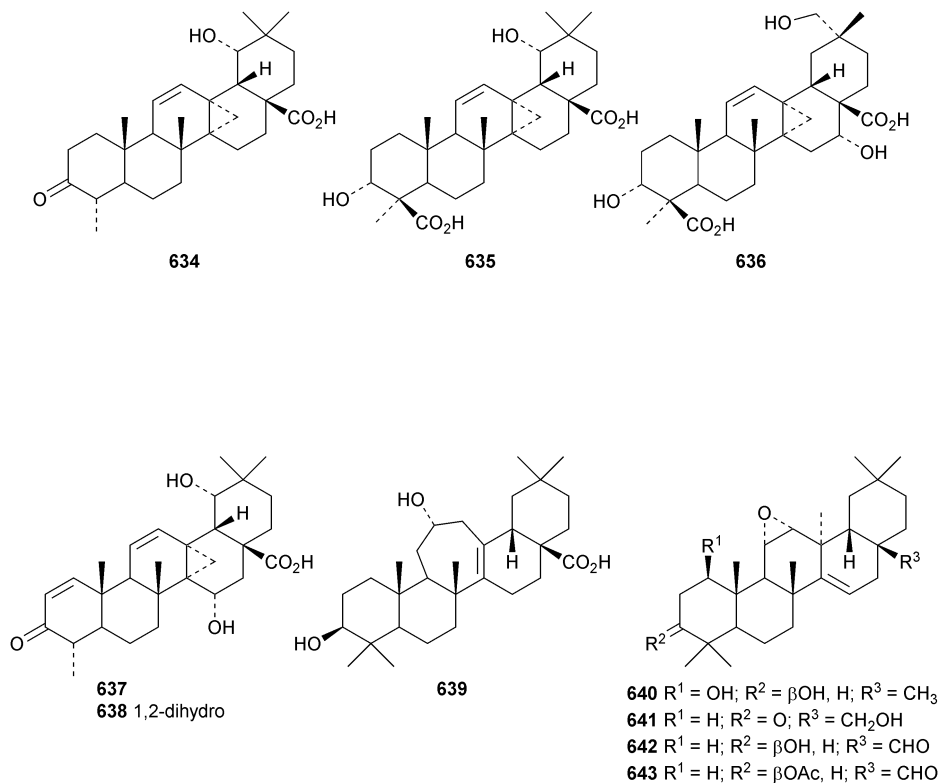
The sources of new oleanane saponins with known genins that have not been assigned trivial names are listed in Table 2.

Pachanosides I1 and D1 are pachanane saponins with known genins from *Isolatocereus dumortieri*.²³⁷ The structures of the 13,27-cyclized oleananes donellanic acids A **634**, B **635** and C **636**, from *Donella ubanguiensis*, were all established by X-ray analyses.²⁹¹ The donellanic acids are accompanied by two

Table 2

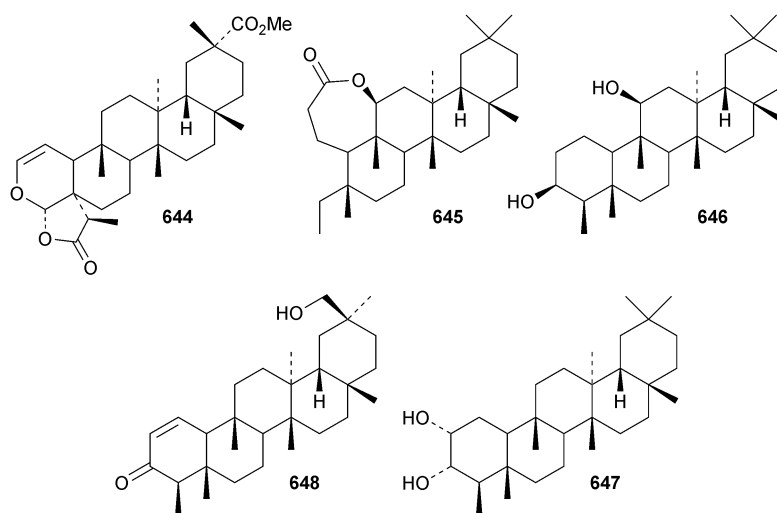
Plant species	Ref.
<i>Abrus precatorius</i>	260
<i>Abuta grandifolia</i>	261
<i>Acanthopanax senticosus</i>	262
<i>Acanthophyllum gypsophiloides</i>	263
<i>Alhagi maurorum</i>	264
<i>Anemone amurensis</i>	265
<i>Aralia elata</i>	266
<i>Aralia taibaiensis</i>	267
<i>Ardisia gigantifolia</i>	268
<i>Callicarpa integerrima</i>	269
<i>Chenopodium foliosum</i>	270
<i>Clematis argenticulida</i>	271 and 272
<i>Cyperus rotundus</i>	273
<i>Dizygotheca elegantissima</i>	274
<i>Eragrostis tef</i>	275
<i>Grangea maderaspatana</i>	276
<i>Gymnema sylvestre</i>	277
<i>Gymnocladus chinensis</i>	278
<i>Gypsophila trichotoma</i>	279
<i>Kalopanax pictus</i>	245
<i>Kalopanax septemlobus</i>	280
<i>Maesa lanceolata</i>	281
<i>Patrinia scabiosifolia</i>	282
<i>Pometia pinnata</i>	283
<i>Salicornia europaea</i>	284
<i>Salicornia herbacea</i>	285
<i>Samanea saman</i>	286
<i>Sideroxylon obtusifolium</i>	287
<i>Tarenna grevei</i>	288
<i>Wedelia chinensis</i>	289
<i>Xanthoceras sorbifolia</i>	290

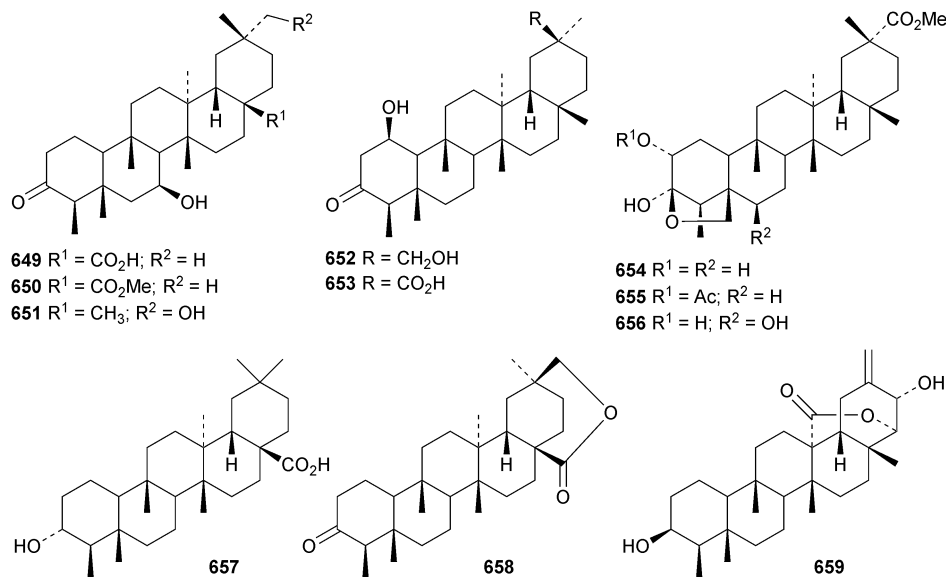




further 13,17-cyclized compounds that have been assigned the tentative structures **637** and **638**. Ilelic acid B **639** is a rearranged oleanane with a seven-membered C-ring from *Ilex latifolia*.²⁹² Four taraxerane derivatives **640–643** have been identified in *Saussurea graminea*.²⁹³

Cassinolide **644**, from *Cassine xylocarpa*, is a 2,3-secofriedelan-3,24-olide derivative.²⁹⁴ *Maytenus robusta* is the source of the 3,4-secofriedelan-3,11β-olide **645** (ref. 295) and friedelane-3β,11β-diol **646**.²⁹⁶ Reissantadiol, from *Reisantia grahamii*, has been identified as friedelane-2α,3α-diol **647**.²⁹⁷

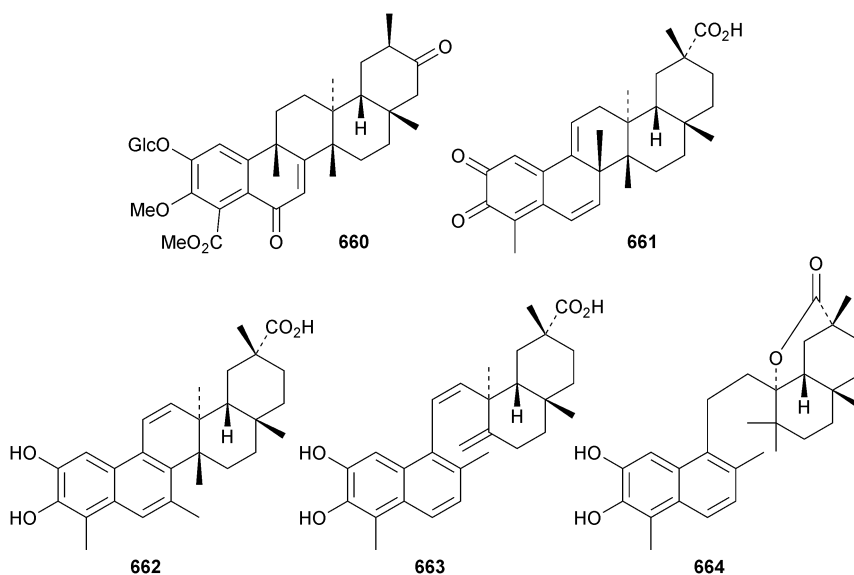


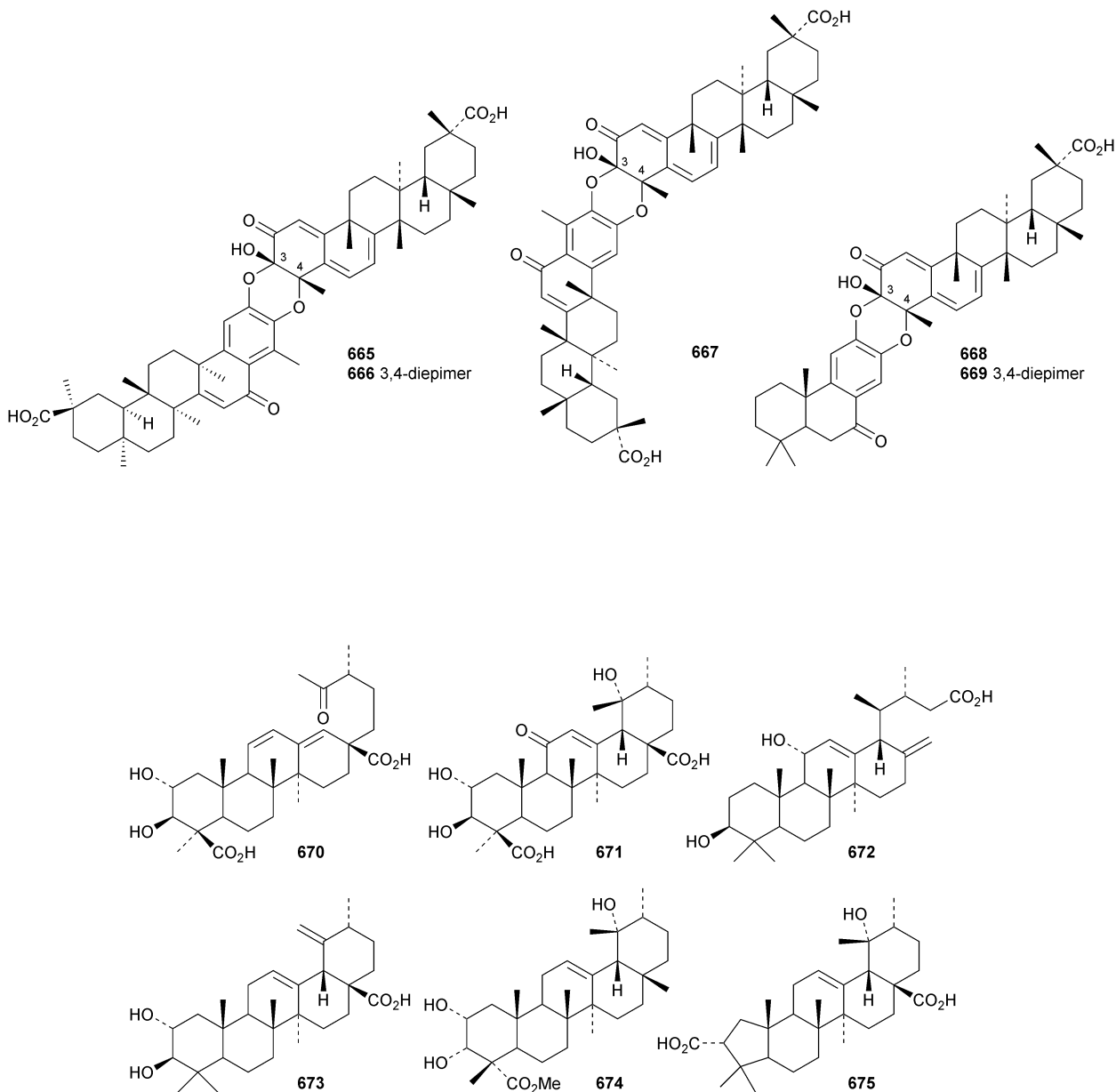


Other simple friedelane triterpenoids include 30-hydroxyfriedel-1-en-3-one **648** from *Salacia hainanensis*,¹²⁴ **649–653** from *Celastrus vulcanicola* and **654–658** from *Maytenus jelskii*²⁹⁸ and glaucalactone **659** from *Caloncoba glauca*.⁶¹

A review of the pharmacology of celastrol, a norfriedelane derivative, has been published.²⁹⁹ Hypoglaside A **660** is a dinorfriedelane glucoside from *Tryperygium hypoglaucum*.³⁰⁰ *Celastrus orbiculatus* is the source of a range of norfriedelane and methyl-migrated derivatives.³⁰¹ The 25(9 → 8)-*abeo*

norfriedelane **661** and the 25(9 → 7)-*abeo* derivative **662** are accompanied by the 8,14-*seco* compounds **663** and **664**. A biosynthetic pathway to these rearranged friedelane derivatives has been proposed. Also present in *Celastrus orbiculatus* are the “dimeric” norfriedelanes celastrolines A α **665** and A β **666** and isocelastrolines A α **667**, together with celastrolines B α **668** and B β **669** that have a linkage to a podocarpane derivative.





7. The ursane group

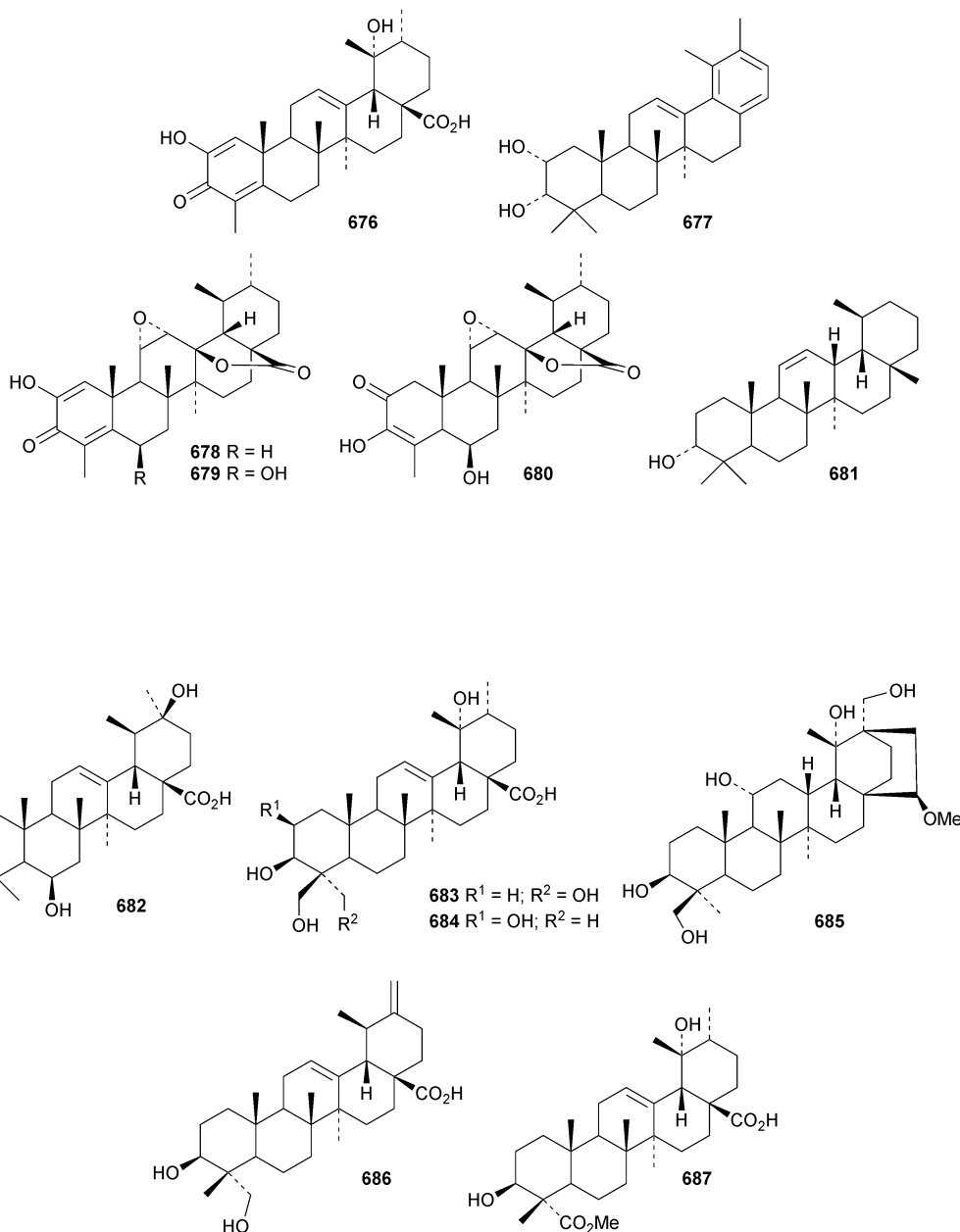
Ursane triterpenoids have shown potential as anticancer drugs.³⁰² Reviews on the anticancer activities of ursolic acid³⁰³ and acetyl-11-keto- β -boswellic acid (AKBA)³⁰⁴ have been published.

The 18,19-secoursane derivative **670** has been isolated from the bark of *Diospyros decandra* together with **671**.¹⁹⁵ The 17,22-*seco* derivative **672** has been found in both *Salvia palaestina* and *Salvia syriaca*.³⁰⁵ Euscaphic acids J **673**, K **674** and L **675** have been isolated from *Euscaphis japonica*.¹⁹⁷ Euscaphic acid L **675** has a contracted ring-A. Negundonorins A **676** and B **677**, from

Vitex negundo, are 24-nor and 28-noruranes, respectively.³⁰⁶ Further 24-norursanes include ulmoidol A **678** from *Eucommia ulmoides*³⁰⁷ and the related compounds **679** and **680** from *Dipsacus chinensis*.³⁰⁸ 30-Norurs-11-en-3 α -ol **681** has been identified in the roots of *Alhagi camelorum*.³⁰⁹

6 β ,20 β -Dihydroxyurs-12-en-28-oic acid **682**, from leaves of *Psidium guajava*, is unusual as it lacks oxygenation at C-3.³¹⁰ The structure of 3 β ,19 α ,23,24-tetrahydroxyurs-12-en-28-oic acid **683**, from *Nauclea officinalis*, was confirmed by X-ray analysis.³¹¹ It is accompanied by the corresponding 2 β ,3 β ,19 α ,24-tetrahydroxy compound **684**. Further simple ursane derivatives include the acetal **685** from *Juglans sinensis*,²⁰⁴ rhododendric acid A **686**



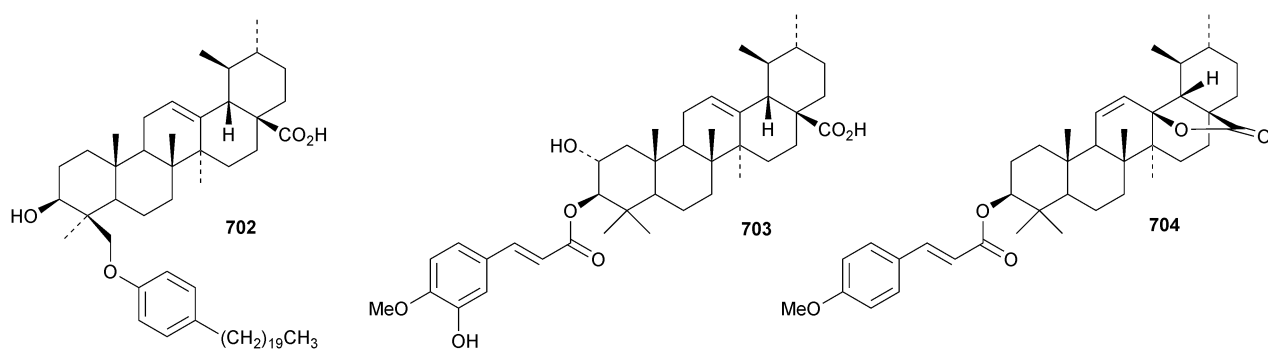
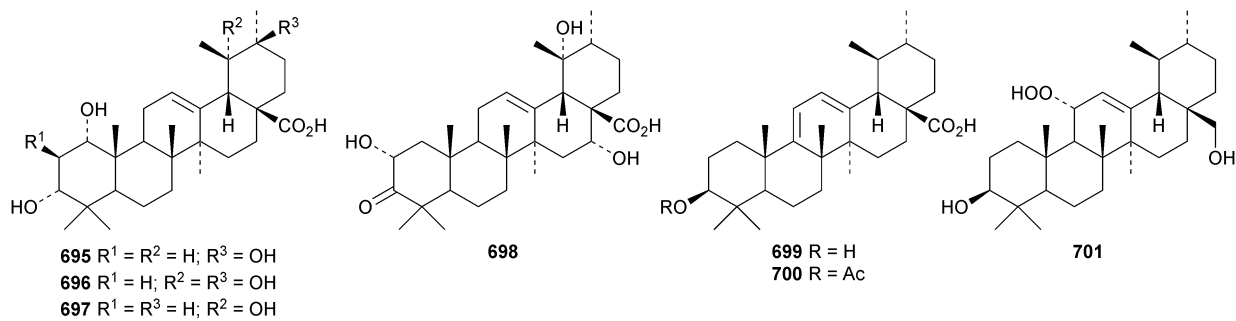
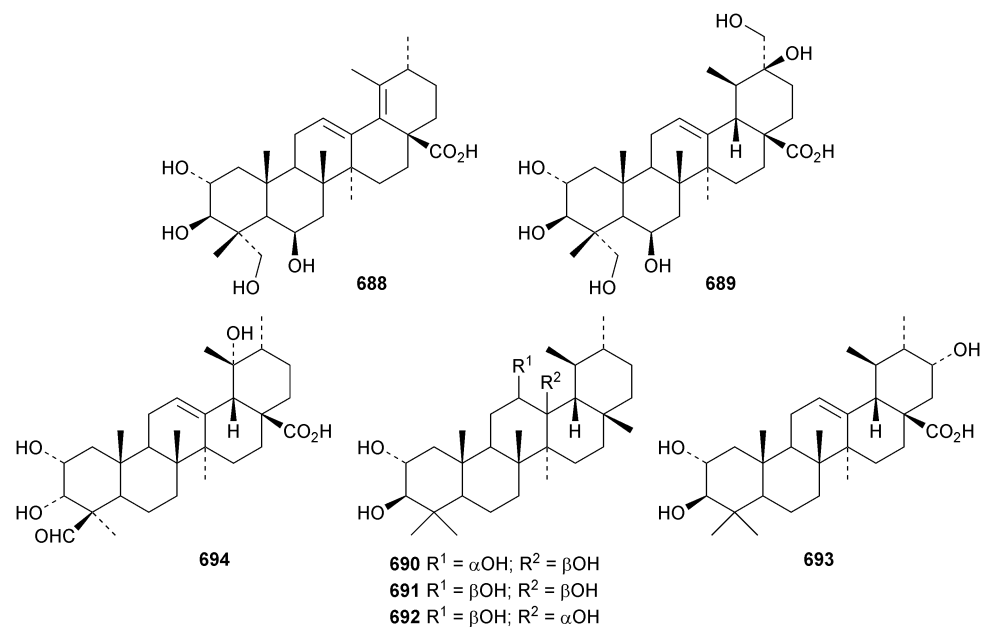


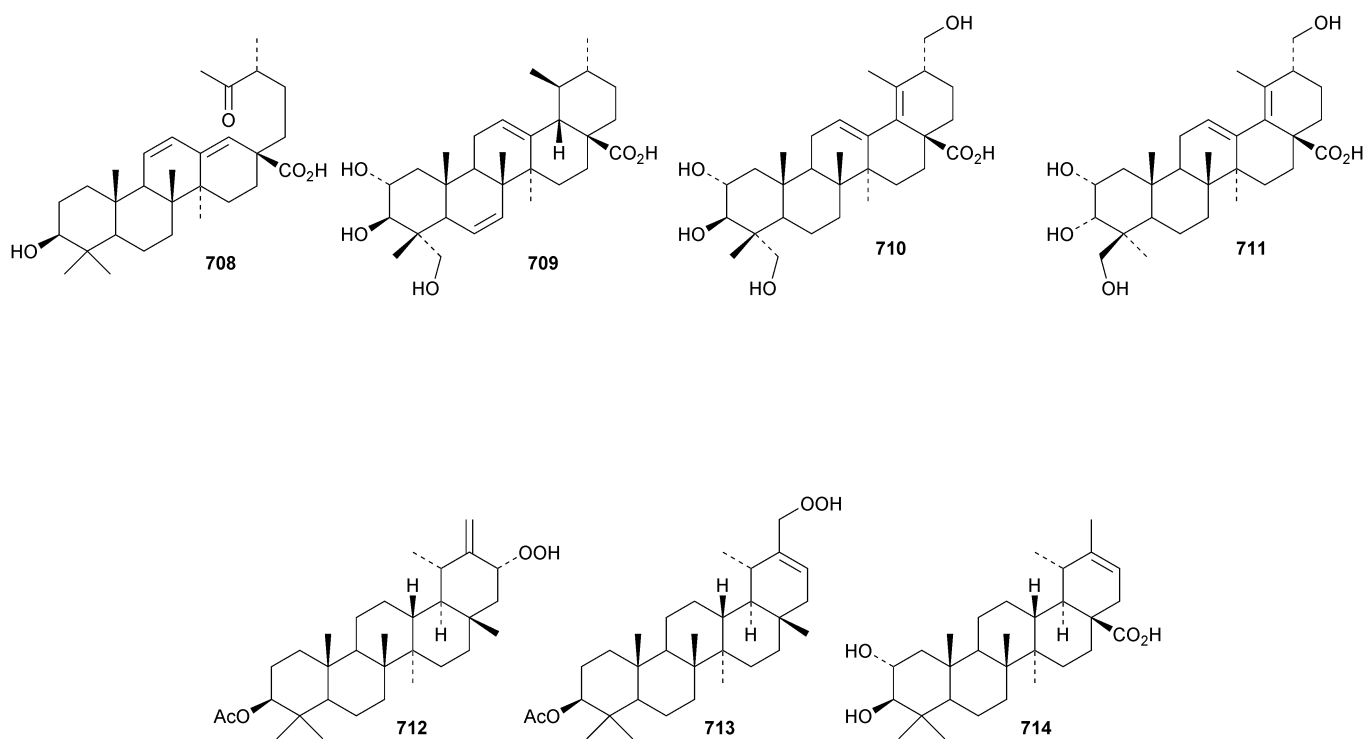
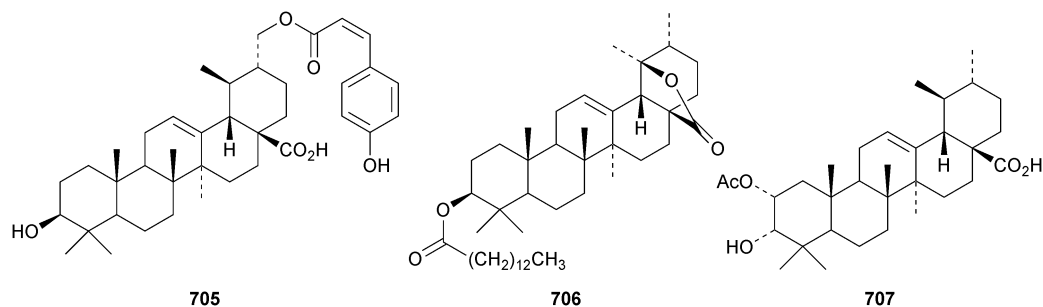
from *Rhododendron brachycarpum*,³¹² uncariursanic acid **687** from *Uncaria macrophylla*,³¹³ 2 α ,3 β ,6 β ,23-tetrahydroxyursa-12,18-dien-28-oic acid **688** from *Kadsura marmorata*,³¹⁴ 2 α ,3 β ,6 β ,20 β ,23,30-hexahydroxyurs-12-en-28-oic acid **689** and psiguanins B **690**, C **691** and D **692** from *Psidium guajava*,³¹⁵ the 2 α ,3 β ,21 α -trihydroxy derivative **693** and the 24-aldehyde **694** from *Berberis koreana*,³¹⁶ the 1 α ,3 α -dihydroxy derivatives **695**–**697** from *Euphorbia kansuensis*,³¹⁷ the 3-ketone **698** from *Albizzia lebbeck*,³¹⁸ loxanic acid **699** and its acetate **700** from *Eucalyptus loxophleba*³¹⁹ and tolpidiol B **701** from *Tolpis proustii* and *Tolpis lagopoda*.³²⁰

Kirmanoic acid **702**, from *Nepeta clarkei*, is an unusual alkylphenyl ether.¹⁸⁵ New ursane esters include the isoferuloyl ester **703** from *Eucalyptus exserta*,²⁰⁵ ehretiolide **704** from *Ehretia longifolia*,³²¹ the 30-*cis*-coumaryl ester **705** from *Rubia schumanniana*,²¹⁶ 3 β -tetradecanoyloxyurs-12-en-28,19 β -olide **706** from *Lysimachia clethroides*,³²² and 3-*epi*-cecropic acid **707** from *Dipterocarpus obtusifolius*.¹⁰⁶

Sanguiside A is an ursane saponin from *Sanguisorba officinalis* with the new 18,19-*seco*-ursane genin **708**.³²³ Centelloside E from *Centella asiatica* has the new genin **709** (ref. 235) and the genins **710** and **711** are present in saponins from *Actinidia valvata*.³²⁴







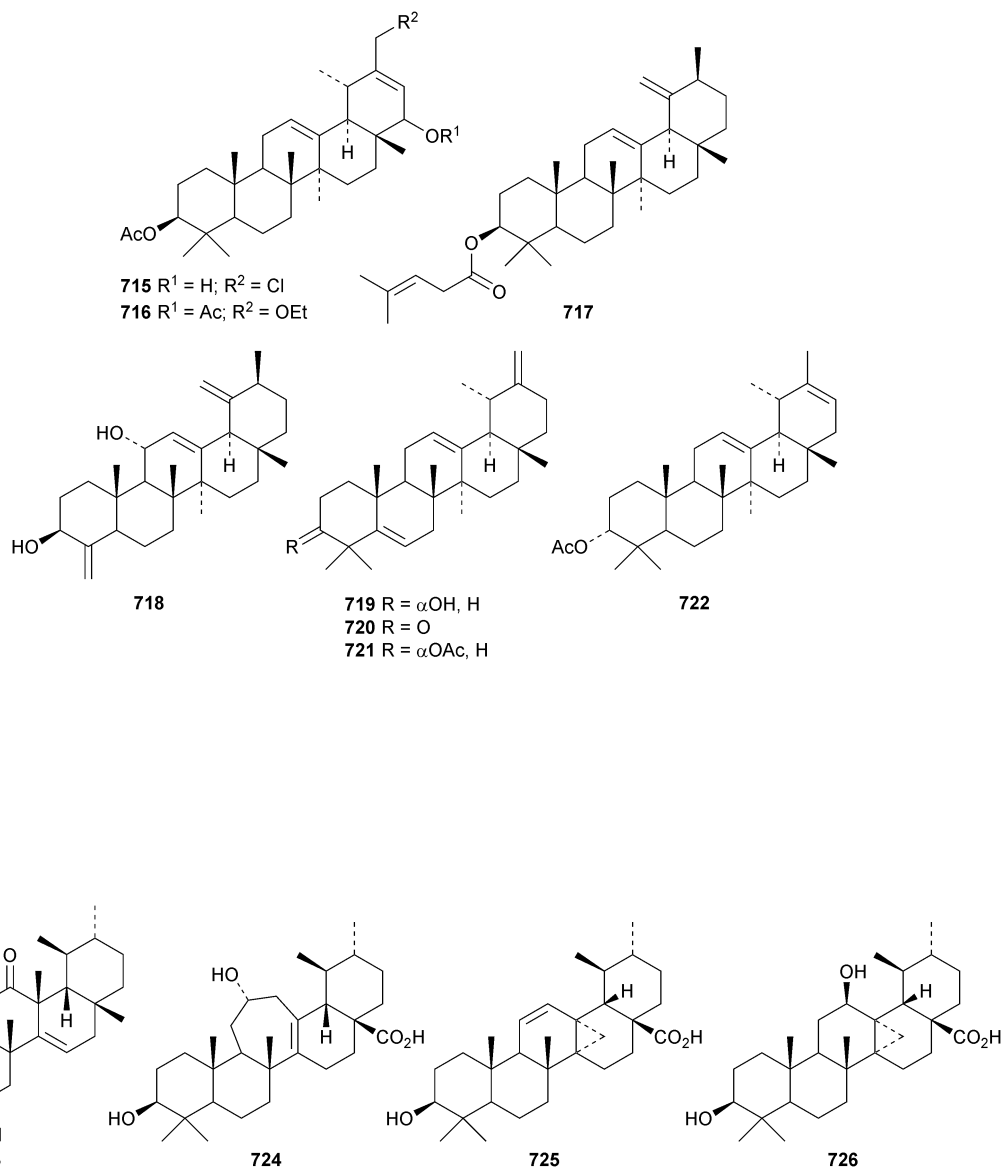
Ursane saponins with known genins include asphorins A and B from *Asphodelus tenuifolius*,³²⁵ asprellanosides A and B from *Ilex asprella*,³²⁶ elasticoside from *Ficus elastica*,³²⁷ ilekudinichosides F and G from *Ilex kudincha*,³²⁸ ilemaminosides A and B from *Ilex mamillata*,³²⁹ ilexasosides A–H from *Ilex asprella*,³³⁰ phylliside A from *Stenocereus eruca*,¹⁸⁰ and unnamed saponins from *Diospyros decandra*,¹⁹⁵ *Juglans sinensis*,²⁰⁴ *Lantana camara*³³¹ and *Psidium guajava*.³³²

The taraxastane hydroperoxide derivatives 712 and 713 have been isolated from the roots of *Taraxacum platycarpum*.¹⁷³ Psi-guanin A, which is 2 α ,3 β -dihydroxytaraxast-20-en-28-oic acid

714, has been found in the leaves of *Psidium guajava*.³¹⁵ Other new taraxastane derivatives include chlorotolpidiol 715 and tolpidiol A 716 from *Tolpis proustii* and *Tolpis lagopoda*,³²⁰ per-gularines A 717 and B 718 from *Pergularia tomentosa*³³³ and calotropoceryl A 719, calotropocerylone A 720 and calotropoceryl acetates A 721 and B 722 from *Calotropis procera*.³³⁴ Two taraxastane saponins with known genins have been found in the roots of *Ilex pubescens*.³³⁵

The 27(14 \rightarrow 13)-abeo-urs-14-enone derivative 723, from *Rubia schumanniana*, has the unusual β -configuration for the migrated methyl.²¹⁶ The rearranged ursanes ilelic acids A 724, C





725 and D 726 have been isolated from *Ilex latifolia*.²⁹² The structure of ilelic acid D 726 was confirmed by X-ray analysis.

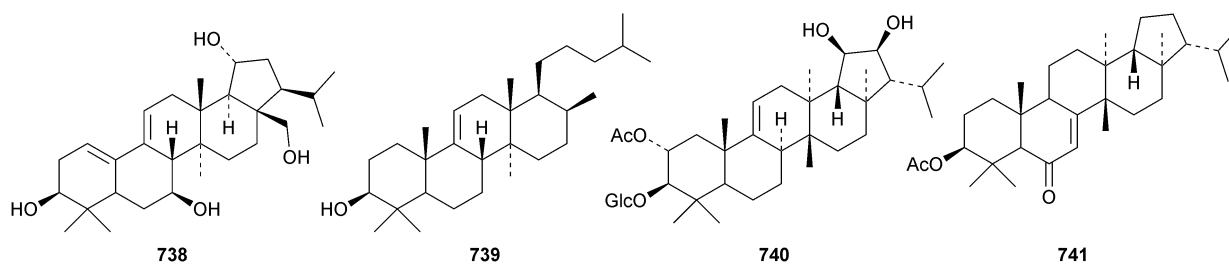
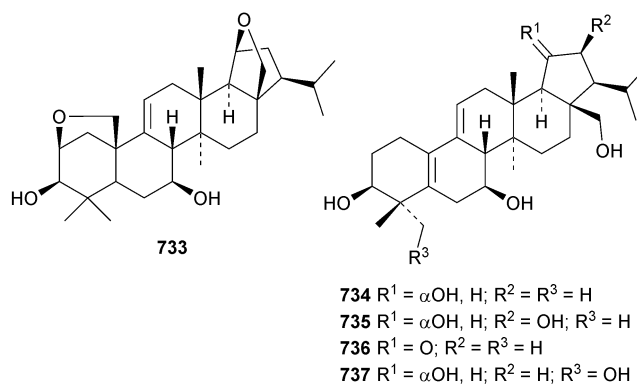
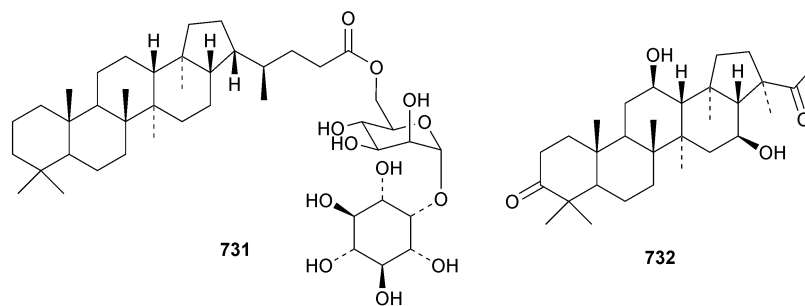
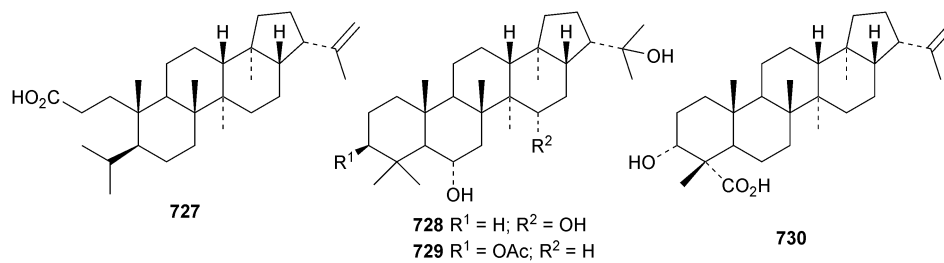
8. The hopane group

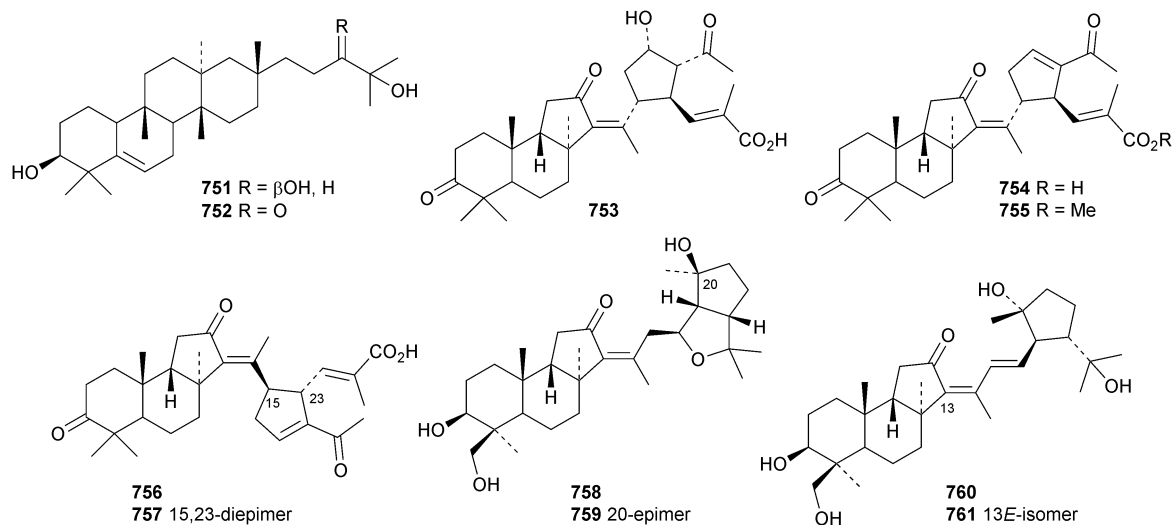
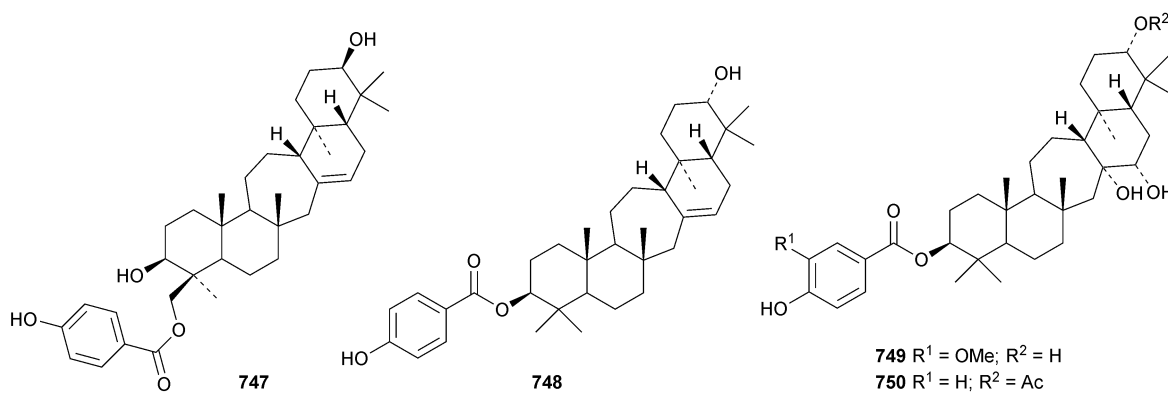
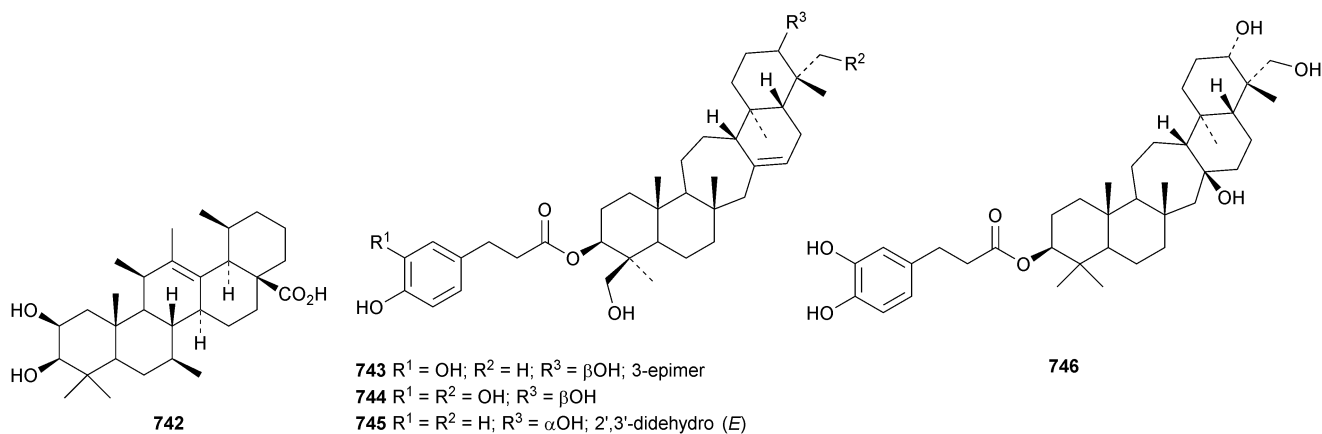
3,4-Secohop-22(29)-en-3-oic acid 727 has been isolated from *Maytenus robusta*.²⁹⁵ The scale insect pathogenic fungus *Aschersonia calendulina* is the source of two hopane metabolites 728 and 729.³³⁶ The leaves of *Hybanthus austro-caledonicus* produce 3-epiwoodwardinic acid 730.³³⁷ Plakohopanoic acid 731, a C₃₂ hopanoic acid, has been isolated from the sponge *Plakortia cf. lita*.³³⁸ The structure of plakohopanoic acid 731 implies that it is of bacterial origin. This is the first example of a biologically produced C₃₂ hopanoic acid. Such

acids were considered to only be geohopanoic acids formed by abiotic degradation of bacteriohopanoic acids. Oppositifolone 732, from *Glinus oppositifolius*, has a 29(22 → 21)-abeo-hopane skeleton and is the 3-ketone of spergulagenin A.³³⁹

Pteroxygonumol 733, from the roots of *Pteroxygonum giraldii*, has been identified as 2 β ,25:19 β ,28-diepoxyarborin-9(11)-ene-3 β ,7 β -diol.³⁴⁰ Five 25-norarborinane derivatives 734–738 have been isolated from bamboo stems, *Sinocalamus affinis*.¹⁸⁷ The structure of 734 was confirmed by X-ray analysis. *Atalantia retusa* is the source of the 17,21-*seco*-arborane derivative retusinol 739.³⁴¹ Peniciside 740 is a fernane metabolite of *Penicillium* sp.¹⁶⁹³⁴² and 3 β -acetoxyfern-7-en-6-one 741 is a constituent of *Scorzonera latifolia*.³⁴³







9. Miscellaneous compounds

The unlikely structure **742** has been proposed for erucaic acid from *Sonchus eruca*.³⁴⁴ The club moss *Lycopodium phlegmaria* is the source of the serratane esters lycophlegmariols A **743**–**D 746** (ref. 345) and four esters **747**–**750** have been found in *Palhinhaea cernua* (syn. *Lycopodium cernuum*).³⁴⁶ The D:B-friedobaccharane derivatives leonatriol **751** and the corresponding ketone leonatriolone **752** have been isolated from *Cassine xylocarpa* and *Celastrus vulcanicola*, respectively.²⁹⁴ Globostellets J **753**–**S 761**, from the marine sponge *Rhabdastrella globostellata*, are isomalabaricanes with cyclopentane side chains.³⁴⁷

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