



Triterpenoids

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This review covers the isolation and structure determination of triterpenoids reported during 2014 including squalene derivatives, lanostanes, holostanes, cycloartanes, cucurbitanes, dammaranes, euphanes, tirucallanes, tetranortriterpenoids, quassinoids, lupanes, oleananes, friedelanes, ursanes, hopanes, serratanes, isomalabaricanes and saponins; 374 references are cited.

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1. Introduction

The interest in the pharmacological activities of triterpenoids continues to be very important.¹ Several reviews have covered the anticancer effects of triterpenoids.^{2–9} Other activities that have been highlighted include anti-HIV,^{10–12} antiinflammatory,¹³ antiviral⁶ and against neurodegenerative disorders.¹⁴ As many of the active compounds are saponins there has been an interest in their synthesis¹⁵ and biosynthesis.¹⁶ Reviews have also appeared covering triterpenoids found in *Astragalus* species,¹⁷ *Gymnema sylvestre*,¹⁸ *Panax* species,^{19,20} *Sapindus* species²¹ and *Siraitia grosvenorii*²² and plants of the Schisandraceae.^{23–25} Triterpenoid biosynthesis in plants²⁶ and the mechanisms of oxidosqualene cyclases²⁷ have also been covered.

2. The squalene group

Two interesting series of polyisoprenoid derivatives, terreolides A 1–F 6 and saponaceolides H 7–P 15, have been reported from

the previously unknown poisonous European mushroom *Tricholoma terreum*.²⁸ The known saponaceolide B 16 was also obtained. The structures of terreolides A 1 and D 4 and saponaceolide B 16 were confirmed by X-ray crystallographic analyses. A complex polyisoprenoid glycoside, from the fruit of *Lycium chinense*, has been assigned the putative structure 17.²⁹

3. The lanostane group

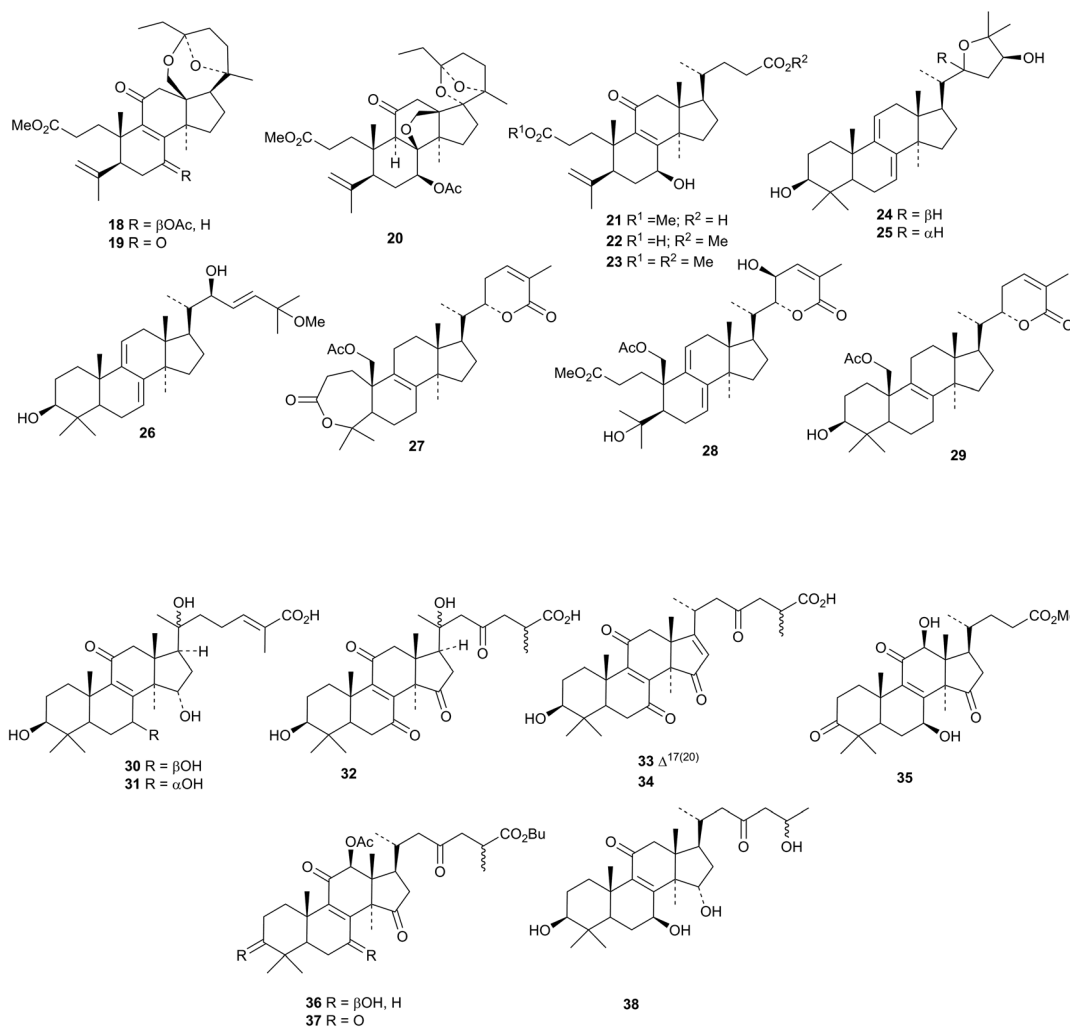
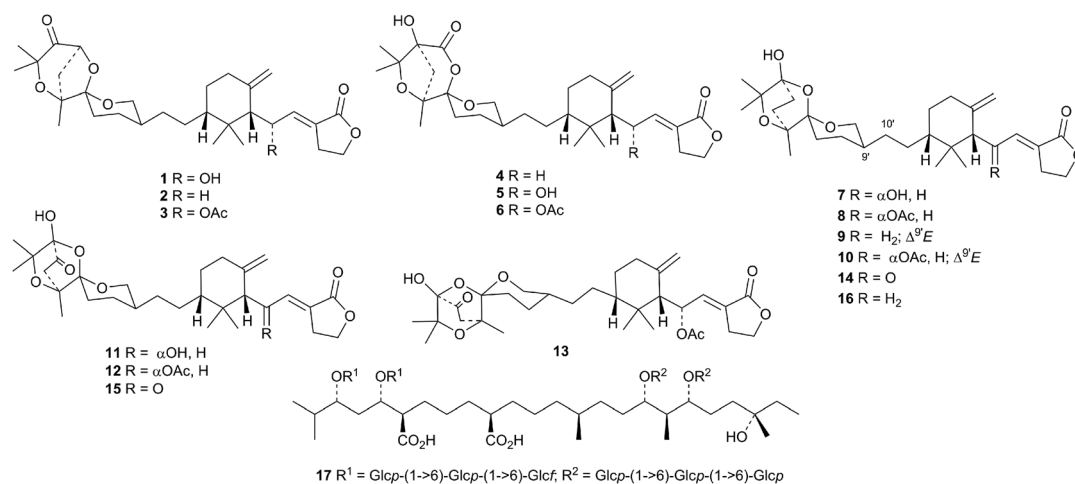
The flow of *Ganoderma* lanostanes continues.³⁰ *Ganoderma boninense* is the source of ganoboninketals A 18, B 19 and C 20.³¹ Fornicatin D 21, E 22 and F 23 and ganodercochlearins A 24, B 25 and C 26 are constituents of *Ganoderma cochlear*.³² The structure of ganodercochlearin B 25 was confirmed by X-ray analysis of the corresponding diacetate. Cultures of *Ganoderma* sp. KM01 produced ganodermalactones B 27, D 28 and E 29.³³ The structure of ganodermalactone B 27 was confirmed by X-ray analysis and was shown to have the same structure as the previously reported colossolactone C, from *Ganoderma colossum*,³⁴ however the pmr and cmr spectra for rings A and B are not in agreement.

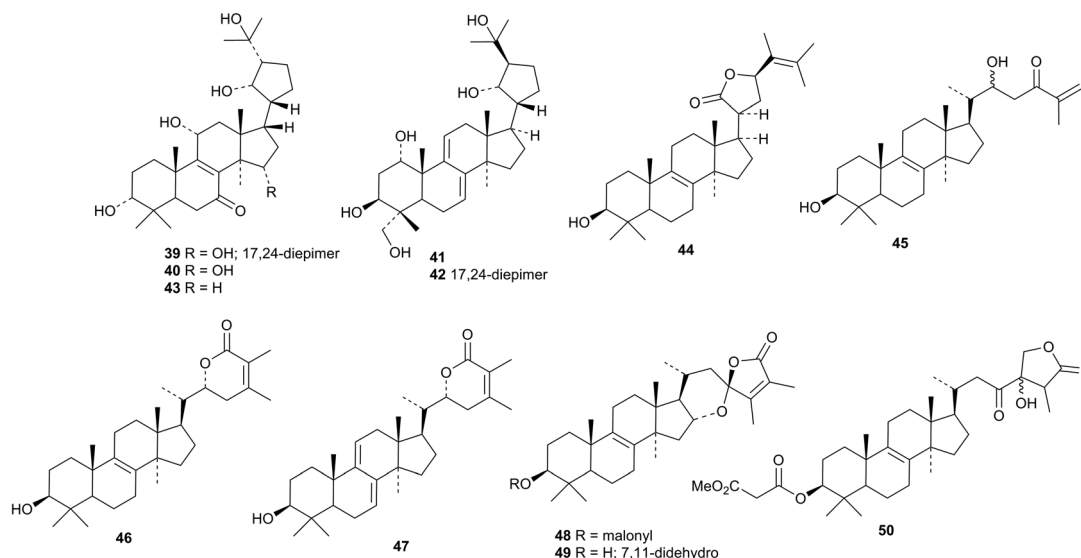
Other *Ganoderma* lanostanes include ganoderic acids XL₁ 30 and XL₂ 31, 20-hydroxyganoderic acid AM₁ 32, ganoderenic acid AM₁ 33 and ganoderesin C 34 from *Ganoderma theaeccolum*,³⁵ methyl lucidenate B 35 (ref. 36) and the butyl esters 36 and 37 (ref. 37) from the fruiting bodies of *Ganoderma lucidum* and the norlanostane 38 from the fruiting bodies of *Ganoderma tropicum*.³⁸ The biological and pharmacological activities of ganoderic acid and lucidenic acid have been covered in a review.³⁹

The mushroom *Inonotus obliquus* is a rich source of the 21,24-cyclolanostanes inonotusols A 39–E 43.⁴⁰ They are accompanied by inonotusols F 44 and G 45. Inonotusols B 40, D 42 and E 43 have unusual configurations at C17 and inonotusol F 44 has an unusual configuration at C20 and methylation at C24. Further C24-methylated metabolites of *Inonotus obliquus* include inotolactones A 46 and B 47.⁴¹ Hexatenuins A 48, B 49

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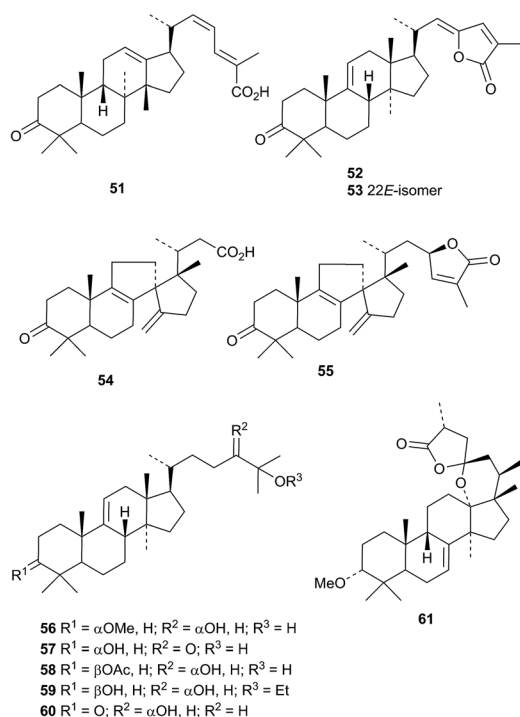






and C 50, from the fruiting body of *Hexagonia tenuis*, also have an extra carbon at C-24.⁴²

The protostane 51, from the bark of *Garcinia ferrea*, is accompanied by the lanostanes garciferolides A 52 and B 53.⁴³ Two rearranged lanostanes 54 and 55 have been isolated from *Abies nukiangensis* together with compounds 56–59.⁴⁴ The structures of 54 and the known 60 were confirmed by X-ray analyses. 3-*O*-Methylabiesatrine A 61 is a rearranged lanostane from *Abies delavayi*.⁴⁵



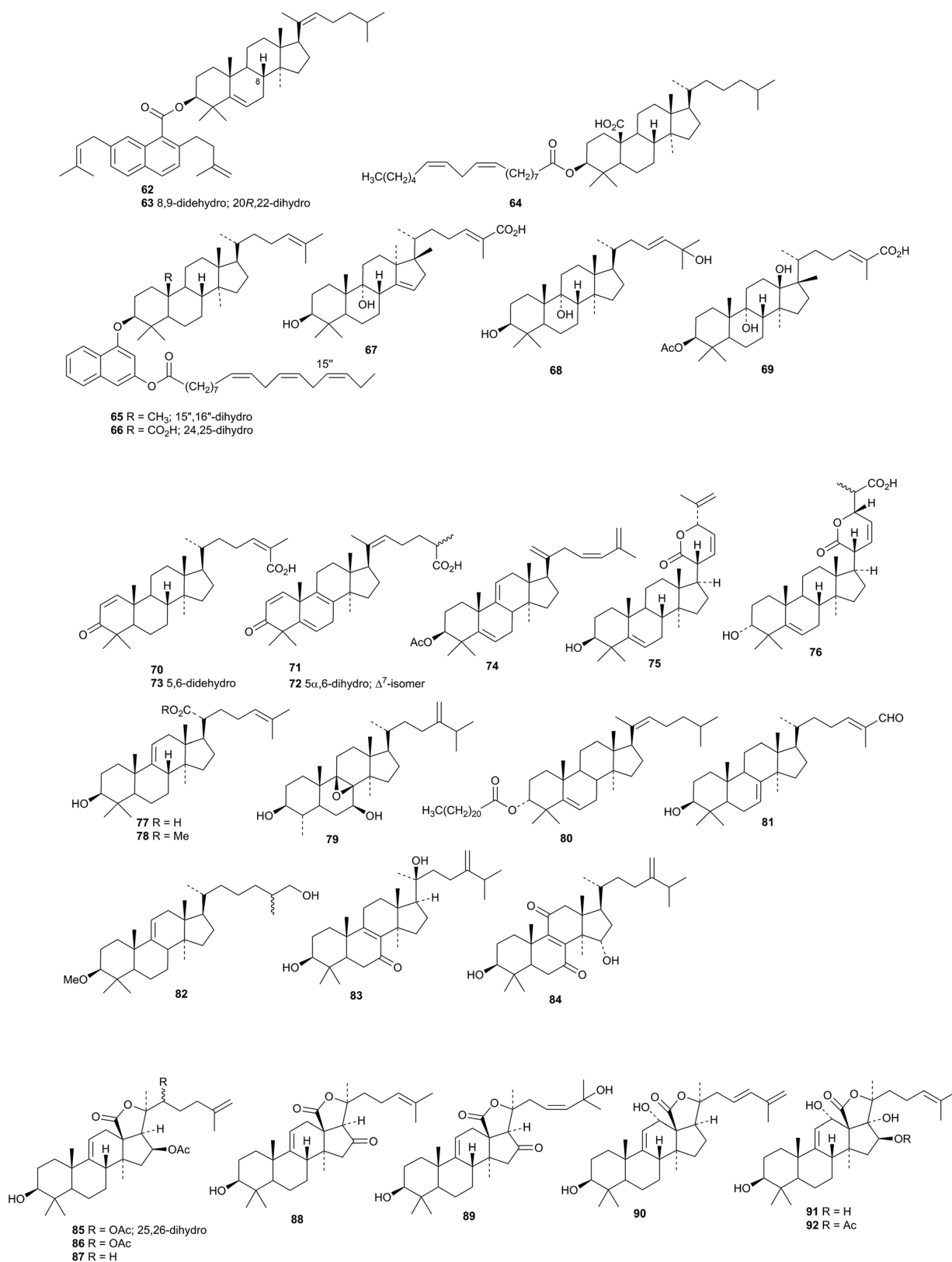
Two naphthalene esters, lanostenyl naphthoates A 62 and B 63 have been reported from the rhizomes of *Acorus calamus*.⁴⁶ The related compounds 64–66 are found in the bark of *Ficus religiosa*.⁴⁷ The mariesane derivative opaciniol B 67 and the lanostane opaciniol C 68 are constituents of *Garcinia opaca*.⁴⁸ Opaciniol B 67 is the same as garchihomebronane K isolated from *Garcinia homebroniana* in 2013.⁴⁹ The rearranged lanostane 69 has been isolated from *Garcinia homebroniana*.⁵⁰

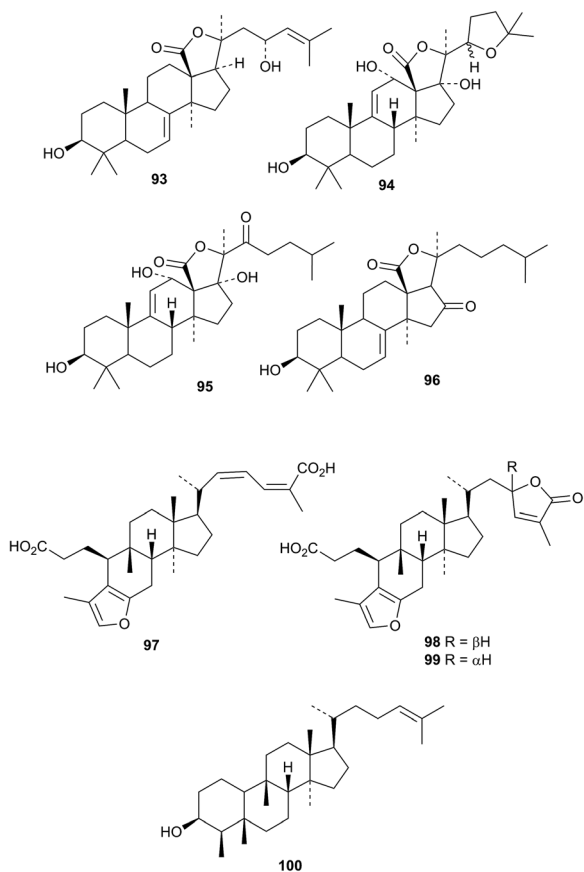
Other lanostanes include manglanostenic acids A 70–D 73 from *Mangifera indica* var. Fazli,⁵¹ myrrhalanostenyl acetate 74, myrrhalanostenol 75, and myrrhalanostenic acid 76 from the oleoresin of *Commiphora myrrha*,⁵² 3β-hydroxylanosta-9(11),24-dien-21-oic acid 77 and its methyl ester 78 from *Protorus longifolia*,^{53,54} the norlanostane 79 from *Euphorbia bupleuroides*,⁵⁵ the ester 80 from the fruit of *Cuminum cyminum*,⁵⁶ kiusianin A 81 from *Tilia kiusiana*⁵⁷ and methyl ether 82 from *Cymbopogon citratus*.⁵⁸ Compounds 83 and 84, from the branches and leaves of *Polyalthia obliquei*, were originally thought to be tirucallane derivatives but are now considered to be lanostanes.^{59,60} Lanostane saponins with known genins have been isolated from *Cuminum cyminum*⁵⁶ and *Panax ginseng*.^{61,62}

Investigations of several sea cucumbers have resulted in the identification of more holostane saponins, some with interesting pharmacological activities.^{63,64} Cladolosides A₁–A₆, from Vietnamese *Cladolabes schmeltzii*, have the new genins 85–89.⁶⁵ Coustesides A–J are new saponins from *Bohadschia cousteaui*.⁶⁶ Coustesides B and G have the new genin 90 and C and D the new genins 91 and 92, respectively. All the others have known genins.

Variagatusides C–F have been isolated from *Stichopus variegates*.⁶⁷ Only variagatuside C has a new genin 93. Holothurins D and E, with the new genin 94 and holothurinoside X, with the new genin 95, are constituents of *Holothuria lessoni* together







with holothurinosides Y and Z with known genins.⁶⁸ The new genin **96** has been reported for pseudocnoside A from *Pseudocnus dubiosus leoninus*.⁶⁹ Holostane saponins with known genins include cucumariosides F₁ and F₂ from *Eupentacta*

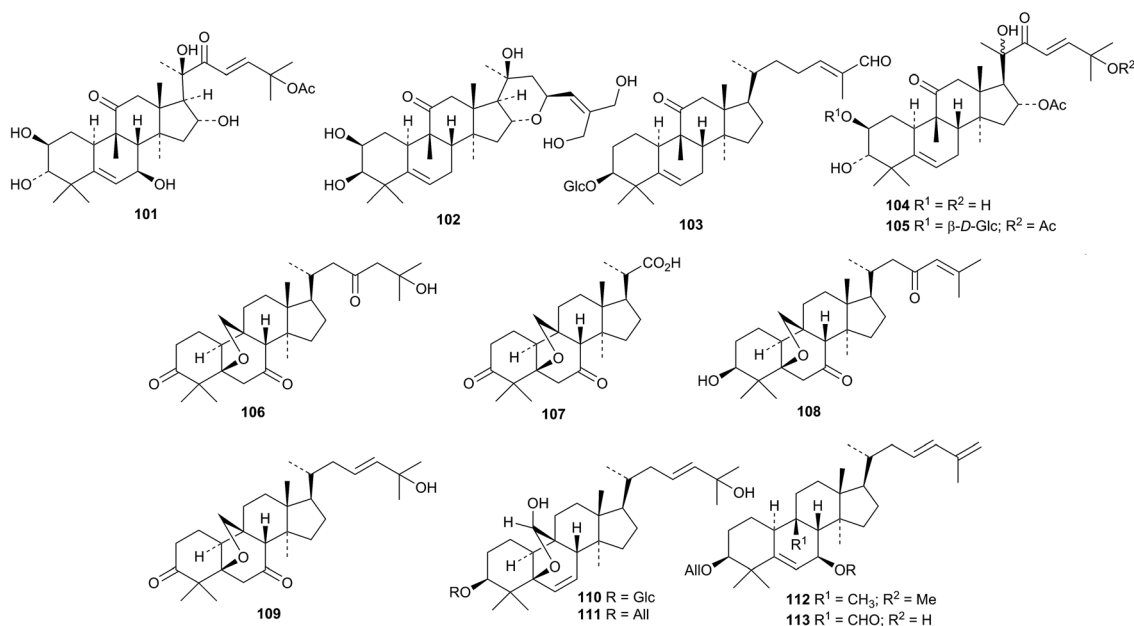
fraudatrix,⁷⁰ kolgaosides A and B from *Kolga hyalina*,⁷¹ stichloroside F from *Stichopus chloronotus*⁷² and violaceosides C, D, E and G from *Pseudocolochirus violaceus*.⁷³

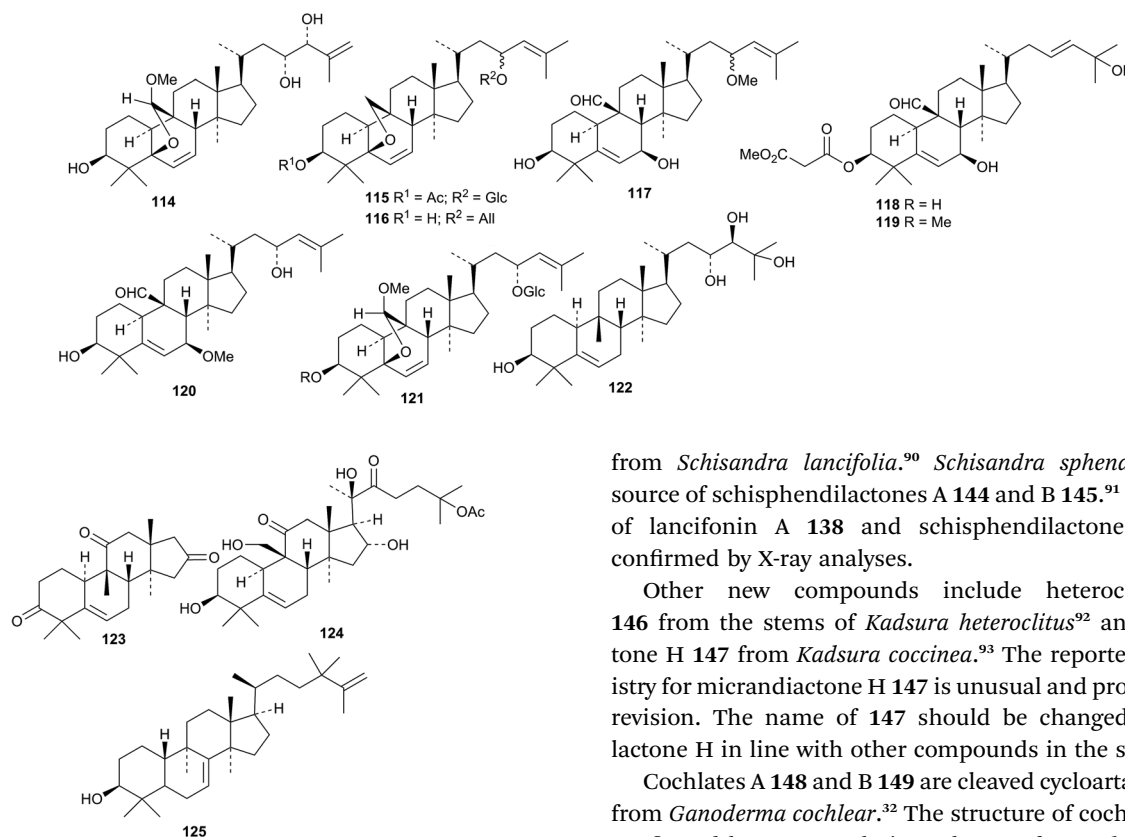
Cucurbitane triterpenoids of mushroom origin have been covered in a review.⁷⁴ Three interesting furanoid cucurbitane derivatives, roseic acid **97** and roseolactones A **98** and B **99**, have been isolated from *Russula aurora* and *Russula minutula*.⁷⁵ *Empetrum nigrum* var. *japonicum* is the source of the migrated cucurbitane nigrum-24-en-3β-ol **100**.⁷⁶

New cucurbitane derivatives isolated from *Hemsleya* species include **101** and **102** from *Hemsleya amabilis*⁷⁷ and hemslepen-side A **103**, 16,25-di-O-acetylcucurbitacin F 2-O-β-D-glucopyranoside **104** and 16-O-acetylcucurbitacin F **105** from *Hemsleya penxianensis*.⁷⁸ New cucurbitanes are still being found in the various parts of *Momordica charantia*.⁷⁹ The fruit is the source of kuguacins T **106**–W **109** (ref. 80) and charantosides D **110**–G **113**.⁸¹ The structure of kuguacin W **109** was confirmed by X-ray analysis.

The leaves and stem yielded karavilagenin F **114**, karavilosides XII **115** and XIII **116** and momordicines VI **117**, VII **118** and VIII **119**.⁸² A separate investigation of the leaves led to the isolation of compounds **120** and **121**.⁸³ Two new glycosides were reported from the seeds, one with the new genin **122**.⁸⁴

Kinoin D **123** is an octanorcucurbitane derivative from the roots of *Ibervillea sonora*.⁸⁵ Minor cucurbitane glycosides from *Siraitia grosvenorii* include 11-deoxymogrosides V and VI and 11-deoxyisomogroside V, all with known genins.⁸⁶ 23,24-Dihydrocucurbitacin C **124** is a new compound from *Cucumis sativus*.⁸⁷ The unlikely stereochemistry of **125** has been proposed for a compound from the leaves and twigs of *Euonymus alatus*.⁸⁸



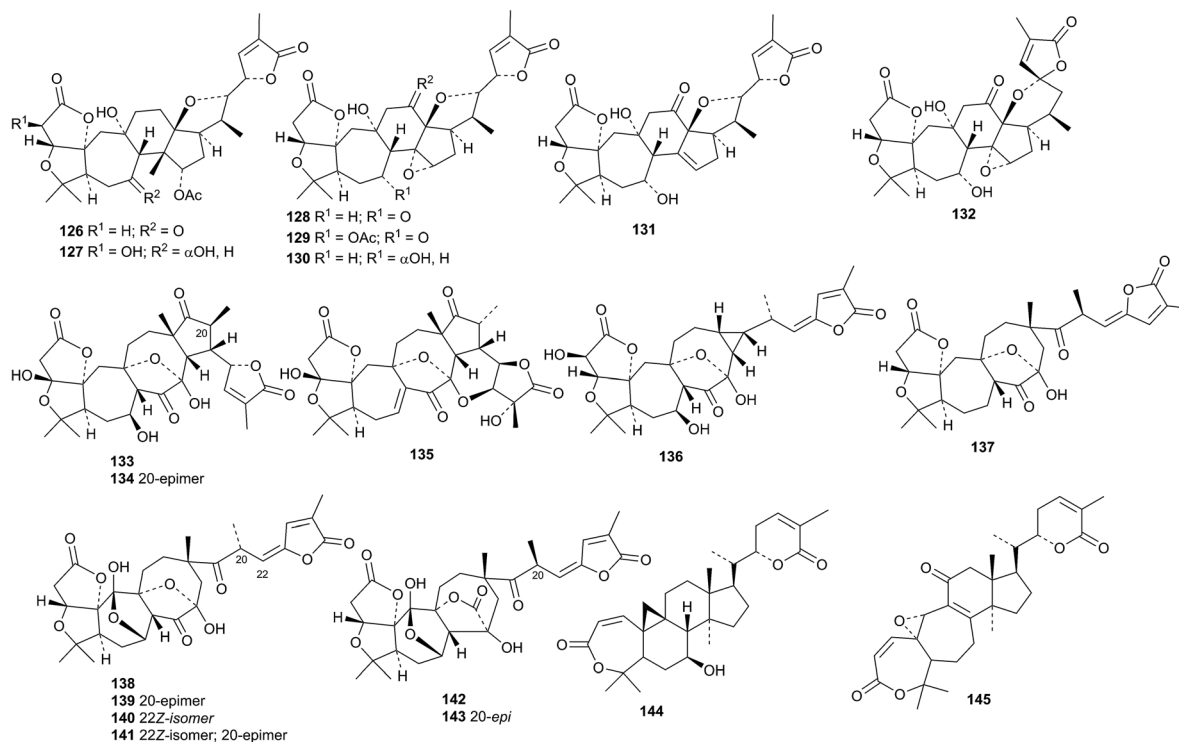


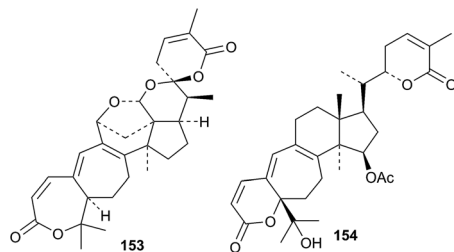
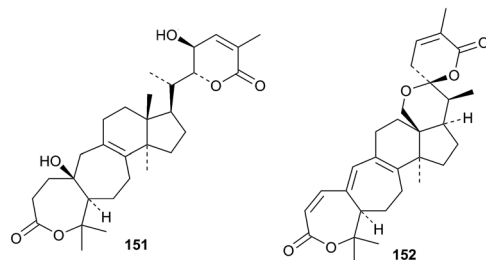
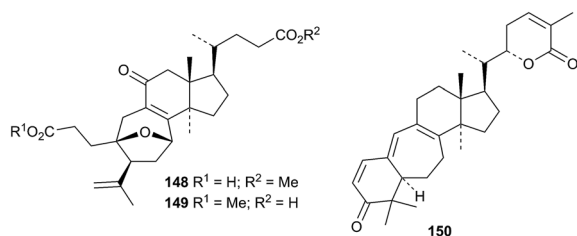
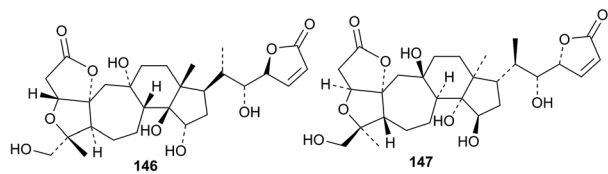
An impressive list of new compounds from *Schisandra chinensis* includes wuweizidilactones J 126–P 132, schindilactones I 133, J 134 and K 135, preschisanartanin N 136 and schisdilactone J 137.⁸⁹ Lancifonins A 138–F 143 are new compounds

from *Schisandra lancifolia*.⁹⁰ *Schisandra sphenanthera* is the source of schispendilactones A 144 and B 145.⁹¹ The structures of lancifonin A 138 and schispendilactone A 144 were confirmed by X-ray analyses.

Other new compounds include heteroclitalactone N 146 from the stems of *Kadsura heteroclita*⁹² and micrandilactone H 147 from *Kadsura coccinea*.⁹³ The reported stereochemistry for micrandilactone H 147 is unusual and probably requires revision. The name of 147 should be changed to micrandilactone H in line with other compounds in the series.

Cochlates A 148 and B 149 are cleaved cycloartane derivatives from *Ganoderma cochlear*.³² The structure of cochlate B 149 was confirmed by X-ray analysis. Cultures of *Ganoderma* sp. KM01 produce further cleaved derivatives ganodermalactones A 150, C 151, F 152 and G 153.³³ The structures of ganodermalactones F 152 and G 153 were confirmed by X-ray analyses. The revised structure 154 has been assigned to colossolactone G, a further metabolite of these cultures.





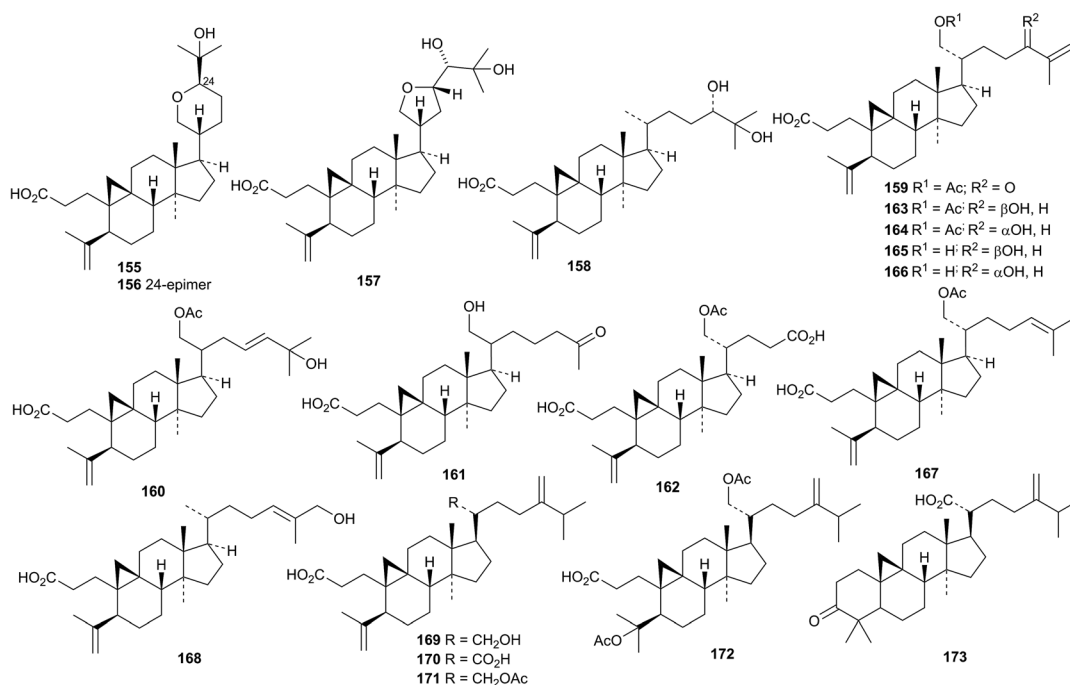
An impressive number of side-chain variations is to be found in the 3,4-secocycloartanes lithocarpic acids A **155**–N **168** from *Lithocarpus polystachyus*.⁹⁴ Lithocarpic acids O **169**–S **173** are further examples from the same source.⁹⁵ The structure of lithocarpic acid A **155** was confirmed by X-ray analysis.

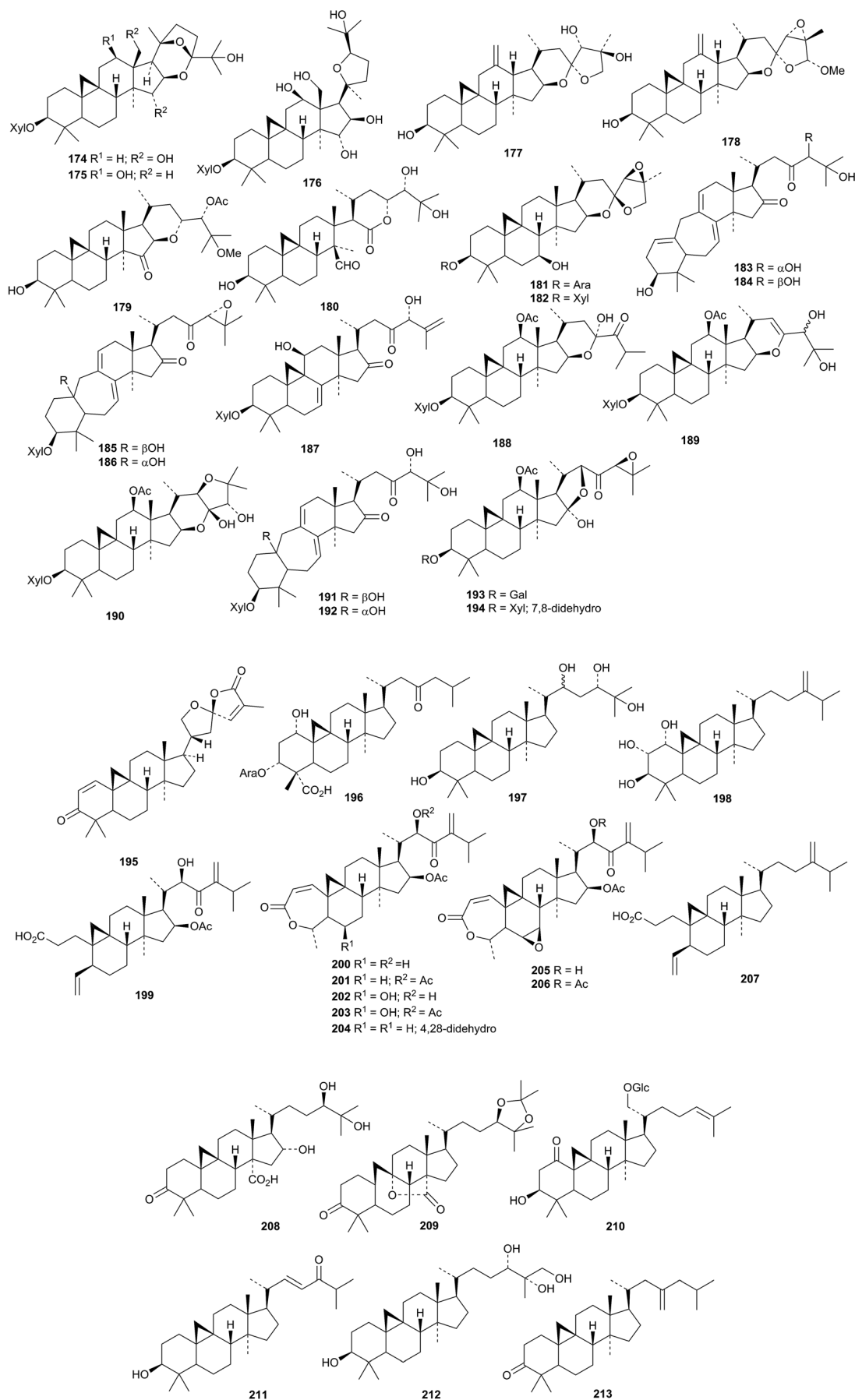
The three cycloartane xylosides **174**–**176**, from *Beesia calthaeifolia*, all have new genins.⁹⁶ New compounds from *Cimicifuga* species include the rearranged cycloartanes yunnanterpene G **177** and 12,18-didehydro-26-methoxyacetol **178**, isodahurinol 24-acetate 25-methyl ether **179**, 15,16-secoshengmanol C **180** and the glycosides **181** and **182** from the aerial parts of *Cimicifuga yunnanensis*,⁹⁷ cimifoetidanols A **183**–H **190** and cimifoetidanosides A **191** and B **192** from the rhizomes of *Cimicifuga foetida*⁹⁸ and glycosides **193** and **194** from the roots of *Cimicifuga simplex*.⁹⁹ The structure of cimifoetidanol A **183** was confirmed by X-ray analysis.

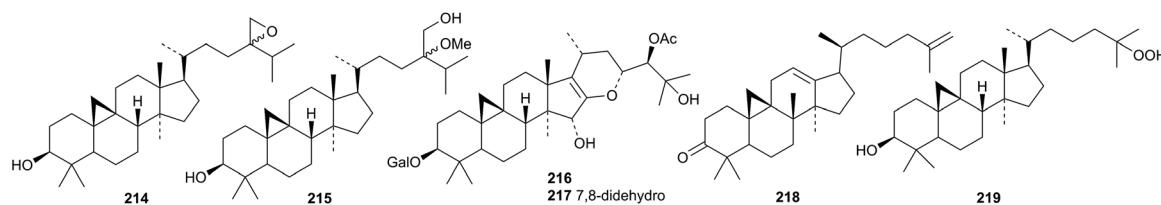
Two new cycloartanes **195** and **196** have been found in *Kleinhovia hospita*.¹⁰⁰ The arabinoside **196** has a new genin. Two new glycosides, one with the new genin **197**, have been reported from *Landoltia punctata*.¹⁰¹ Neomacrotriol **198** and the 29-nor-cycloartanes neomacroin **199**, neomacrolactone **200** and related compounds **201**–**206** have been isolated from *Neoboutonia macrocalyx*.¹⁰² The related 29-nor-derivative **207** has been found in *Cinnamosma fragrans*.¹⁰³

Other new cycloartanes include caloncobic acid C **208** and caloncobalactone C **209** from the leaves of *Caloncoba glauca*,¹⁰⁴ the glucoside rhizostyloside **210**, with a new genin, from *Rhizophora stylosa*,¹⁰⁵ compound **211** from *Cassia italica*,¹⁰⁶ and the tetrol **212** from the leaves and twigs of *Walsura yunnanensis*.¹⁰⁷ The unusual 23-methylene structure **213** has been proposed for a constituent of *Piper thomsonii*.¹⁰⁸

Compounds **214** and **215** have been isolated as mixtures of 24-epimers from *Euphorbia fischeriana*.¹⁰⁹ Two glycosides **216** and **217** from the roots of *Cimicifuga simplex* are described as







galactopyranosides but drawn as furanosides.⁹⁹ Cycloarta-12,25-dien-3 β -ol has been claimed as a constituent of Cameroonian brown propolis but the structure drawn is actually the 9(19)-cyclodammarane **218**.¹¹⁰ 25-Hydroperoxycycloartanol **219** is a constituent of *Euphorbia bupleuroides*.⁵⁵

Cycloartane saponins with known genins include krugianoside A from *Astragalus plumosus* var. *krugianus*¹¹¹ and riparsaponin from *Homonoia riparia*¹¹² and saponins from *Beesia calthaeifolia*,¹¹³ *Cimicifuga foetida*¹¹⁴ and *Euphorbia boissierana*.¹¹⁵

4. The dammarane group

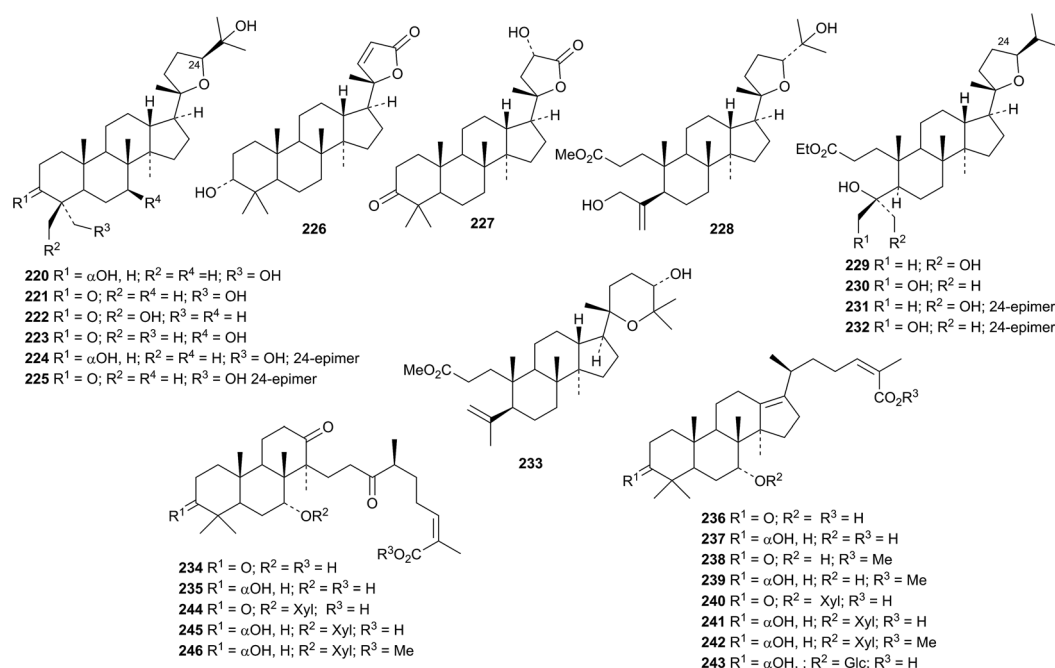
An interesting group of new dammaranes **220–233** has been reported from the stems of *Dysoxylum binectiferum*.¹¹⁶ Several 13,17-secodammaranes are among the 20-epi-derivatives dysotriflorins A **234–M** **246** from *Dysoxylum densiflorum*.¹¹⁷ The structure of dysotriflorin I **242** was confirmed by X-ray analysis.

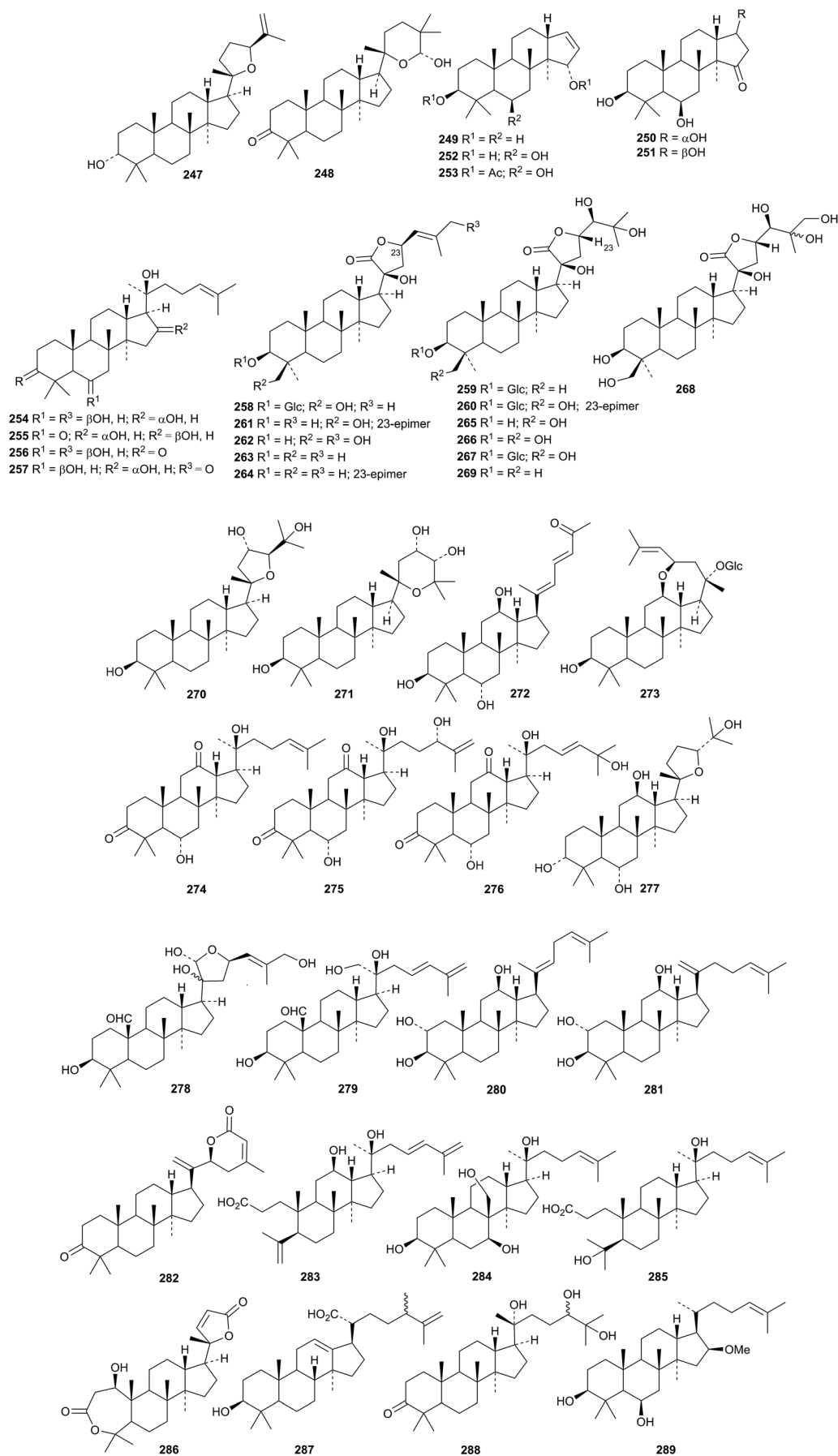
Dysomollisol **247** and dysomollisone **248** are constituents of the fruit of *Dysoxylum mollissimum*.¹¹⁸ Dysomollisone **248** has been assigned an unusual rearranged side-chain. The octanor-derivative rosanol A **249** has been found in the roots of *Rosa rugosa*.¹¹⁹ Horipenoids A **250–H** **257**, from *Homonoia riparia*, include several other octanor-derivatives.¹²⁰ The structure of

horipenoid E **254** was confirmed by X-ray analysis. Thirteen new dammarane saponins have been isolated from *Gentianella azurea* including the glucosides **258–260** whose structures were confirmed by X-ray analyses.¹²¹ Glucosides **258–260** have new genins. Further new genins **261–265** are found in the new dammarane saponins. The known gentirigenic acid and gentirigeoside A were also obtained from *Gentianella azurea* and their structures have been revised to **266** and **267**, respectively, on the basis of X-ray analyses. The genins of the known gentirigeosides B and E were also revised to **268** and **269**, respectively.

Phlomisumbrosides A and B are new glycosides from *Phlomis umbrosa* with the new genins **270** and **271**.¹²² The 27-nordammarane **272** and the glucoside **273**, with a known genin, are further constituents of the leaves of *Panax ginseng*.¹²³ The three 3,12-diketones **274–276** were obtained from the same source.¹²⁴ The epoxydammaranetetrol **277** has been isolated from the stems and leaves of American ginseng and given the erroneous name 3 α -ocotillol (ocotillol is an epoxydammaranediol).¹²⁵

New compounds from *Gynostemma pentaphyllum* include two saponins with new genins **278** and **279**,¹²⁶ the saponins damulins C and D with the new genins **280** and **281** (ref. 127)

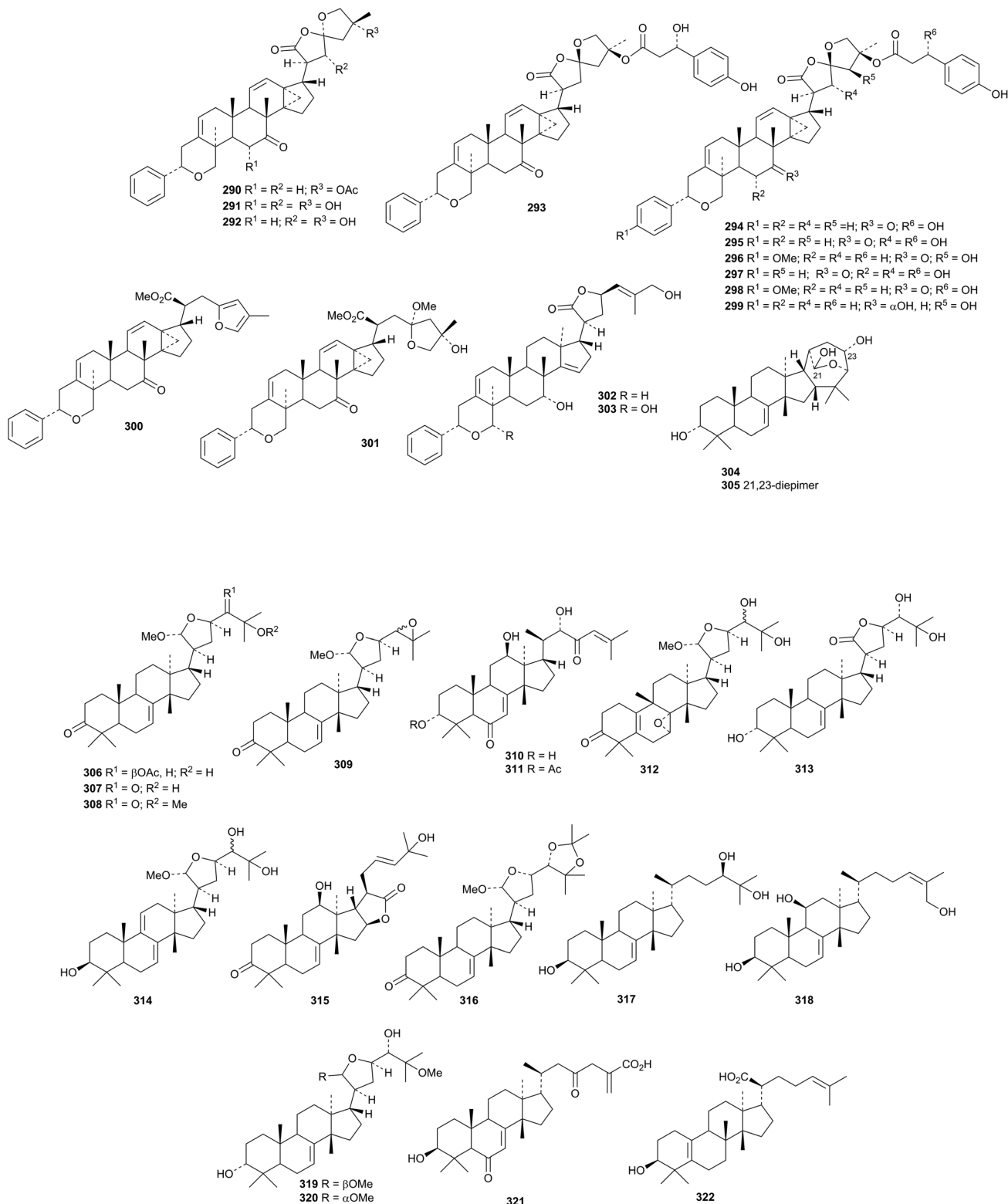


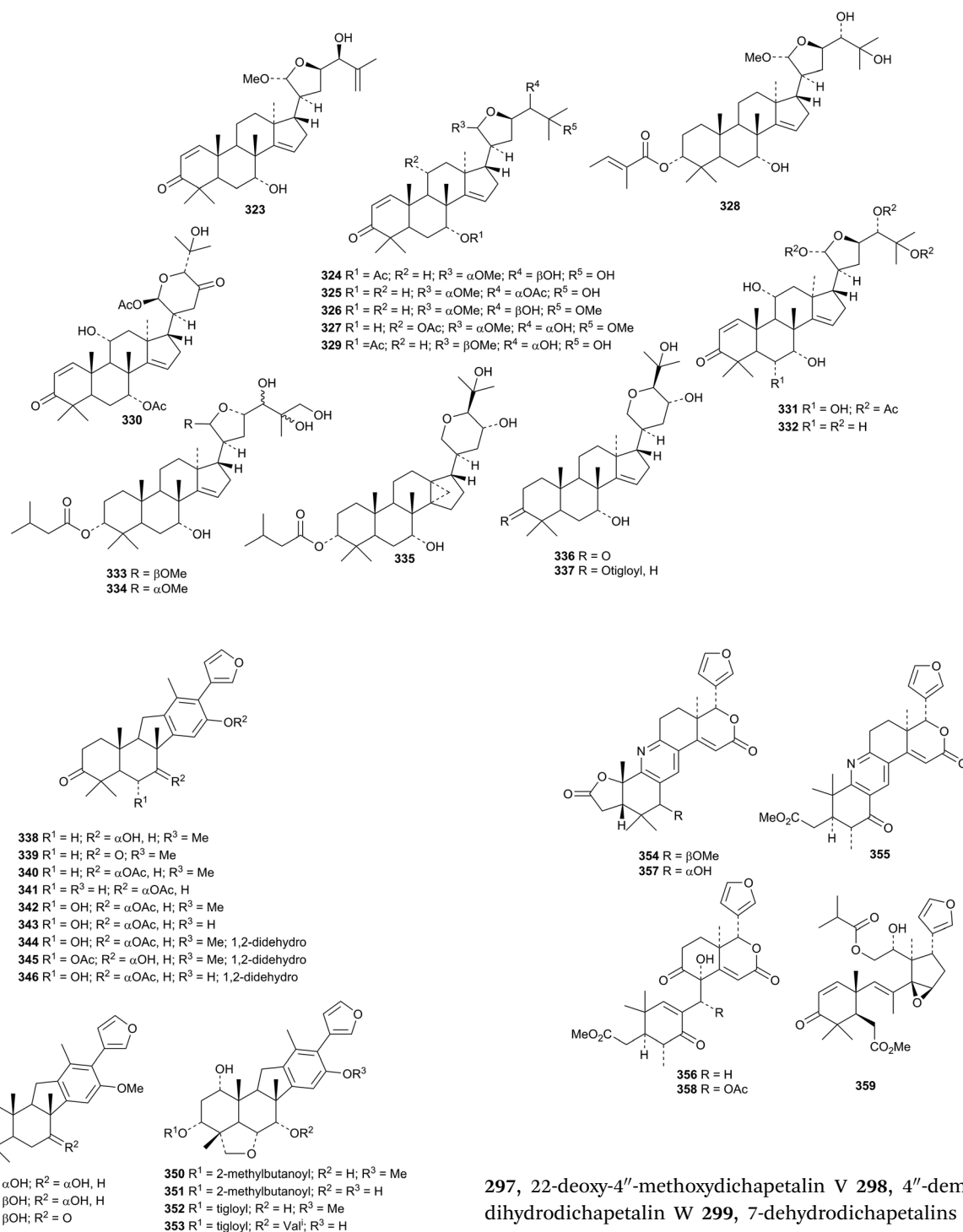


and the keto-lactone **282**.¹²⁸ Cyclocarioside K, from *Cyclocarya paliurus*,¹²⁹ and tubeimoside C, from *Bolbostemma paniculatum*,¹³⁰ also have new genins, **283** and **284**, respectively. Other new dammaranes include the ring A-cleaved derivative **285** from *Aglaia abbreviata*,¹³¹ deacetylbrachycarpon-22-ene **286** from *Cleome arabica*,¹³² the 30-nor-24-methyl derivative

floccosic acid **287** from *Nepeta floccosa*,¹³³ the keto-triol **288** from the root bark of *Ailanthus altissima*¹³⁴ and farmanol **289** from *Nepeta suaveis*.¹³⁵

New dammarane saponins with known genins include cyclocarioside J from *Cyclocarya paliurus*,¹³⁶ jujubosides D and E (duplicate names) from *Ziziphus jujuba*,¹³⁷ notoginsenosides FZ,





LX and LY from *Panax notoginseng*¹³⁸ and saponins from *Aralia elata*¹³⁹ and *Panax notoginseng*.¹⁴⁰ The pharmacological activities and production of saponins from *Centella asiatica* have been reviewed.

Fourteen new dichapetalin derivatives have been obtained from *Dichapetalum gelonioides* including 22-deoxydichapetalin P 290, 25-deacetyldichapetalins M 291 and P 292, dichapetalins T 293, U 294, V 295 and W 296, 6 α -hydroxydichapetalin V

297, 22-deoxy-4''-methoxydichapetalin V 298, 4''-demethoxy-7-dihydrodichapetalin W 299, 7-dehydrodichapetalins E 300, G 301 and Q 302 and 29 α -hydroxy-21-dehydrodichapetalin Q 303.¹⁴¹ The structure of 22-deoxydichapetalin P 290 was confirmed by X-ray analysis. The unusual 16,25-cyclised tirucallane structures 304 and 305 have been proposed for asperols A and B from *Canarium asperum*.¹⁴²

Other new tirucallane derivatives include the acetals 306–309 from *Dysoxylum binectariferum*,¹⁴³ trichostemonol 310 and the corresponding 3-acetate 311, trichostemonate, from the stem bark of *Walsura trichostemon*,^{144,145} indicililacols A 312–D 315 from the fruits of *Azadirachta indica*,¹⁴⁶ toosendansin D 316 from *Melia toosendan*,¹⁴⁷ compounds 317 and 318 from



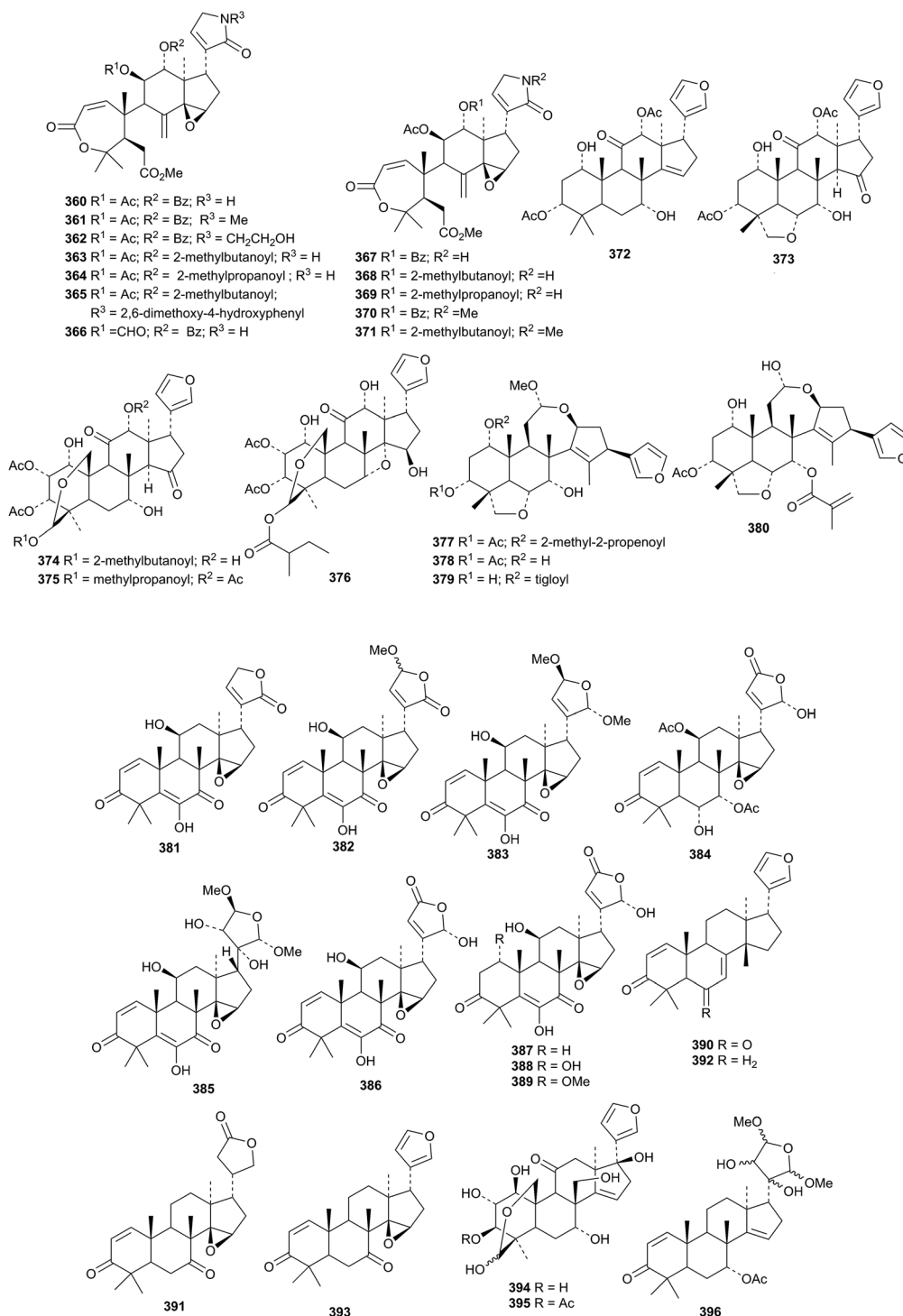
Celastrus stylosus,¹⁴⁸ the 21-epimers paramignyols A **319** and B **320** from *Paramignya scandens*¹⁴⁹ and dysoxylum A **321** (duplicate name) from *Dysoxylum densiflorum*.¹⁵⁰ The unusual structure **322** has been ascribed to a constituent of *Melia azedarach*.¹⁵¹

Xylogranatamines A **323**–G **328** are new apotirucallenes from the Chinese mangrove *Xylocarpus granatum*.¹⁵² Other members of this class are represented by compounds **330**–**332** from the leaves of *Walsura trichostemon*,¹⁵³ dictamnins A **333** and B **334**,

21-epimers from the bark of *Dictamnus dasycarpus*,¹⁵⁴ cedrodorols A **335** and B **336** from *Cedrela odorata*¹⁵⁵ and compound **337** from *Melia azedarach*.¹⁵⁶

4.1 Tetranortriterpenoids

There is a strong interest in the biological activities of limonoids.^{157–160} Anticancer^{161,162} and pesticidal¹⁶³ activities of limonoids have also been highlighted. The publication of new

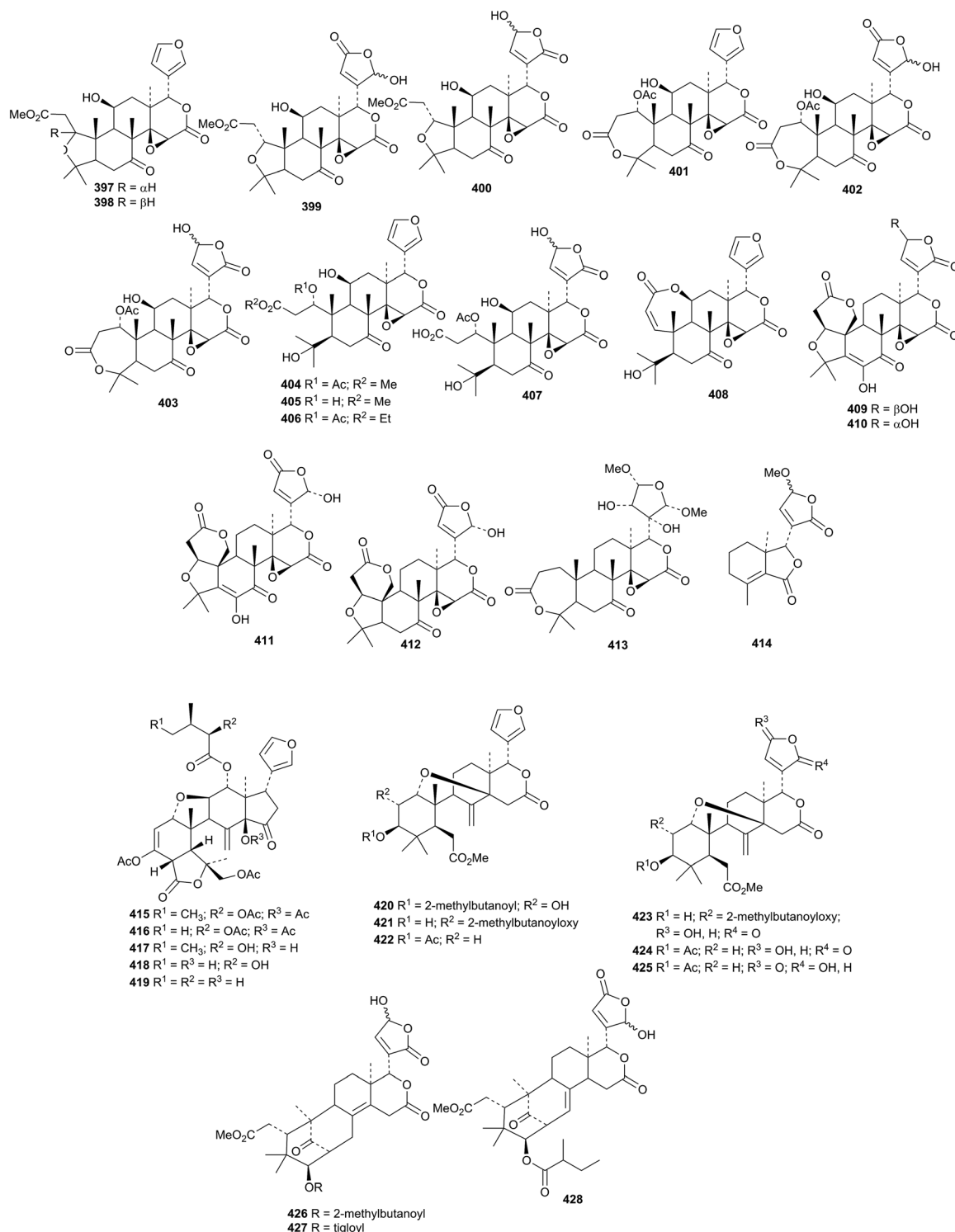


members of this class continues unabated. Walsucochinoids C 338–R 353, from *Walsura cochinchinensis*, form an interesting group of rearranged derivatives.¹⁶⁴ The structures of walsuchinoids C 338 and L 347 were confirmed by X-ray analyses.

Xylogranatopyridines A 354, B 355 and prexylogranatopyridine 356, from the Chinese mangrove *Xylocarpus granatum*, are closely related to the known xylogranatin F 357 and

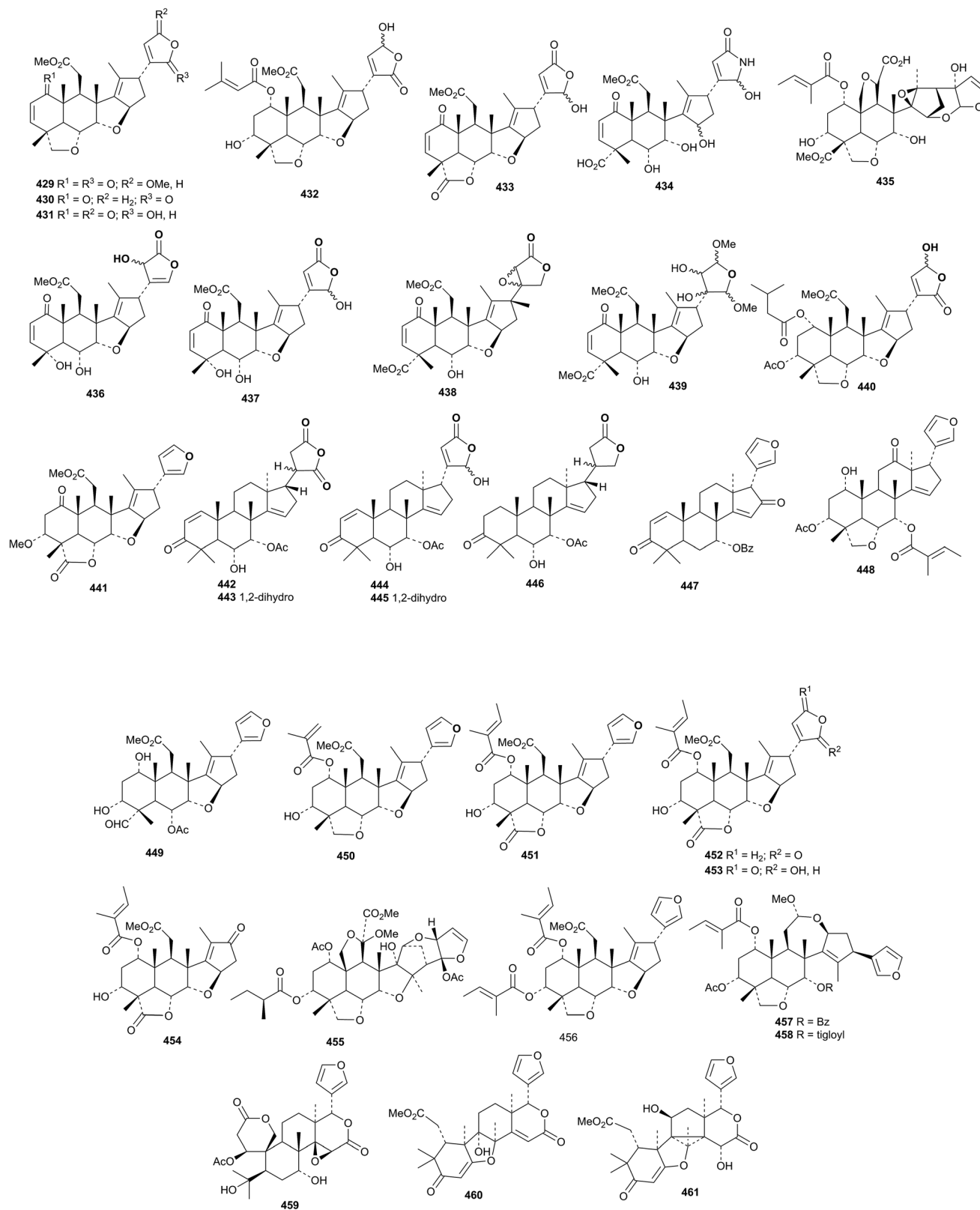
hainangranatumin D 358.¹⁶⁵ The unusual 9,11-seco-derivative toonasecone A 359 has been isolated from *Toona ciliata*.¹⁶⁶

A series of amides, amooramides A 360–L 371, has been reported from the twigs and leaves of *Amoora tsangii*.¹⁶⁷ The highly oxygenated tetranortriterpenoids 372–376, from the fruits of *Melia toosendan*, are accompanied by the ring-C cleaved derivatives 377–379.¹⁶⁸ Compound 378 has also been isolated from *Melia azedarach* together with 380.¹⁶⁹



Nine new cedrelone derivatives, walsuranolide B **381**, 11 β -hydroxy-23-O-methylwalsuranolide **382**, yunnanolides A **383** and B **384**, yunnanol A **385**, the isowalsuranolide derivatives **386–389**, have been isolated from the leaves and twigs of

Walsura yunnanensis.¹⁰⁷ Dysoxylamins B **390**, C **391** (duplicate names) and compounds **392** and **393** are constituents of *Dysoxylum densiflorum*.¹⁵⁰ Other derivatives with intact skeletons include flexuosoids A **394** and B **395** from *Phyllanthus*

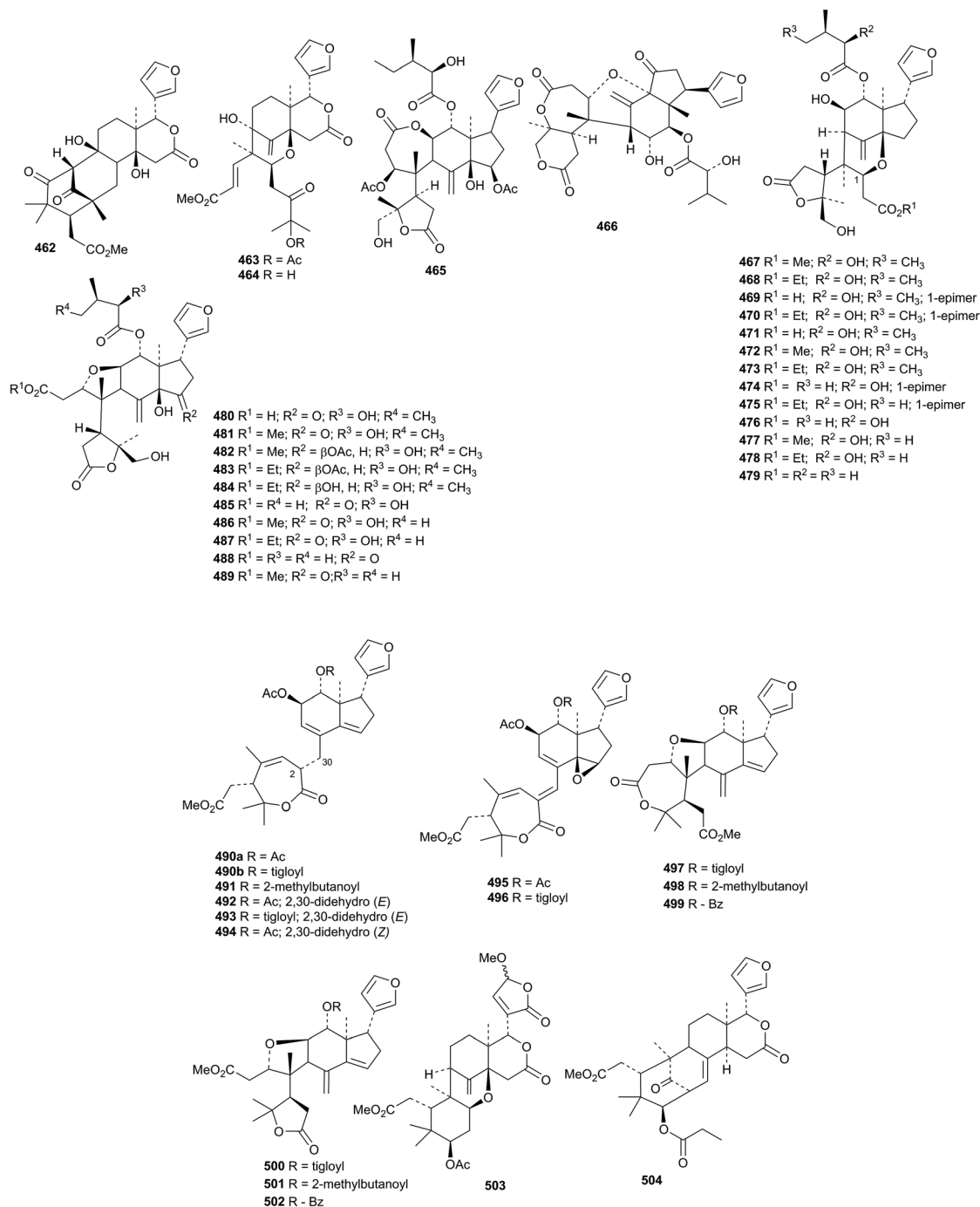


*flexuosus*¹⁷⁰ and compound **396** from the flowers of *Azadirachta indica* var. *siamensis*.¹⁷¹

The A,D-seco derivatives clauemargines A **397**–**L 408** have been isolated from the stems of *Clausena emarginata*.¹⁷² The structure of clauemargine A **397** was confirmed by X-ray analysis. Other A,D-seco derivatives include euodirutaecins A **409** and B **410**, as an inseparable mixture, evodirutaenin A **411** and shihulimonin A1 **412** from the rhizomes of *Coptis chinensis* and *Euodia rutaecarpa*¹⁷³ and kihadanin C **413** from the root bark of *Dictamnus dasycarpus*.¹⁷⁴ 23-O-Methyl dasylactone B **414** is a further constituent of *Dictamnus dasycarpus*.¹⁷⁴

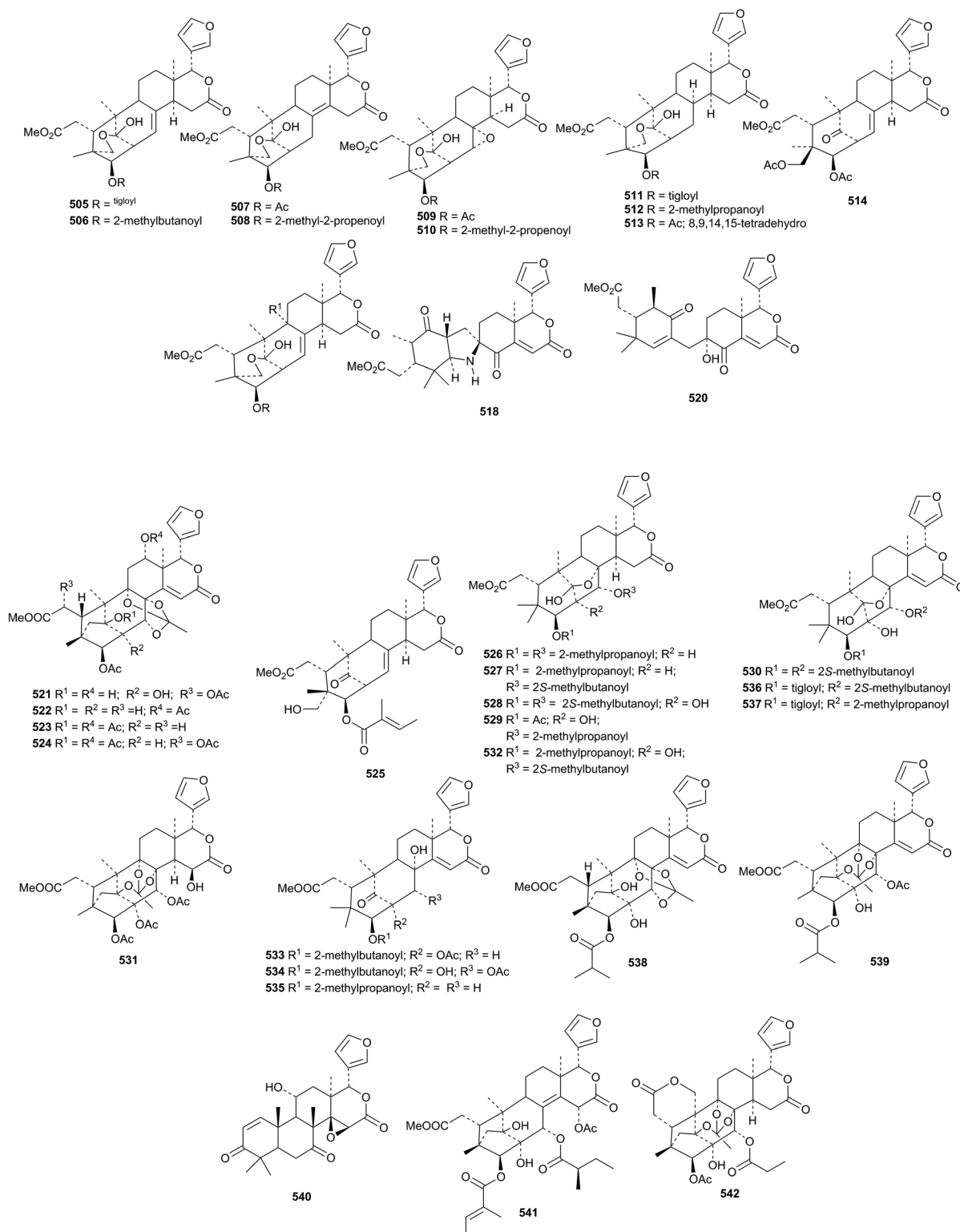
Ring B-cleaved derivatives are represented by aphagranols D **415**–**H 419** from the fruits of *Aphanamixis grandifolia*¹⁷⁵ and the methyl angolensate derivatives cipaferens E **420**–**J 425** from the seeds of *Cipadessa baccifera*.¹⁷⁶ The mexicanolide derivatives, cipaferens K **426**, L **427** and M **428**, were also isolated together with the known compounds cipadesin A and 2*R*-methylbutanoylproceranolide whose structures were confirmed by X-ray analyses.

The seemingly endless investigations of the constituents of *Azadirachta indica* have, unsurprisingly, produced more unremarkable ring C-cleaved derivatives. These include the 28-



deoxynimbolide derivative **429**,¹⁷⁷ compounds **430–432**,¹⁷⁸ nimbolide B **433** and nimbic acid B **434** (ref. 179) and compounds **435–437** from *Azadirachta indica*¹⁸⁰ and compounds **438–441** from *Azadirachta indica* var. *siamensis*.¹⁸¹ The uncleaved derivatives **442–446** (ref. 180) and **447** and **448** (ref. 181) were also obtained.

Three new ring C-cleaved derivatives **449–451**, along with a host of known compounds, have been reported from the fruits of *Melia azedarach*.¹⁸² The leaves and bark are the source of the new derivatives **452–454** (ref. 183) while the meliacarpin derivative **455** was found in the leaves.¹⁵⁶ Toosendansins A **456**, B **457** and C **458** are constituents of *Melia toosendan*.¹⁴⁷



The ichangin derivative **459**, 9 α -hydroxyhortolide A **460** and 11 β -hydroxyhortolide C **461** were isolated from *Hortia orcadia*.¹⁸⁴

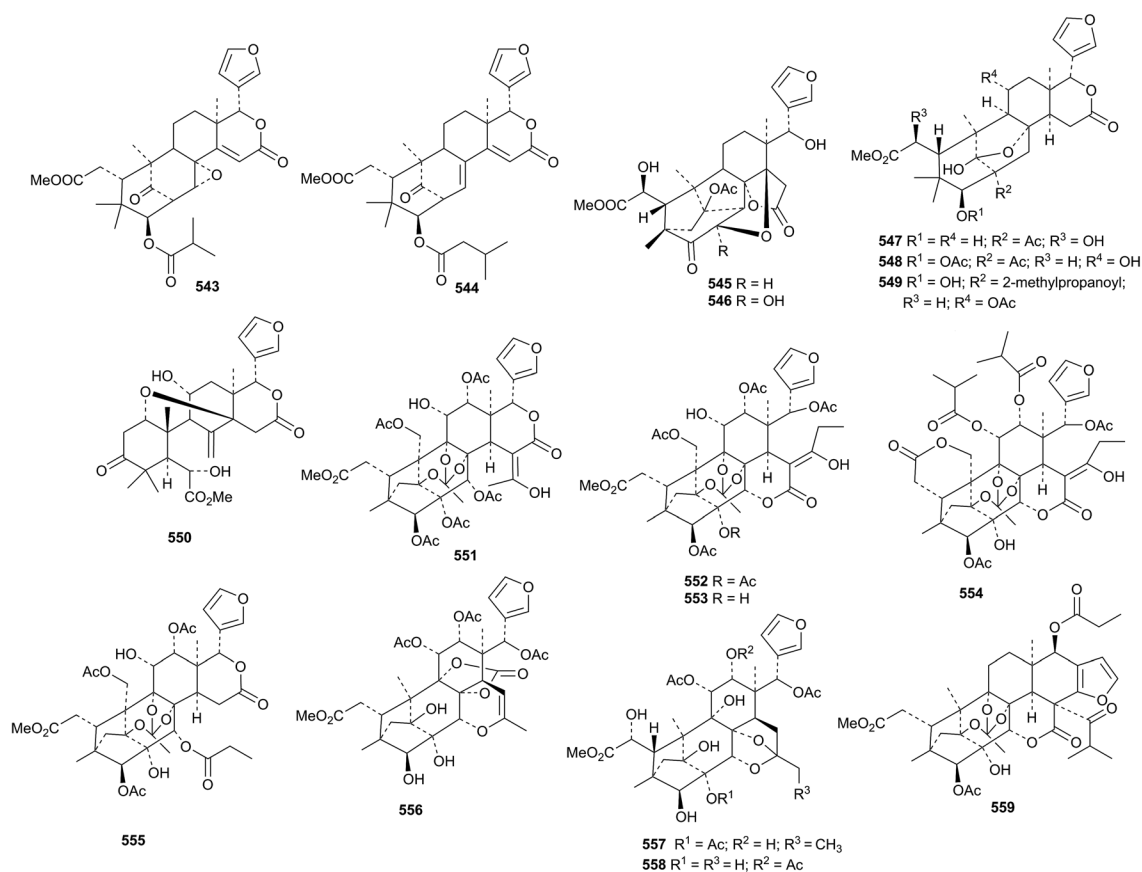
New skeletal variations of rearranged limonoids continue to appear. The structures of trichiconins A **462** and B **463**, from *Trichilia connaroides*, were confirmed by X-ray analyses.¹⁸⁵ They were accompanied by trichiconin C **464**. Zaphaprinins A **465**–Y **489** are modified prieurianin derivatives from the fruits of *Aphanamixis grandifolia*.¹⁸⁶ The structures of zaphaprinins B **466**, E **469** and P **480** were confirmed by X-ray analyses. Eight members of this group are ethyl esters and are presumably artefacts of the extraction process.

A similar group of compounds, aphanamixoids C **490a**–P **502**, has been reported from *Aphanamixis polystachya*.¹⁸⁷ Cine-racipadesin G **503** (ref. 188) and the swietenine derivative **504** (ref. 189) are constituents of *Cipadessa cinerascens*.

525.¹⁹⁴ Xylorumphins E **526**–J **531** and 2-hydroxyxylorumphin F **532** are constituents of the seeds of *Xylocarpus rumphii*.¹⁹⁵ The structure of xylorumphin G **528** was confirmed by X-ray analysis.

Carapanolides C **533**–I **539** (ref. 196) and carapanolides J **540**, K **541** and L **542** (ref. 197) have been reported from the seeds of *Carapa guianensis*. The structure of carapanolide F **536** was confirmed by X-ray analysis.

Further investigations of *Khaya ivorensis* have resulted in the isolation of 14,15-didehydroruageanin A **543** and 3-O-(3-methylbutanoyl)seneganolide A **544** (ref. 198) and ivorenoids A **545**–F **550**.¹⁹⁹ Velutinasins A **551**–H **558** are phragmalin derivatives from *Chukrasia tabularis* var. *velutina*.²⁰⁰ Velutinalide C **559** is another new compound from this source.²⁰¹

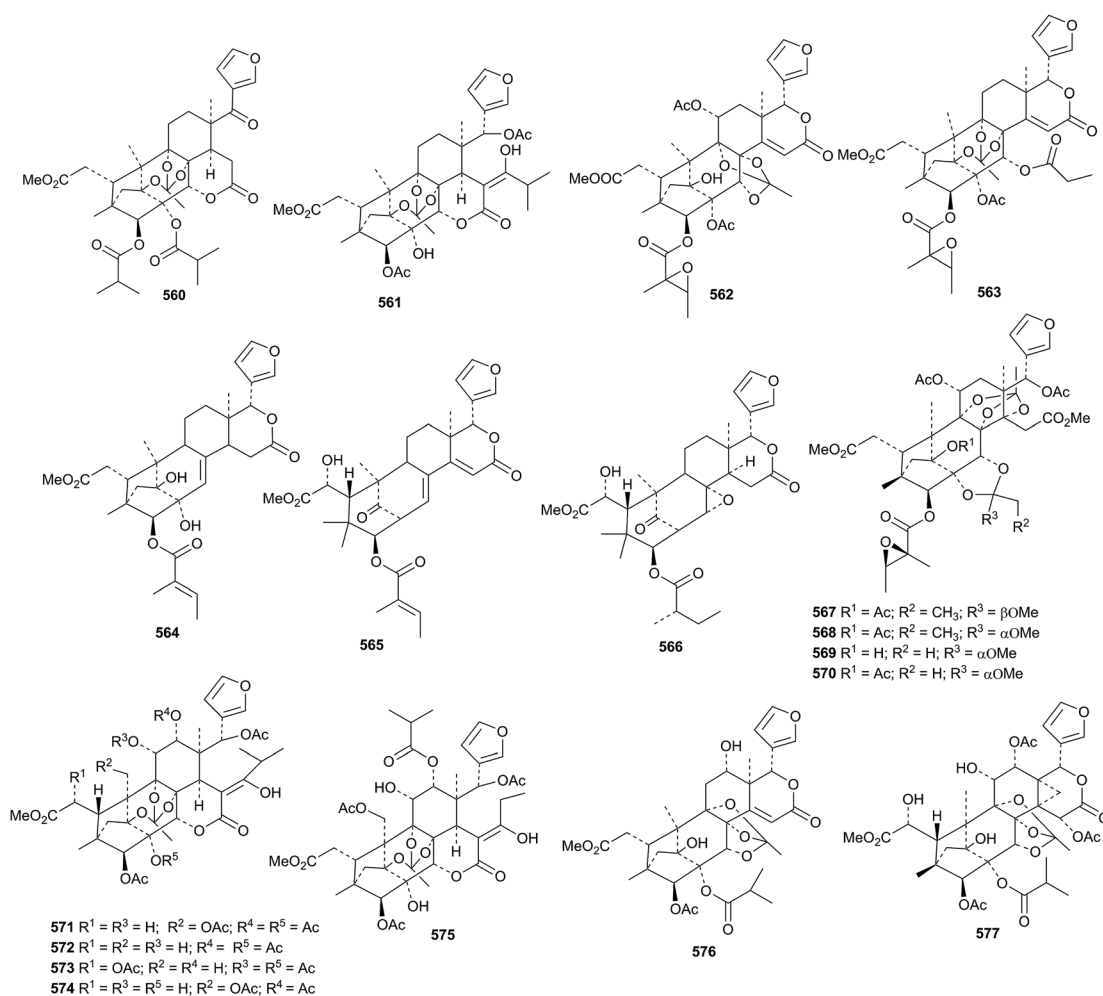


Compounds from an Indian *Xylocarpus granatum* include granatamins L **505**–U **514** (ref. 190) and granatamins V **515**–Y **518**.¹⁹¹ The structures of granatamins L **505** and Y **518** were confirmed by X-ray analyses. Granatamins M **506** and V **515** have also been isolated from *Xylocarpus granatum* by another group and named xylomexicanins H and G, respectively.¹⁹² They occur with xylomexicanins E **519** and F **520** that were drawn with the wrong absolute configuration in the reference.

Other constituents of *Xylocarpus granatum* include the phragmalin derivatives **521**–**524** (ref. 193) and xylocartin C

Neobeguea mahafalensis is the source of the phragmalin derivatives libiguin A **560** and libiguin B **561** (in equilibrium with its keto tautomer).²⁰² These compounds are reported to have aphrodisiac properties. 2-Acetylsoymidin B **562** and soymidins D **563** and E **564** are constituents of *Soymida febrifuga*.²⁰³ Swielimonoids A **565**–F **570** are additional constituents of *Swietenia macrophylla* seeds.²⁰⁴ Chukvelutilides I **571**–O **577** are further new phragmalin derivatives from the seeds of *Chukrasia tabularis*.²⁰⁵ Synthetic studies have indicated that the biosynthesis of the 1,8,9-orthoester moiety in phragmalins involves intermediates with an ester at C-1.²⁰⁶





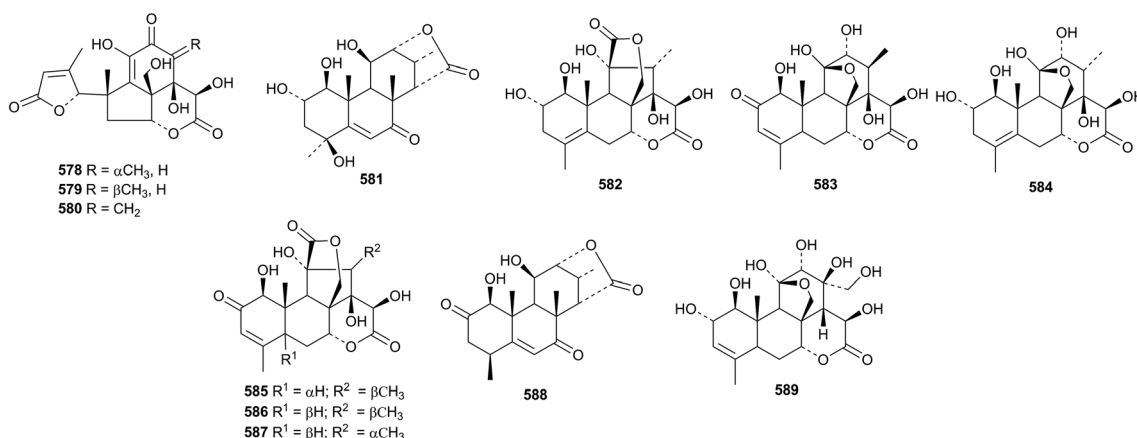
4.2 Quassinoids

Eurylactones E 578, F 579 and G 580, eurycomalides D 581, and E 582 and 13 α ,18-dihydroeurycomanone 583 are new constituents of the roots of *Eurycoma longifolia*.²⁰⁷ Other constituents of *Eurycoma longifolia* include Δ^4 -14-hydroxyglaucaol 584, 5-isoeurycomadilactone 585, eurycomadilactone 586 and 13-epieurycomadilactone 587 (ref. 208) and eurycomalide C 588.²⁰⁹ The structures of

Δ^4 -14-hydroxyglaucaol 584 and 5-isoeurycomadilactone 585 were confirmed by X-ray analyses. Shinjulaolone O 589 has been isolated from the root bark of *Ailanthus altissima*.²¹⁰

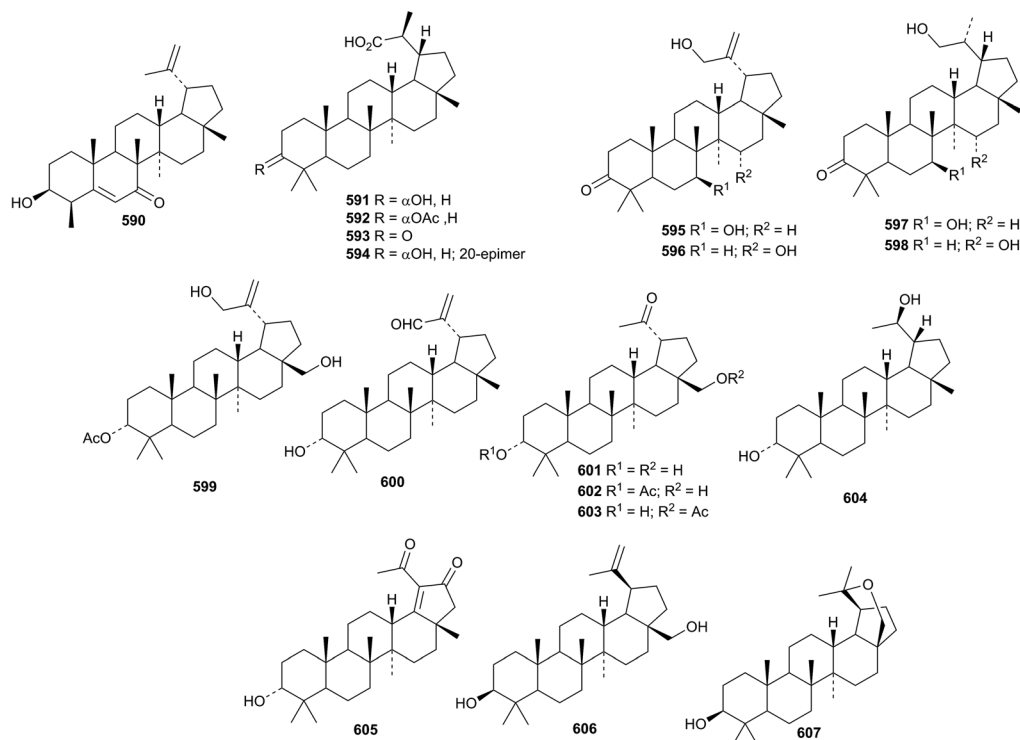
5. The lupane group

Betulinic acid has been reported to have a variety of pharmacological activities including antitumour activity.^{211,212} The first



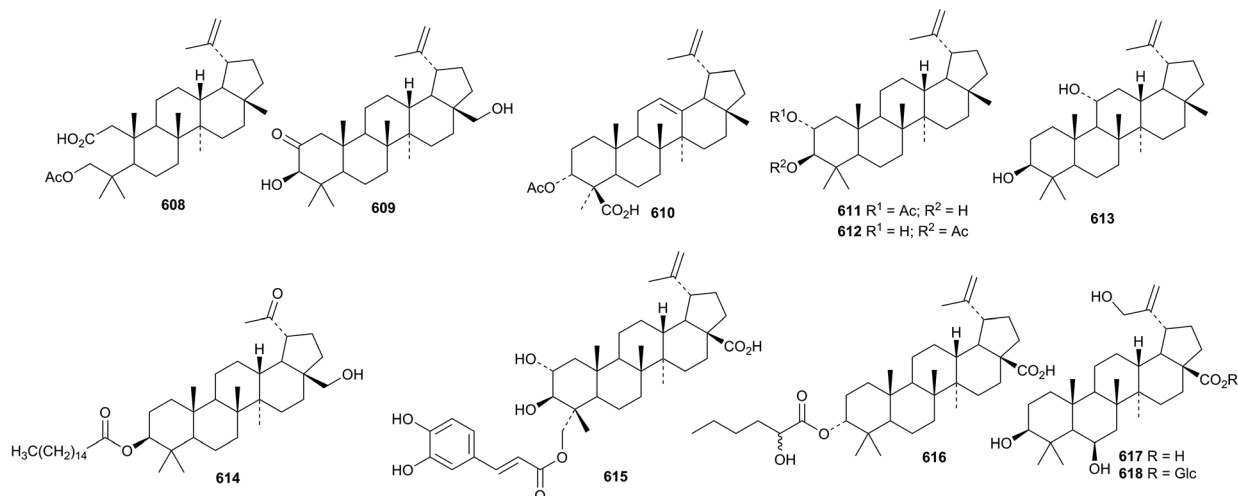
example of a 23-norlupane, 3-hydroxy-23-nor-5,20(29)-lupadien-7-one **590**, has been reported from *Lagerstroemia indica*.²¹³ *Euonymus carnosus* is a prolific source of lupane triterpenoids. Fifteen new compounds **591**–**605**, including the 30-nor-derivatives **601**–**605**, have been isolated.²¹⁴ The structure of **591** was confirmed by X-ray analysis. 19-Epibetulin **606** and 19-*epi*-20,28-epoxy-3-lupanol **607** have been reported from *Hibiscus syriacus*.²¹⁵

20(29)-lupene-3 β ,11 α -diol **613** together with its 3-palmitate and the 30-norlupane palmitate **614** from *Saussurea phyllocephala*,²¹⁹ sorbanolic acid **615** from *Sorbus lanata*²²⁰ and the 2-hydroxyhexanoyl ester of 3-epibetulinic acid **616** from *Dillenia indica*.²²¹ 3 β ,6 β ,29-Trihydroxy-20(30)-lupen-28-oic acid **617** and its β -D-glucopyranosyl ester **618** are constituents of *Licania cruegeriana*.²²² Lupane saponins with known genins include schekwangsiensides F and G



Other simple lupane derivatives include salacinins A **608** and B **609** from *Salacia hainanensis*,²¹⁶ the acetates **610** from *Boswellia sacra*²¹⁷ and **611** and **612** from *Salvia viridis*,²¹⁸

from *Schefflera kwangsiensis*²²³ and saponins from *Eryngium agavifolium*.²²⁴



6. The oleanane group

Oleanane triterpenoids and their saponins have a wide range of pharmacological activities.^{225–227} Oleanolic acid^{228–231} and maslinic acid²³² have been well studied, particularly for their anti-tumour effects.

Cyclocaric acid A, from *Cyclocarya paliurus*, was claimed to have the structure **619** with an oxetane ring.²³³ Synthesis of the oxetane **619** and re-examination of the original literature report indicates that cyclocaric acid A is identical with hederagenin **620**.²³⁴ The 2,3-seco-derivative **621** has been found in *Ligularia przewalskii*,²³⁵ and the 2,3-seco anhydride **622** is a constituent of *Microtropis fokiensis* where it is accompanied by the intact oleananes **623**, **624** and the 18-oleanene derivative **625**.²³⁶ Further 18-oleanene derivatives include 2 α ,3 β -dihydroxy-18-oleanen-28-oic acid **626** from *Lawsonia inermis*²³⁷ and the corresponding 29-oic acid **627** from *Mentha suaveolens*.²³⁸

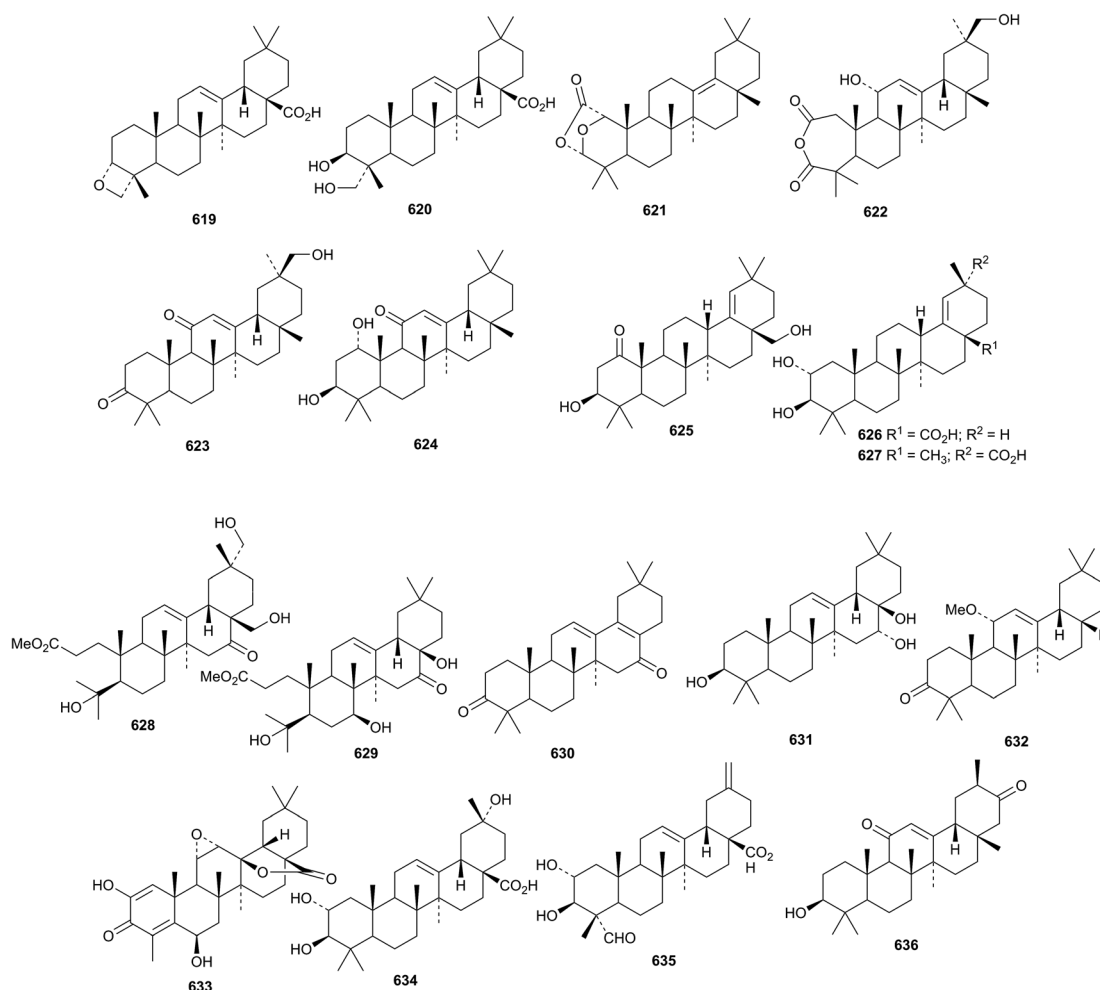
The 3,4-seco-derivatives camelliaoleans A **628** and B **629**, together with the 28-noroleanane derivatives **630** and **631**, have been isolated from *Camellia japonica*.²³⁹ Liquidaformone **632** is another 28-noroleanane from fruits of *Liquidambar formosana*.²⁴⁰ Asprellol C **633** is a 24-noroleanane from *Ilex*

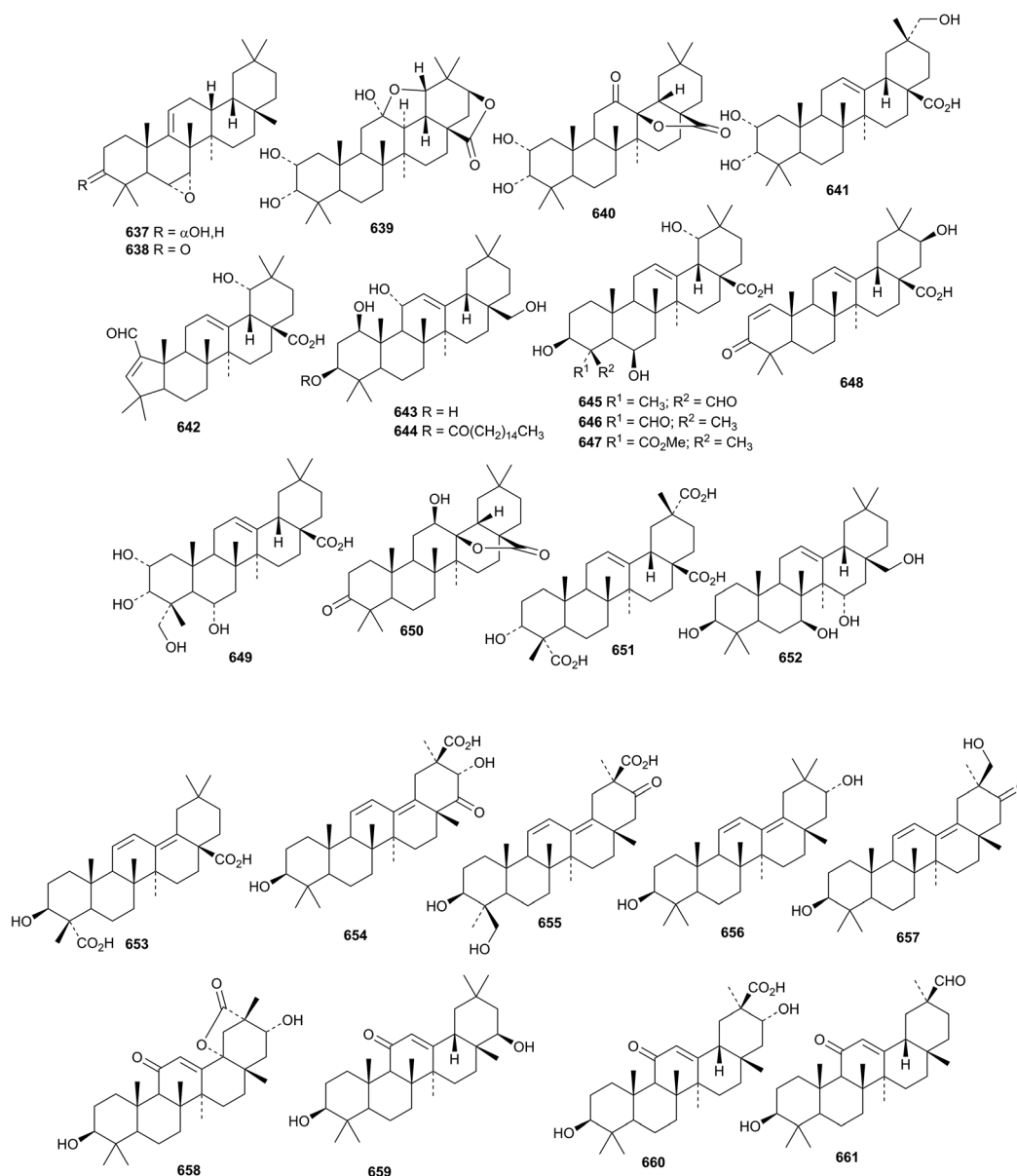
asprella,²⁴¹ whereas the noroleananes **634** and **635** have been found in *Akebia trifoliata*²⁴² and glyyunnansapogenin I **636** is from *Glycyrrhiza yunnanensis*.²⁴³

Two unusual 9(11)-oleanene derivatives **637** and **638**, lacking a ketone at C-12, have been isolated from *Boswellia ovalifoliata*.²⁴⁴ Cannabifolin A **639**, from *Vitex negundo* var. *cannabifolia*, has unusual *cis*-fused C/D rings.²⁴⁵ It is accompanied by cannabifolins E **640** and F **641**. Rusaic acid B **642**, from the roots of *Rosa rugosa*, has a contracted ring A.¹¹⁹

Other simple oleanane derivatives include 12-oleanene-1 β ,3 β ,11 α ,28-tetrol **643** and its 3-palmitate **644** from *Saussurea phyllocephala*,²¹⁹ uncarinic acids F **645**, G **646** and H **647** from *Uncaria rhynchophylla*,²⁴⁶ schekwangsiensin **648** from *Schefflera kwangsiensis*,²²³ glaucescic acid **649** from *Terminalia glaucescens*,²⁴⁷ the 28,13-olide **650** from *Ekebergia capensis*,²⁴⁸ 3 α -hydroxy-12-oleanene-23,28,29-trioic acid **651** from *Acanthopanax gracilistylus*²⁴⁹ and 12-oleanene-3 β ,7 β ,15 α ,28-tetrol **652** from *Salvia argentea* var. *aurasiaca*.²⁵⁰

3 β -Hydroxy-11,13(18)-oleanadiene-23,28-dioic acid **653**, previously identified as the genin of saponarioside J, has been isolated from *Anoectochilus elwesii*.²⁵¹ Yunganosides L, M, N₁, N₂, O and P are saponins from *Glycyrrhiza yunnanensis* with the new genins yunganogenins L **654**–P **658**.²⁴³ Licorice-





saponins M3 and N4, from *Glycyrrhiza glabra*, have the new genin **659**.²⁵² Licorice-saponin M3 is the same as uralsaponin T that has been isolated from *Glycyrrhiza uralensis* together with uralsaponins P–S and W that have the new genins **660** and **661**, respectively.²⁵³

Other oleanane saponins with new genins include centellasaponins E and I, from *Centela asiatica*, with the genins **662** and **663**,²⁵⁴ hippophosides A–D, from *Hippophae rhamnoides* ssp. *sinensis*, with the genins **664** and **665**,²⁵⁵ oleiferasaponin B₂, from *Camellia oleifera*, with the genin **666**,²⁵⁶ tubeimosides A and B, from *Bolbostemma paniculatum*, with the genins **667** and **668**,¹³⁰ saponins from *Akebia trifoliata* with the noroleanane genins **669** and **670**,²⁵⁷ *Entada phaseoloides* with the genins **671–673**,²⁵⁸ *Eclipta prostrata* with the genin 12-oleanene-3 β ,16 β ,29-triol **674** (ref. 259) and *Silphium asteriscus* also with the genin **674** together with eleven related genins **675–685**.²⁶⁰

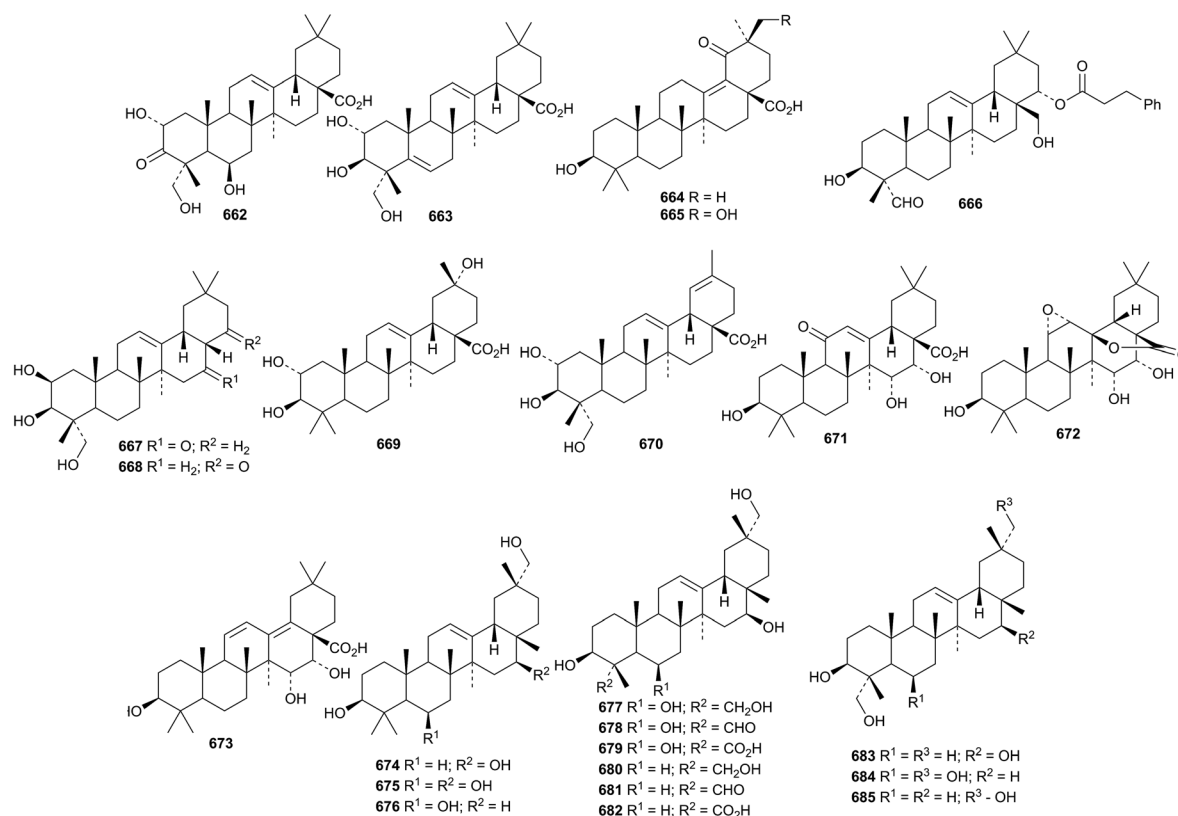
New oleanane saponins with known genins that have been assigned trivial names are listed in Table 1.

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

The unlikely acetone hemiacetal **686** has been reported as a constituent of *Isodon adenantha*.³¹⁵ 11,21-Dihydroxy-1-oleananone **687** and four esters **688–691** are claimed to be substituents of *Coriandrum sativum*.³¹⁶ Other new oleanane esters include the 3-palmitoyl ester of 3 β ,28-dihydroxy-12-oleanen-11-one (procerenone) from *Omphalocarpum procerum*,³¹⁷ and the oleoyl ester 12,18-oleanadien-3 β -ol.³¹⁸ Leonurusoleanolides E **692–J** **697**, from *Leonurus japonicus*, are further esters of the 19(18 $\rightarrow$ 17)-abeo-28-noroleanane phlomis-tetraol B.³¹⁹

Malaytaxerate **698**, from *Sapium baccatum*, is a ring-E contracted nortaraxerane derivative.³²⁰ *Davidia involucrata* is the





source of the ring-A contracted nortaraxeranes davinvolumols A **699** and B **700** and davinolunone A **701** together with the intact taraxeranes davinolunones B **702** and C **703**.³²¹ The structure of the 2,3-secotaraxerane pycanocarpine **704**, from *Pleiocarpa pycnantha*, was established by X-ray analysis.³²² A taraxerane saponin with a known genin has been isolated from the roots of *Clematis argentea*.³²³ The structures of

both the multiflorane derivative turraoic acid **705** and turraenine **706**, from a *Turraea* species, were also established by X-ray analysis.³²⁴ Turraenine **706** is an unusual nitrogen-containing dimeric normultiflorane. Three multiflorane esters **707–709** have been isolated from seeds of *Cucurbita maxima*.³²⁵ The glutinane derivative klorol A **710**, from *Kleinia odorata*, is 5 α -hydroxydebdropanoxide.³²⁶ The authors

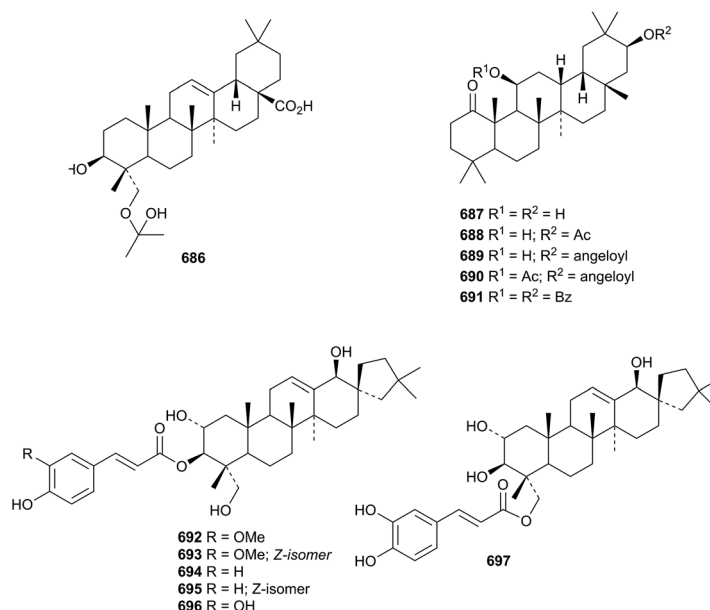


Table 1 Trivial names and sources of new oleanane saponins with known genins

Trivial name	Plant species	Reference
Angulasaponins A–D	<i>Vigna angularis</i>	261
Aristatosides A–C	<i>Cephalaria aristata</i>	262
Bafouoside C	<i>Cussonia bancoensis</i>	263
Caspicaosides E–K	<i>Gliditsia caspica</i>	264
Celosins H–J	<i>Celosia argentea</i>	265
(celosin I is a duplicate name)		
Clematiunicinosides A–H	<i>Clematis uncinata</i>	266
Comastomasaponins A–H	<i>Comastoma pedunculatum</i>	267
Conyzasaponins R, S	<i>Conyza japonica</i>	268
Conyzasaponins T, U	<i>Conyza japonica</i>	269
Davisianosides A, B	<i>Cephalaria davisiana</i>	270
Flaccidosides V–VII	<i>Anemone flaccida</i>	271
Grindeliosides A–C	<i>Grindelia argentina</i>	272
Ilexasprellanosides D–F	<i>Ilex asprella</i>	273
Ilexpublesnin R	<i>Ilex pubescens</i>	274
Leptocarposide	<i>Ludwigia leptocarpa</i>	275
Licorice-saponin O4	<i>Glycyrrhiza glabra</i>	252
Lobeliodosides A–D	<i>Lysimachia lobelioides</i>	276
Lonicerosides F–J	<i>Lonicera japonica</i>	277
Officinoterpenoside D	<i>Rosmarinus officinalis</i>	278
Oleiferosides A–H	<i>Camellia oleifera</i>	279
Oleiferoside B ₁	<i>Camellia oleifera</i>	256
Paradoxosides A–E	<i>Vitellaria paradoxa</i>	280
Pittangretosides N, O, P	<i>Pittosporum angustifolium</i>	281
Pittangretosides A ₁ , B ₁ , J, K, M, Q–Z	<i>Pittosporum angustifolium</i>	282
Potentillanoside F	<i>Potentilla anserina</i>	283
Salbiges A, B	<i>Salicornia herbacea</i>	284
Sarconepaside C	<i>Sarcopyramis nepalensis</i>	285
Schefflesides A–H	<i>Schefflera kwangsiensis</i>	286
Schefflesides I–L	<i>Schefflera kwangsiensis</i>	287
Sieboldisaponin B	<i>Stachys sieboldii</i>	288
Simenoside A	<i>Gypsophila simonii</i>	289
Schekwangsiensides A–E	<i>Schefflera kwangsiensis</i>	223
Uralsaponins M, N, O, U, V, Y	<i>Glycyrrhiza uralensis</i>	253
Yemuosides YM ₃₆ , YM ₃₇	<i>Stauntonia chinensis</i>	290
Yunganoside E ₃	<i>Glycyrrhiza yunnanensis</i>	243

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

Plant species	Reference
<i>Acacia auriculiformis</i>	291
<i>Anemone rivularis</i> var. <i>flore-minore</i>	292
<i>Callicarpa nudiflora</i>	293
<i>Centratherum anthelminticum</i>	294
<i>Clematis argentea</i>	295
<i>Croton lachnocarpus</i>	296
<i>Eclipta prostrata</i>	259 and 297
<i>Entada phaseoloides</i>	258
<i>Eryngium planum</i>	298
<i>Ganophyllum giganteum</i>	299
<i>Garcinia hanburyi</i>	300
<i>Gymnema sylvestre</i>	301
<i>Gypsophila arrostii</i>	302
var. <i>nebulosi</i> , <i>Gypsophila bicolor</i>	
<i>Manilkara hexandra</i>	303
<i>Melissa officinalis</i>	304
<i>Momordica charantia</i>	305
<i>Paonychia anatolica</i> ssp. <i>balansae</i>	306
<i>Patrinia scabra</i>	307
<i>Polycarpha corymbosa</i> var. <i>eriantha</i>	308
<i>Polygala tenuifolia</i>	309
<i>Pycnanthemum flexuosum</i>	310
<i>Sapindus mukorossi</i>	311
<i>Silene rubicunda</i>	312
<i>Silphium asteriscus</i>	260
<i>Tremastelma palaestinum</i>	313
<i>Xanthoceras sorbifolia</i>	314

7. The ursane group

The antitumour activity of ursolic acid has been highlighted.^{334,335} The unusual 9,25-cyclo-12-ursen-3 β -ol **721** has been reported from Cameroonian brown propolis.¹¹⁰ The ring-A modified ursanes davinvolunic acids **A 722**, **B 723** and **C 724** have been isolated from *Davidia involucrata*.³³⁶ Davinvolunic acid **C 724** contains an unusual methyl hemiacetal. The leaves of *Vitex negundo* var. *cannabifolia* are the source of cannabifolins **A 725**, **C 726** and **D 727**.²⁴⁵ The structure of cannabifolin **A 725** was confirmed by X-ray analysis to have *cis*-fused rings C and D. Two ursane derivatives **728** and **729**, with the unusual 20 α H-configuration, have been identified in *Ilex cornuta*.³³⁷ Asprellols **A 730** and **B 731**, from *Ilex asprella*, are 24-norursane derivatives.²⁴¹ Urs-12-ene-2 α ,3 β ,19 α -triol **732**, from *Terminalia arjuna*, has been named torment.³³⁸

Other simple ursane derivatives include cymosic acid **733** from *Rosa cymosa*,³³⁹ elatunic acid **734** from *Omphalocarpum elatum*,³⁴⁰ erandione **735** from *Ricinus communis*,³⁴¹ klodorone **A 736** from *Kleinia odora*,³²⁶ meyanthic acid **737** and urs-12-ene-2 α ,3 α ,19 α ,24,28-pentol **738** from *Meyna (Vangueria) spinosa*,³⁴² uncarinic acids **H 739** and **I 740** from *Uncaria rhynchophylla*,²⁴⁶ 3 α ,6 β ,19 α -trihydroxyurs-12-en-28-oic acid **741** from *Mitragyna diversifolia*,³⁴³ 3 β ,20 β -dihydroxyursan-28-oic acid **742** from *Malus domestica*,³⁴⁴ 3 α ,11 β -dihydroxyurs-12-en-28-oic acid **743**

draw klodorol **A 710** with incorrect stereochemistry at C-13 and C-14.

The structures of the friedelane triterpenoids found in *Maytenus* species have been summarised.³²⁷ Glaucalactone **B 711** is a 29-norfriedelane 27,20-lactone from *Caloncoba glauca*¹⁰⁴ and hainanenone **712** is a 23-norfriedelane derivative from *Drypetes hainanensis*.³²⁸ The 23,24-dinorfriedelane pristimerol **713**, from *Celastrus aculeatus*, has been given the same name as the reduction product of pristimerin.³²⁹ Galphimines **K 714** and **L 715** are further 3,4-seco-derivatives from *Galphimia glauca*.³³⁰ Other friedelane derivatives include salacinin **C 716** from *Salacia hainanensis*,²¹⁶ the 3-ketones **717** and **718** from *Maytenus robusta*³³¹ and the esters **718** and **720** from *Drypetes hoanensis*.³³² The structure of **717** was confirmed by X-ray analysis. The known norfriedelane celastrol from *Triperygium wilfordii* has shown interesting antitumour activity.³³³



from *Gentiana veitchiorum*,³⁴⁵ three compounds **744–746** from *Zizyphus jujuba*,³⁴⁶ three compounds **747–749** from *Microtropis fokiensis*²³⁶ and nine ursanes **750–758** from *Salvia argentea* var. *aurasiaca*.²⁵⁰

Centrellasaponin J, from *Cenrella asiatica*, has the new ursane genin **759**.²⁵⁴ Further new ursane genins include **760** from *Callicarpa nudiflora*,²⁹³ **761** from *Clematis argentea*,³²³ **762** and **763** from *Panax ginseng*⁶¹ and **764–766** from *Schefflera heptaphylla*.³⁴⁷

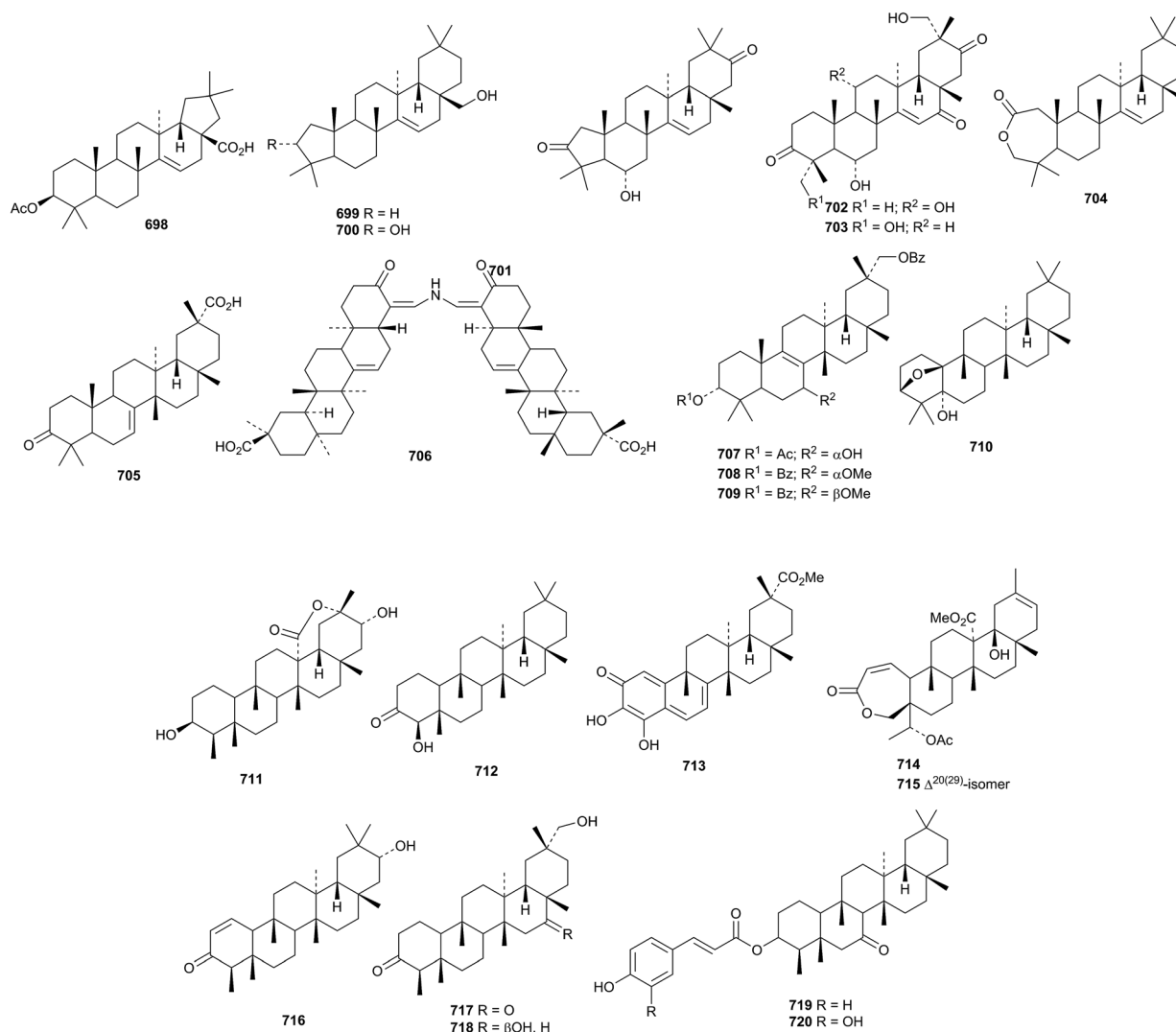
Named ursane saponins with known genins include fag-onoside A from *Fagonia cretica*,³⁴⁸ grandoside from *Syzygium grande*,³⁴⁹ ilexosaponins G and H from *Ilex pubescens*,³⁵⁰ ilexasprellanosides A–C from *Ilex asprella*,²⁷³ ilexpubescensins N–Q (Q is the same as zygoeichwaloside H isolated in 2007(ref. 351)) from *Ilex pubescens*,²⁷⁴ officinoterpenoside C from *Rosmarinus officinalis*,²⁷⁸ potentillanosides A–E²⁸³ and G³⁵² from *Potentilla anserina*, sieboldisaponins A³⁵³ and C²⁸⁸ from *Stachys sieboldii*, and zygofaboside C from *Zygo-phyllum fabago*.³⁵⁴ Unnamed saponins with known genins have been isolated from *Eucommia ulmoides*,³⁵⁵ *Ilex*

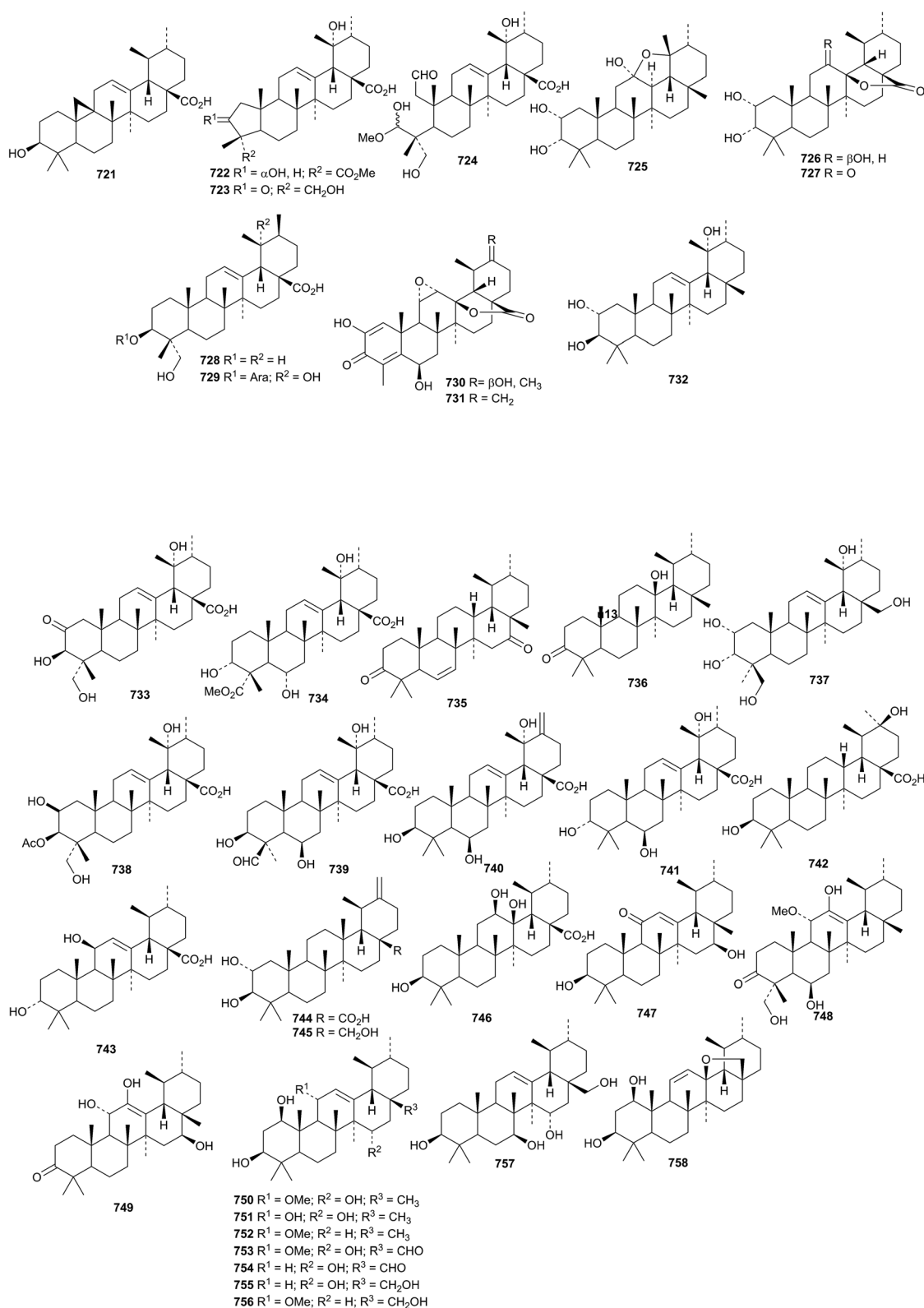
cornuta,^{356,357} *Melissa officinalis*,³⁰⁴ *Schefflera heptaphylla*³⁴⁷ and *Vitex negundo*.³⁵⁸

Further ursane esters include the acetate **767** from *Boswellia sacra*,²¹⁷ the acetate **768** from *Mentha suaveolens*,²³⁸ ferulates **769** and **770** from *Ampelopsis japonica*.³⁵⁹ and the palmitate **771** from *Inula cappa*.³⁶⁰ Flaccidoside IV is a taraxastane saponin with a known genin from *Anemone flaccida*.²⁷¹ The unusual 3 β -acetoxy-22,28-cyclobauer-7-ene **772** has been identified in *Ixeris chinensis*.³⁶¹

8. The hopane group

The 2,3-seco-21 α H-hopane derivatives **773** and **774** have been isolated from *Megacodon stylophorus*.³⁶² The structure of **773** was confirmed by X-ray analysis. Ribosylhopane **775**, which has been postulated as a precursor of C₃₅ bacteriohopanepolyols in *Streptomyces coelicolor*, has now been found in blocked mutants.³⁶³ Two fernane derivatives **776** and **777** have been reported from *Lonicera quinquelocularis* however the structures are drawn lacking C-28 in the reference.³⁶⁴ A fernane saponin, from *Spergula fallax*, has the new genin **778**.³⁶⁵



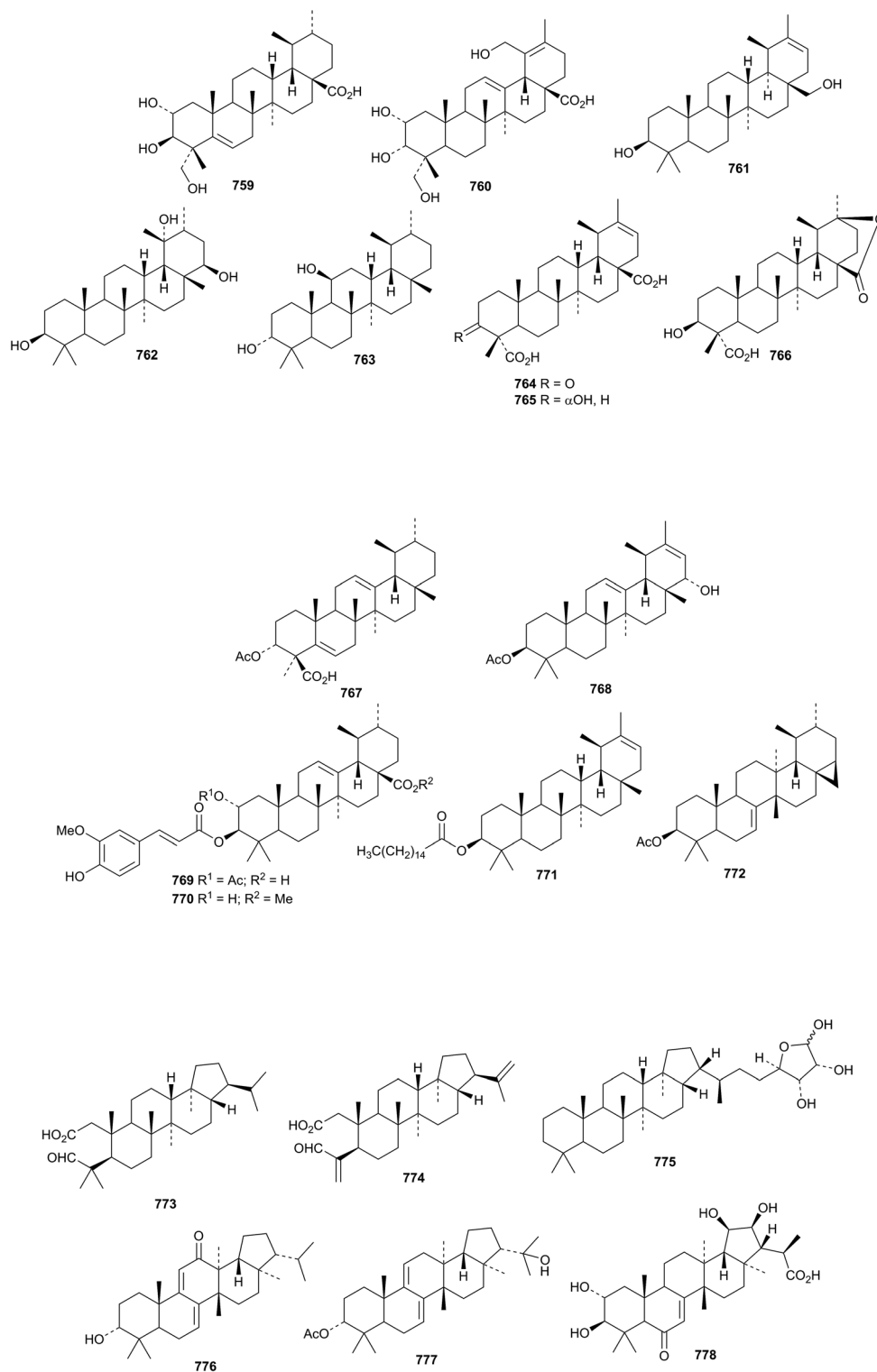


9. Miscellaneous compounds

The unlikely structure 779 has been assigned to a triterpene rhamnoside from *Sesbania aculeata*.³⁶⁶ Three gammacerane

saponins, from *Spergula fallax*, have the new genin **780**.³⁶⁵ *Lycopodium japonicum* is the source of the serratane derivatives lycojaponicumins A **781**–**F 786** (ref. 367) and the formate esters **787** and **788**.³⁶⁸

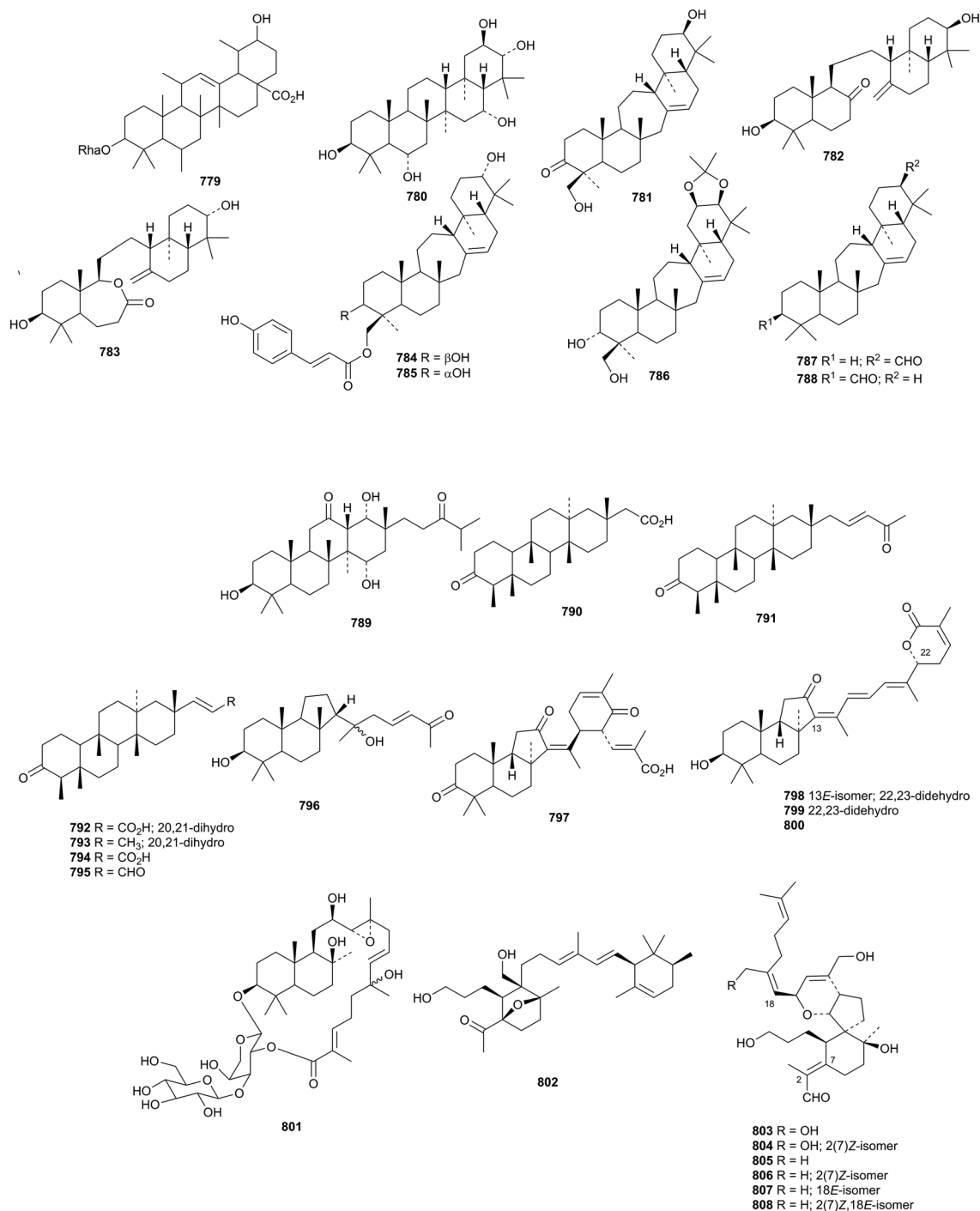




Fatsioside A, from fruit of *Fatsia japonica*, has the new bacchane genin **789**.³⁶⁹ The structure of the norshionane derivative astershionone A **790**, from *Aster tataricus*, was established by X-ray analysis.³⁷⁰ The related astershionones B **791**–**795** were

also isolated. Opaciniol A **796**, from *Garcinia opaca*, is a hex-normalabaracane derivative.⁴⁸ Further isomalabaricane derivatives, jaspiferins C **797**–**799**, **800** have been found in the South China Sea sponge *Jaspis stellifera*.³⁷¹ Phyteujaposide **801** is an





unusual polypodane cyclic saponin from *Phyteuma japonicum*.³⁷² Further iridal triterpenoids from *Iris* species include irisgermanone **802** from *Iris germanica*³⁷³ and spiroiridotectals A **803**–F **808** from *Iris tectorum*.³⁷⁴

10. Conflicts of interest

There are no conflicts of interest.

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