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REVIEW

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Triterpenoids

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Covering 2014. Previous review: *Nat. Prod. Rep.*, 2017, **34**, 90–122

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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.

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] antiviral[6] and against neurodegenerative disorders.[14] As many of the active compounds are saponins there has been an interest in their synthesis[15] and biosynthesis.[16] Reviews have also appeared covering triterpenoids found in *Astragalus* species,[17] *Gymnema sylvestre*,[18] *Panax* species,[19,20] *Sapindus* species[21] and *Siraitia grosvenorii*[22] and plants of the Schisandraceae.[23–25] Triterpenoid biosynthesis in plants[26] and the mechanisms of oxidosqualene cyclases[27] 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]

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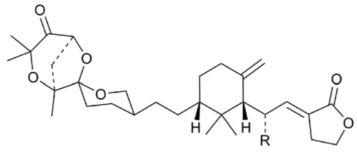
3. The lanostane group

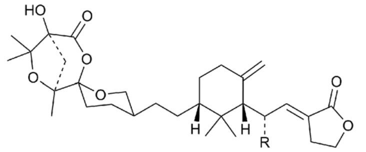
The flow of *Ganoderma* lanostanes continues.[30] *Ganoderma boninense* is the source of ganoboninketals A **18**, B **19** and C **20**.[31] Fornicatins D **21**, E **22** and F **23** and ganodercochlearins A **24**, B **25** and C **26** are constituents of *Ganoderma cochlear*.[32] The structure 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 XL_1 **30** and XL_2 **31**, 20-hydroxyganoderic acid AM_1 **32**, ganoderenic acid AM_1 **33** and ganoderesin C **34** from *Ganoderma theaecolum*,[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]

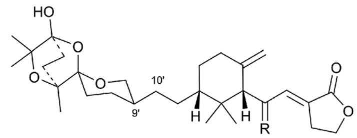
The mushroom *Inonotus obliquus* is a rich source of the 21,24-cyclolanostanes inonotusols A **39**–E **43**.[40] They are accompanied by inonotusols F **44** and G **45**. Inonotusols B **40**, D **42** and E **43** have unusual configurations at C17 and inonotusol F **44** has an unusual configuration 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**



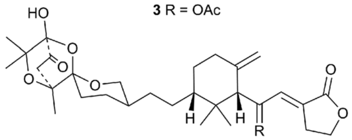
1 R = OH
2 R = H
3 R = OAc



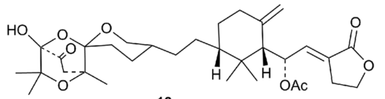
4 R = H
5 R = OH
6 R = OAc



7 R = αOH, H
8 R = αOAc, H
9 R = H_2; $\Delta^{9'}E$
10 R = αOAc, H; $\Delta^{9'}E$
14 R = O
16 R = H_2



11 R = αOH, H
12 R = αOAc, H
15 R = O



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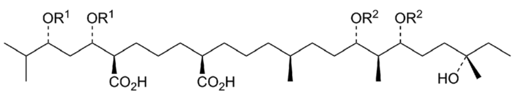
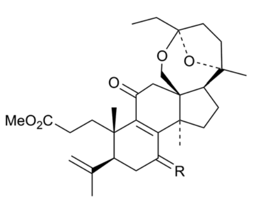
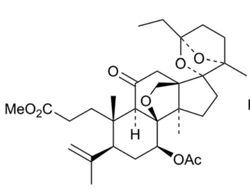


17 R^1 = Glc*p*-(1->6)-Glc*p*-(1->6)-Glc*f*; R^2 = Glc*p*-(1->6)-Glc*p*-(1->6)-Glc*p*



18 R = βOAc, H
19 R = O



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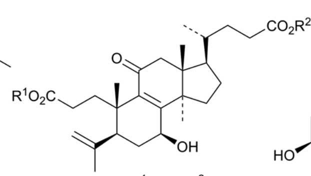
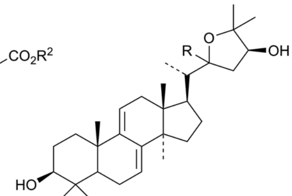
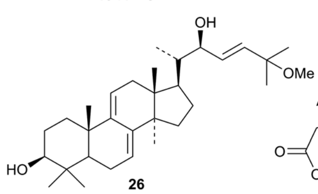


21 R^1 =Me; R^2 = H
22 R^1 =H; R^2 = Me
23 R^1 = R^2 = Me



24 R = βH
25 R = αH



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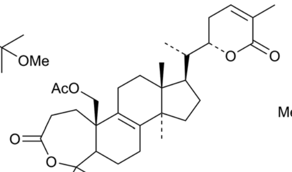

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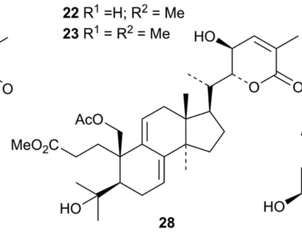

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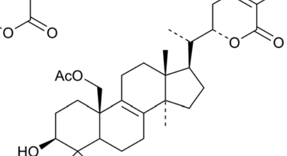

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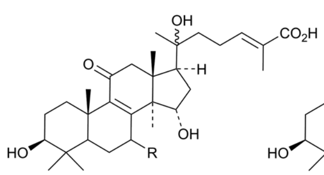
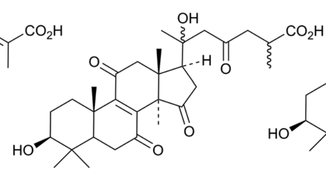
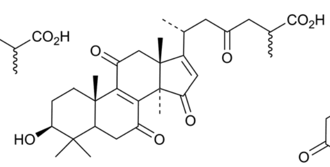


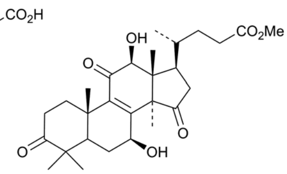
30 R = βOH
31 R = αOH



32



33 $\Delta^{17(20)}$
34



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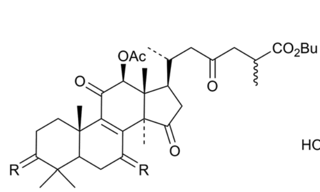
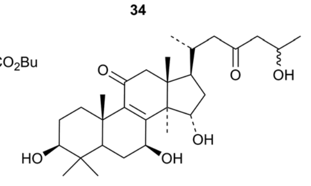
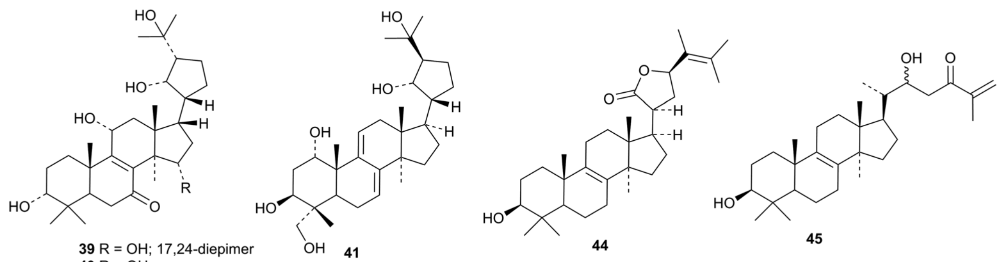


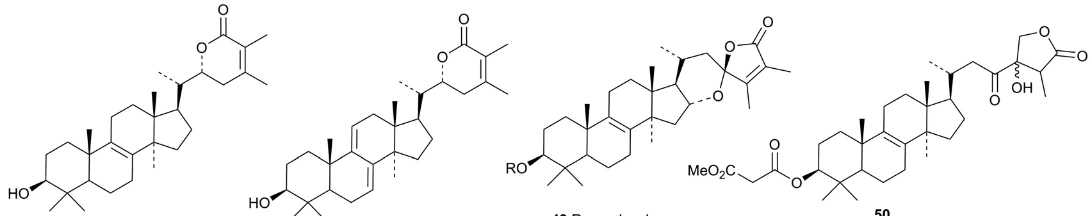
36 R = βOH, H
37 R = O



38



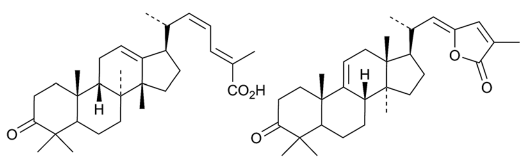
39 R = OH; 17,24-diepimer
40 R = OH
43 R = H
41
42 17,24-diepimer
44
45



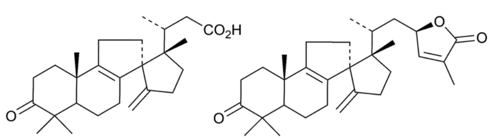
46
47
48 R = malonyl
49 R = H; 7,11-didehydro
50

and C **50**, from the fruiting body of *Hexagonia tenuis*, also have an extra carbon at C-24.[42]

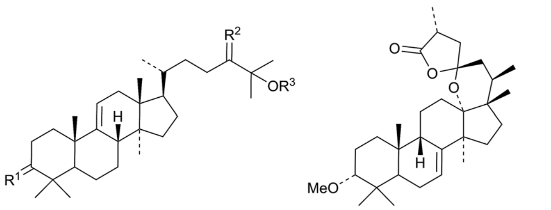
The protostane **51**, from the bark of *Garcinia ferrea*, is accompanied by the lanostanes garciferolides A **52** and B **53**.[43] Two rearranged lanostanes **54** and **55** have been isolated from *Abies nukiangensis* together with compounds **56–59**.[44] The structures of **54** and the known **60** were confirmed by X-ray analyses. 3-*O*-Methylabiesatrine A **61** is a rearranged lanostane from *Abies delavayi*.[45]



51
52
53 22*E*-isomer



54
55



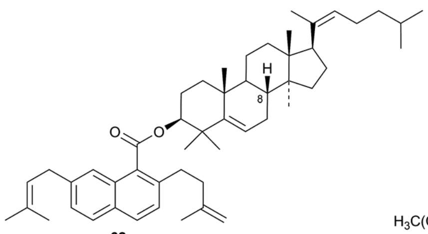
56 R^1 = αOMe, H; R^2 = αOH, H; R^3 = H
57 R^1 = αOH, H; R^2 = O; R^3 = H
58 R^1 = βOAc, H; R^2 = αOH, H; R^3 = H
59 R^1 = βOH, H; R^2 = αOH, H; R^3 = Et
60 R^1 = O; R^2 = αOH, H; R^2 = H
61

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 garcihombronane K isolated from *Garcinia hombroniana* in 2013.[49] The rearranged lanostane **69** has been isolated from *Garcinia hombroniana*.[50]

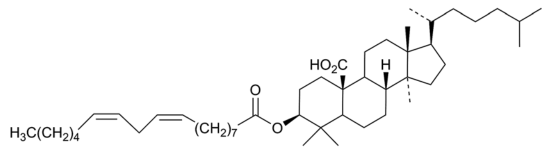
Other lanostanes include manglanostenoic acids A **70**–D **73** from *Mangifera indica* var. Fazli,[51] myrrhalanostenyl acetate **74**, myrrhalanostenol **75**, and myrrhalanostenoic acid **76** from the oleoresin of *Commiphora myrrha*,[52] 3β-hydroxylanosta-9(11),24-dien-21-oic acid **77** and its methyl ester **78** from *Protorhus 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 A_1–A_6, 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.

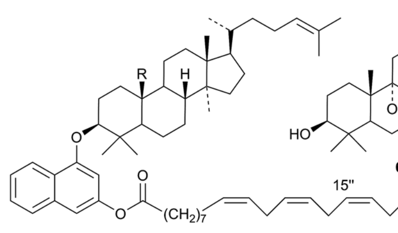
Variegatusides C–F have been isolated from *Stichopus variegates*.[67] Only variegatuside C has a new genin **93**. Holothurins D and E, with the new genin **94** and holothurinoside X, with the new genin **95**, are constituents of *Holothuria lessoni* together



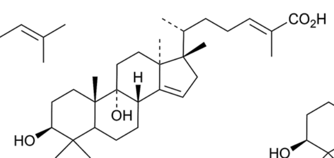
62
63 8,9-didehydro; 20*R*,22-dihydro



64



65 R = CH_3; 15'',16''-dihydro
66 R = CO_2H; 24,25-dihydro



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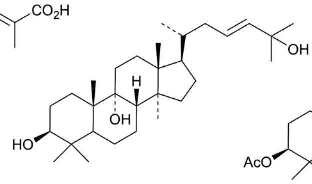

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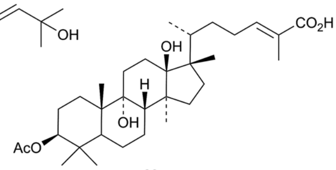

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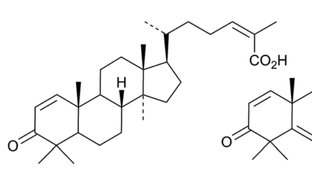
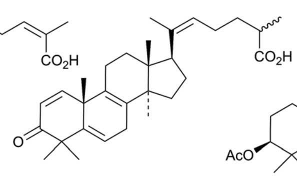
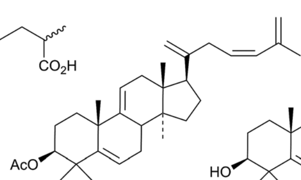


70
73 5,6-didehydro



71
72 5α,6-dihydro; Δ^7-isomer



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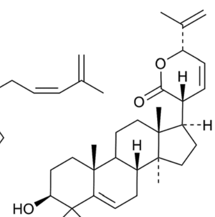

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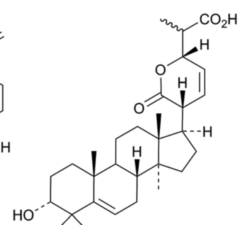

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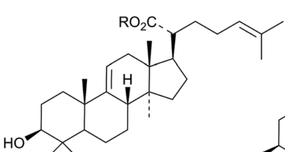
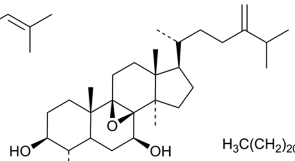


77 R = H
78 R = Me



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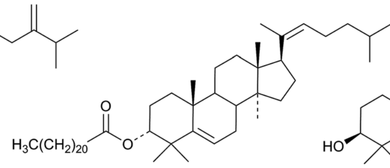

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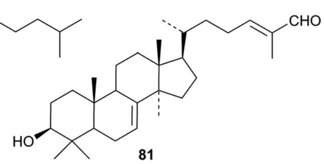

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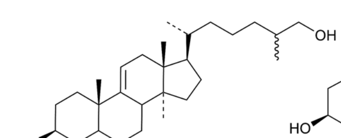

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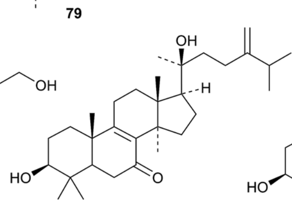

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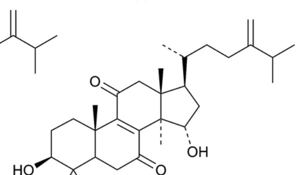

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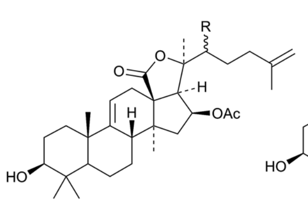
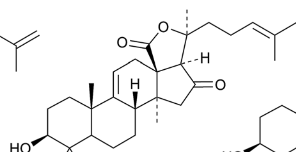


85 R = OAc; 25,26-dihydro
86 R = OAc
87 R = H



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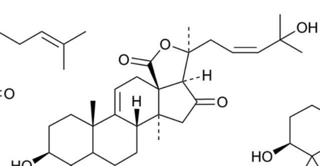

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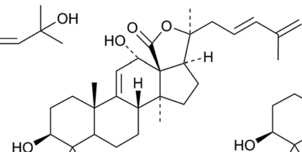

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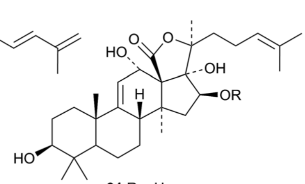
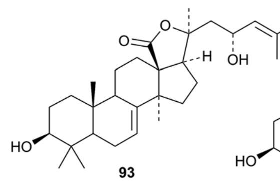


91 R = H
92 R = Ac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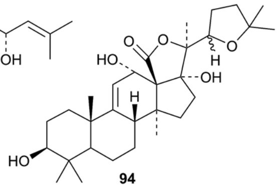
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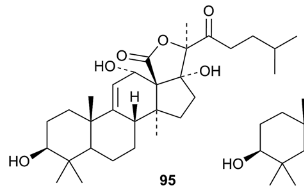
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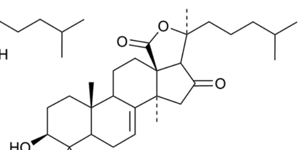
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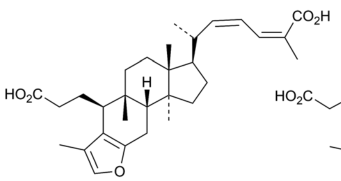
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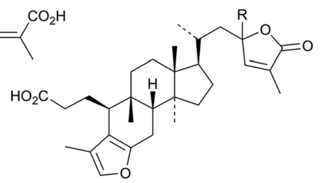
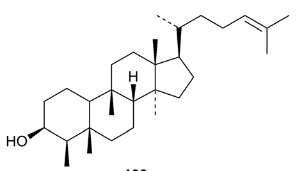

98 R = βH
99 R = αH


100

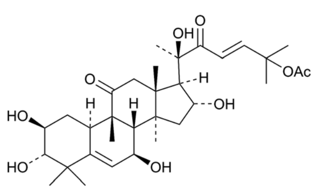
with holothurinosides Y and Z with known genins.[68] The new genin **96** has been reported for pseudocnoside A from *Pseudocnus dubiosus leoninus*.[69] Holostane saponins with known genins include cucumariosides F_1 and F_2 from *Eupentacta fraudatrix*,[70] kolgaosides A and B from *Kolga hyalina*,[71] stichloroside F from *Stichopus chloronotus*[72] and violaceusosides 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] *Empetrun 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 hemslepenside 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 sonorae*.[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 *Cucumus sativus*.[87] The unlikely stereochemistry of **125** has been proposed for a compound from the leaves and twigs of *Euonymus alatus*.[88]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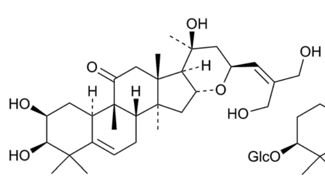
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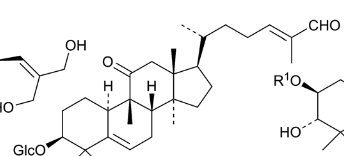
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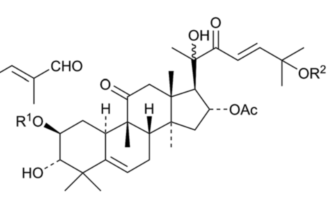
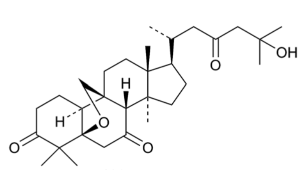

104 $R^1 = R^2 = H$
105 R^1 = β-*D*-Glc; R^2 = Ac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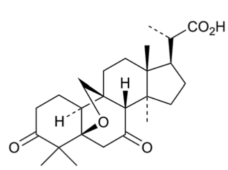
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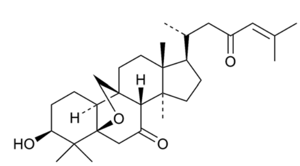
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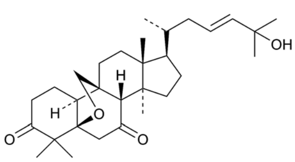
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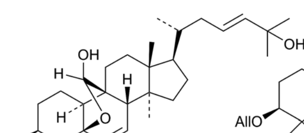
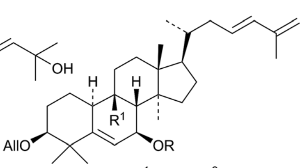
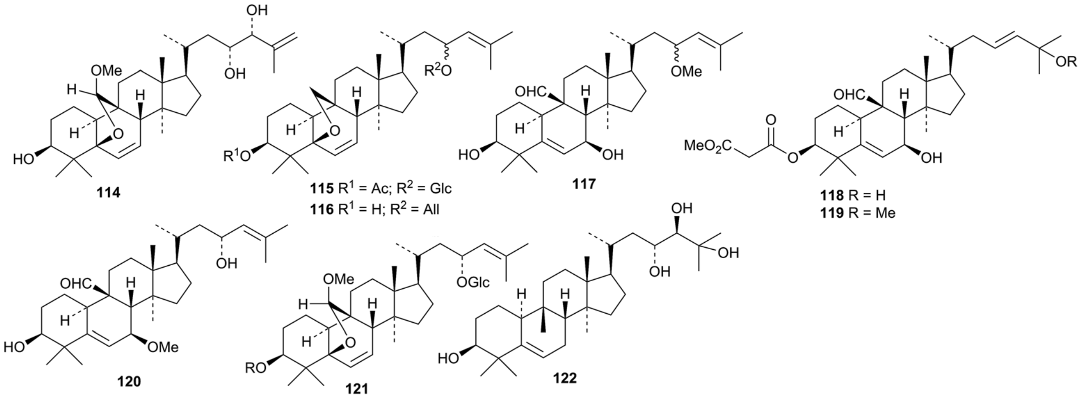
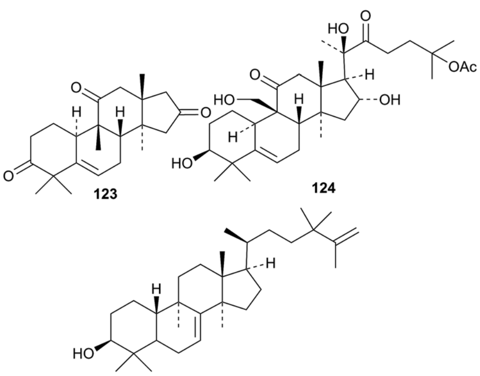

110 R = Glc
111 R = All


112 $R^1 = CH_3$; R^2 = Me
113 R^1 = CHO; R^2 = H



114; 115 R^1 = Ac; R^2 = Glc; 116 R^1 = H; R^2 = All; 117; 118 R = H; 119 R = Me; 120; 121; 122

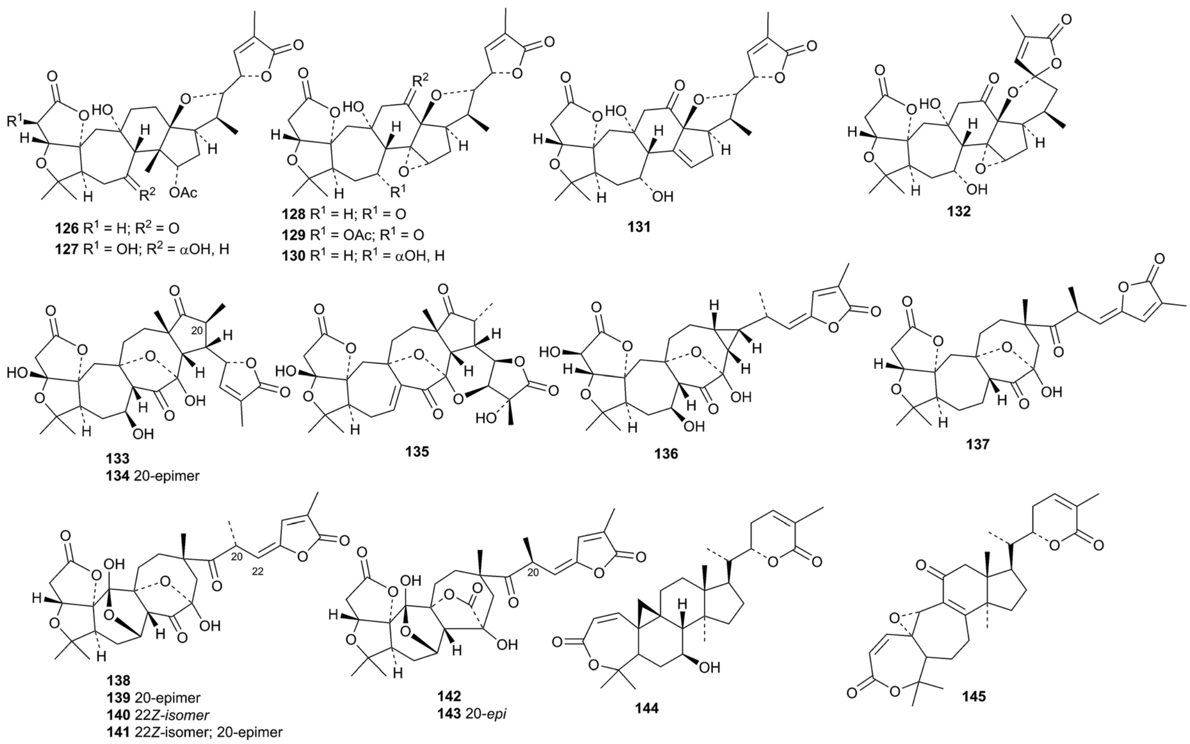


123; 124; 125

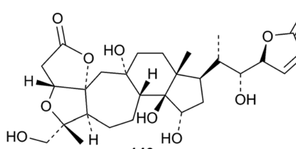
An impressive list of new compounds from *Schisandra chinensis* includes wuweizidilactones J **126**–P **132**, schindilactones I **133**, J **134** and K **135**, preschisanartanin N **136** and schisdilactone J **137**.[89] Lancifonins A **138**–F **143** are new compounds from *Schisandra lancifolia*.[90] *Schisandra sphenanthera* is the source of schisphendilactones A **144** and B **145**.[91] The structures of lancifonin A **138** and schisphendilactone A **144** were confirmed by X-ray analyses.

Other new compounds include heteroclitalactone N **146** from the stems of *Kadsura heteroclitus*[92] and micrandiactone H **147** from *Kadsura coccinea*.[93] The reported stereochemistry for micrandiactone 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.



126 R^1 = H; R^2 = O; 127 R^1 = OH; R^2 = αOH, H; 128 R^1 = H; R^1 = O; 129 R^1 = OAc; R^1 = O; 130 R^1 = H; R^1 = αOH, H; 131; 132; 133; 134 20-epimer; 135; 136; 137; 138; 139 20-epimer; 140 22*Z-isomer*; 141 22*Z*-isomer; 20-epimer; 142; 143 20-*epi*; 144; 145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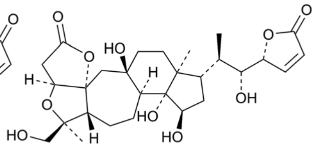
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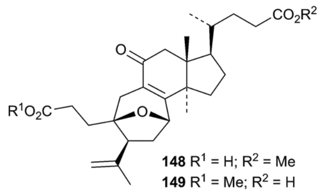
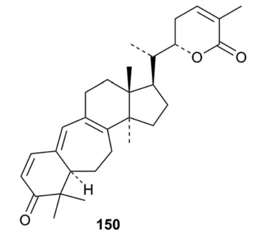

148 R^1 = H; R^2 = Me
149 R^1 = Me; R^2 = H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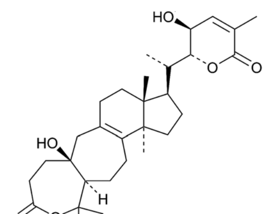
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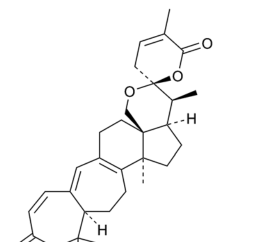
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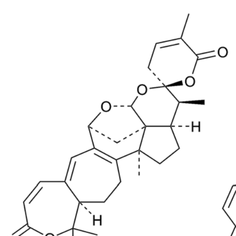
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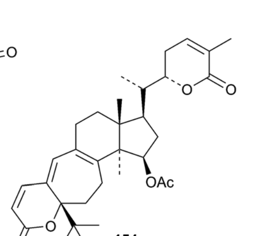

154

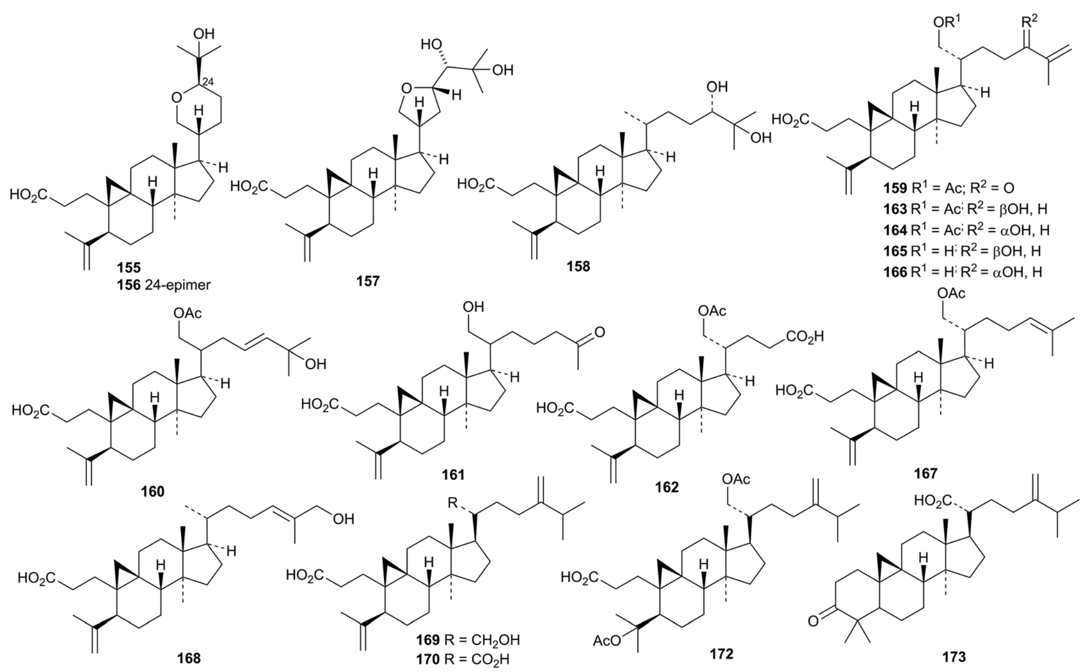
An impressive number of side-chain variations is to be found in the 3,4-secocycloartanes lithocarpic acids A **155**–N **168** from *Lithocarpus polystachyus*.[94] Lithocarpic acids O **169**–S **173** are further examples from the same source.[95] The structure of lithocarpic acid A **155** was confirmed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

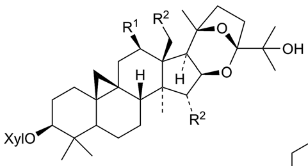
The three cycloartane xylosides **174–176**, from *Beesia calthaefolia*, all have new genins.[96] New compounds from *Cimicifuga* species include the rearranged cycloartanes yunnanterpene G **177** and 12,18-didehydro-26-methoxyacetol **178**, isodahurinol 24-acetate 25-methyl ether **179**, 15,16-secoshengmanol 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-norcycloartanes 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]

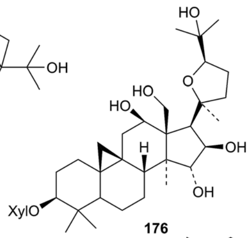
Other new cycloartanes include caloncobic acid C **208** and caloncobalactone C **209** from the leaves of *Caloncoba glauca*,[104] the glucoside rhizostyloside **210**, with a new genin, from *Rhizophora stylosa*,[105] compound **211** from *Cassia italica*,[106] and the tetrol **212** from the leaves 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


155
156 24-epimer
157
158
159 R^1 = Ac; R^2 = O
163 R^1 = Ac; R^2 = βOH, H
164 R^1 = Ac; R^2 = αOH, H
165 R^1 = H; R^2 = βOH, H
166 R^1 = H; R^2 = αOH, H
160
161
162
167
168
169 R = CH_2OH
170 R = CO_2H
171 R = CH_2OAc
172
173



174 R[1] = H; R[2] = OH
175 R[1] = OH; R[2] = H



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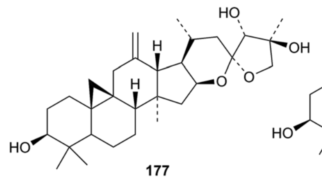

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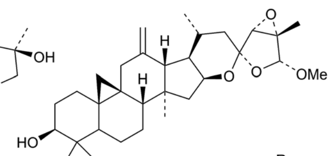

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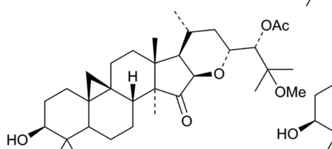

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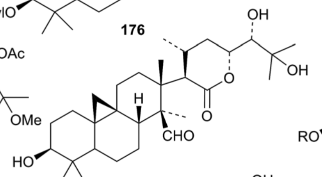
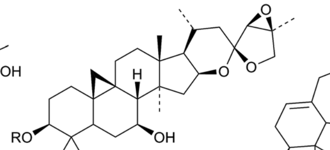
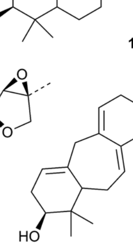


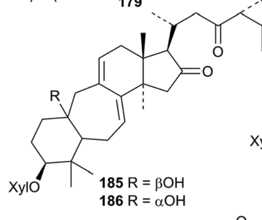
180



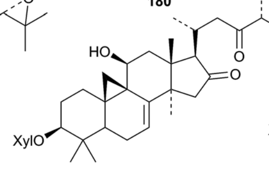
181 R = Ara
182 R = Xyl



183 R = αOH
184 R = βOH



185 R = βOH
186 R = αOH



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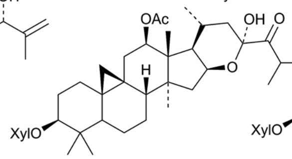

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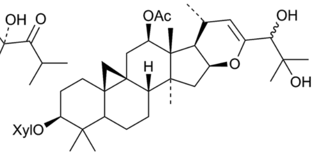

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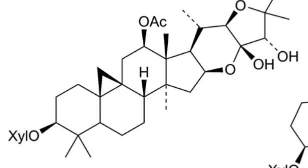

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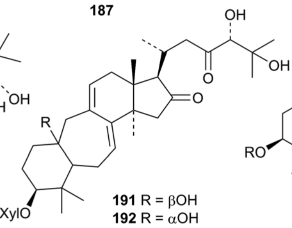
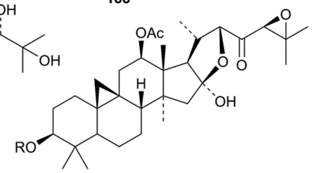
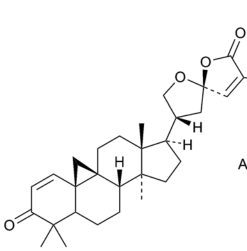


191 R = βOH
192 R = αOH



193 R = Gal
194 R = Xyl; 7,8-didehydro



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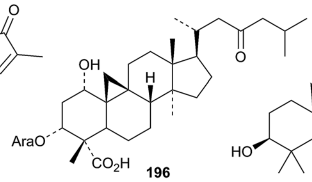

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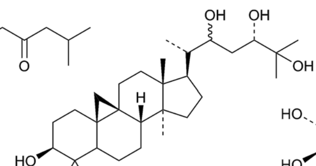

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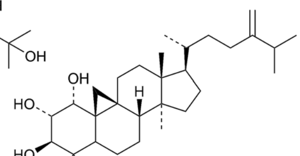

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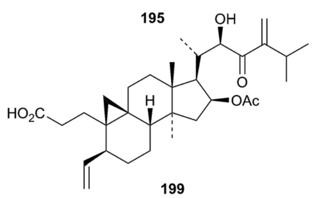

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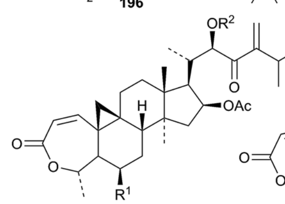
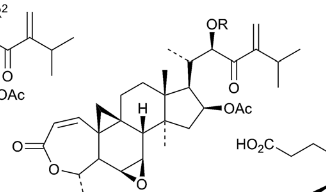
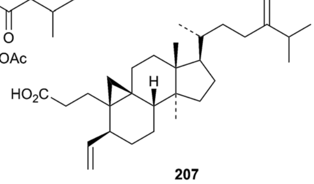


200 R[1] = R[2] =H
201 R[1] = H; R[2] = Ac
202 R[1] = OH; R[2] = H
203 R[1] = OH; R[2] = Ac
204 R[1] = R[1] = H; 4,28-didehydro



205 R = H
206 R = Ac



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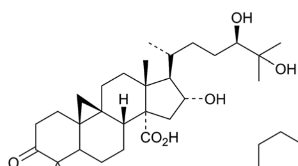

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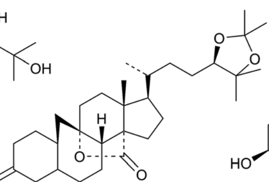

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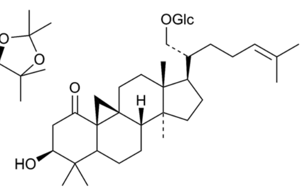

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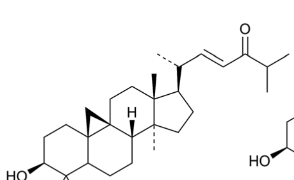

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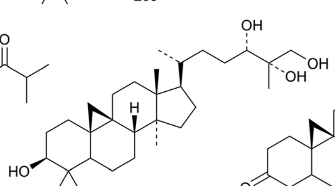

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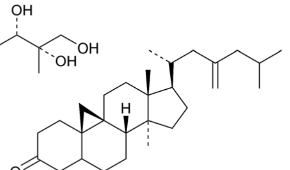

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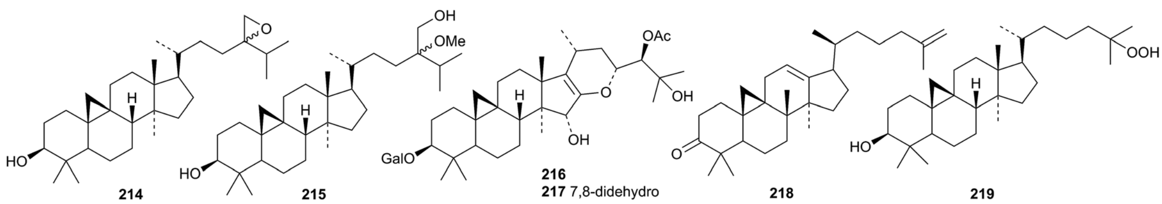


214 215 216 217 7,8-didehydro 218 219

galactopyranosides but drawn as furanosides.[99] Cycloarta-12,25-dien-3β-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 calthaefolia*,[113] *Cimicifuga foetida*[114] and *Euphorbia boissierana*.[115]

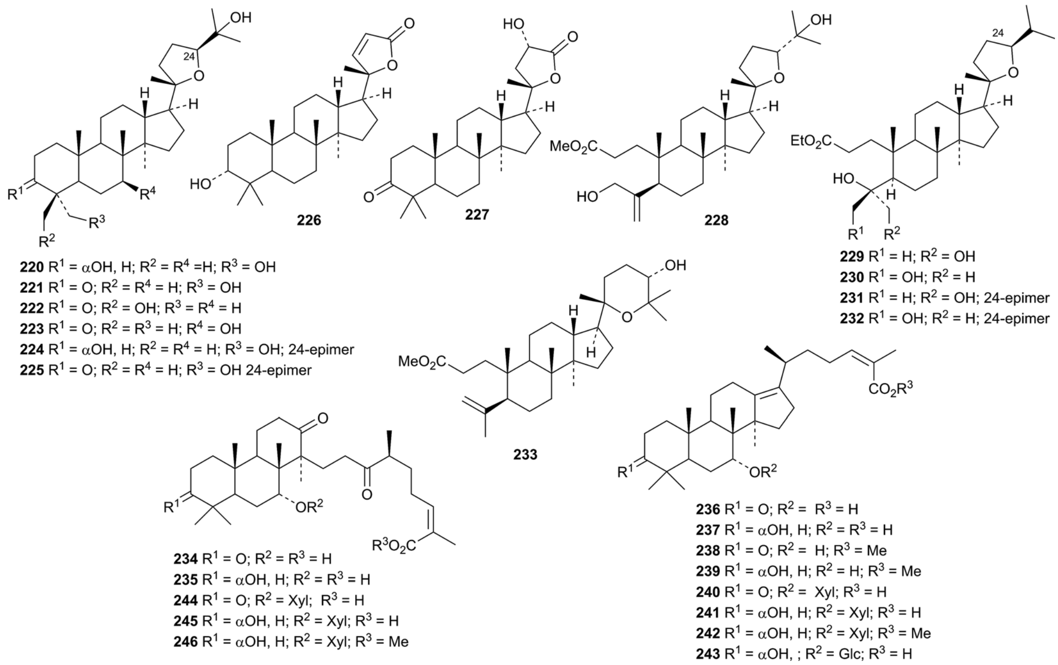
4. The dammarane group

An interesting group of new dammaranes **220–233** has been reported from the stems of *Dysoxylum binecteriferum*.[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.

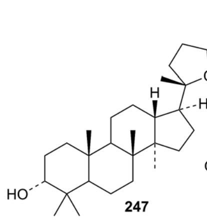
Dysomollisol **247** and dysomollisone **248** are constituents of the fruit of *Dysoxylum mollissimum*.[118] Dysomollisone **248** has been assigned an unusual rearranged side-chain. The octanor-derivative rosanol A **249** has been found in the roots of *Rosa rugosa*.[119] Horipenoids A **250**–H **257**, 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 3α-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)



220 R1 = αOH, H; R2 = R4 =H; R3 = OH
221 R1 = O; R2 = R4 = H; R3 = OH
222 R1 = O; R2 = OH; R3 = R4 = H
223 R1 = O; R2 = R3 = H; R4 = OH
224 R1 = αOH, H; R2 = R4 = H; R3 = OH; 24-epimer
225 R1 = O; R2 = R4 = H; R3 = OH 24-epimer
226 227 228
229 R1 = H; R2 = OH
230 R1 = OH; R2 = H
231 R1 = H; R2 = OH; 24-epimer
232 R1 = OH; R2 = H; 24-epimer
233
234 R1 = O; R2 = R3 = H
235 R1 = αOH, H; R2 = R3 = H
244 R1 = O; R2 = Xyl; R3 = H
245 R1 = αOH, H; R2 = Xyl; R3 = H
246 R1 = αOH, H; R2 = Xyl; R3 = Me
236 R1 = O; R2 = R3 = H
237 R1 = αOH, H; R2 = R3 = H
238 R1 = O; R2 = H; R3 = Me
239 R1 = αOH, H; R2 = H; R3 = Me
240 R1 = O; R2 = Xyl; R3 = H
241 R1 = αOH, H; R2 = Xyl; R3 = H
242 R1 = αOH, H; R2 = Xyl; R3 = Me
243 R1 = αOH, ; R2 = Glc; R3 = H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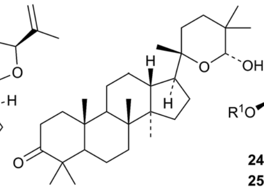
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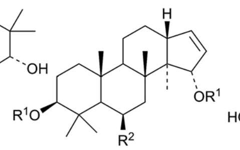
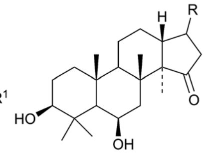
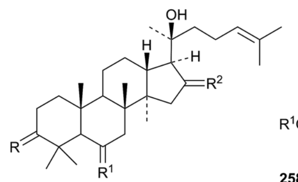
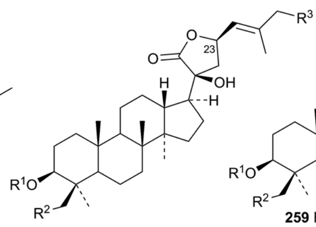
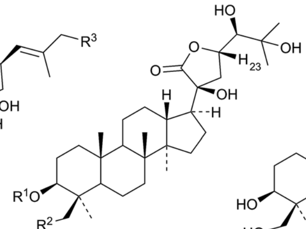
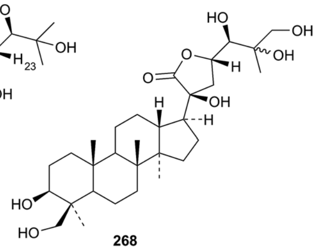

249 $R^1 = R^2 = H$
252 $R^1 = H$; $R^2 = OH$
253 $R^1 = Ac$; $R^2 = OH$


250 R = αOH
251 R = βOH


254 $R^1 = R^3 =$ βOH, H; $R^2 =$ αOH, H
255 $R^1 = O$; $R^2 =$ αOH, H; $R^2 =$ βOH, H
256 $R^1 = R^3 =$ βOH, H; $R^2 = O$
257 $R^1 =$ βOH, H; $R^2 =$ αOH, H; $R^3 = O$


258 $R^1 = Glc$; $R^2 = OH$; $R^3 = H$
261 $R^1 = R^3 = H$; $R^2 = OH$; 23-epimer
262 $R^1 = H$; $R^2 = R^3 = OH$
263 $R^1 = R^2 = R^3 = H$
264 $R^1 = R^2 = R^3 = H$; 23-epimer


259 $R^1 = Glc$; $R^2 = H$
260 $R^1 = Glc$; $R^2 = OH$; 23-epimer
265 $R^1 = H$; $R^2 = OH$
266 $R^1 = R^2 = OH$
267 $R^1 = Glc$; $R^2 = OH$
269 $R^1 = R^2 = H$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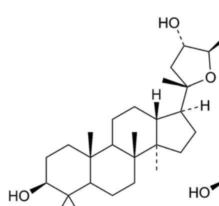
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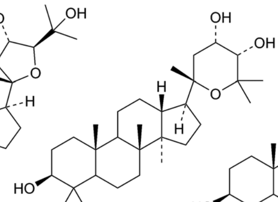
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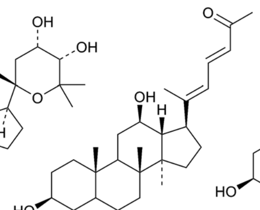
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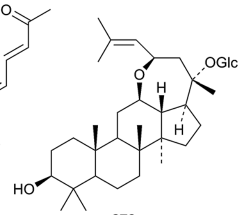
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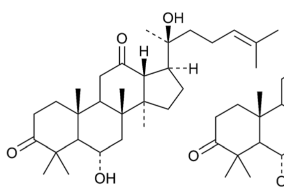
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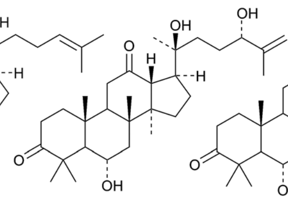
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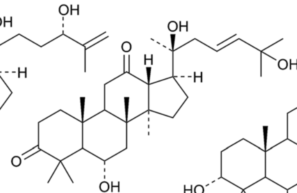
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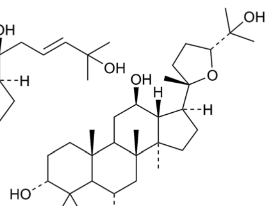
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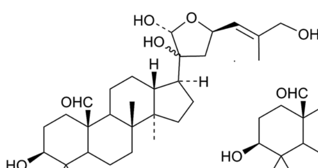
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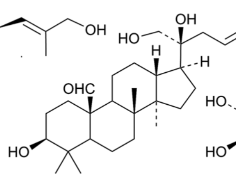
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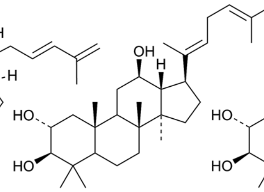
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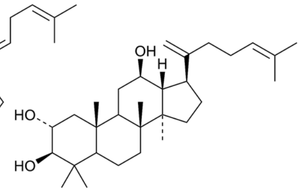
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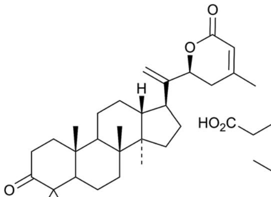
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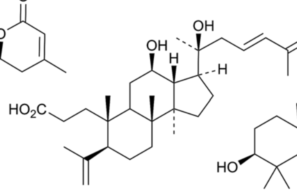
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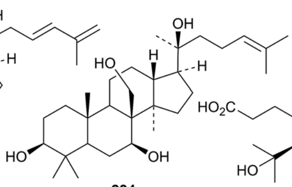
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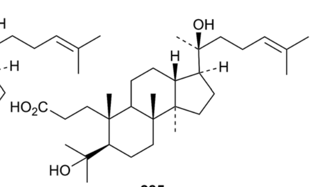
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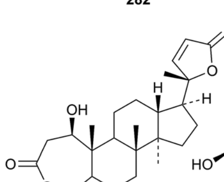
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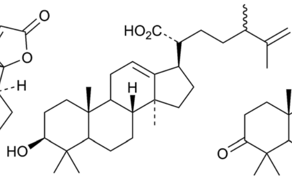
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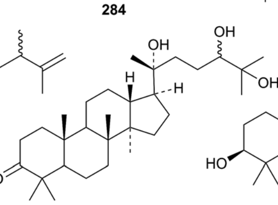
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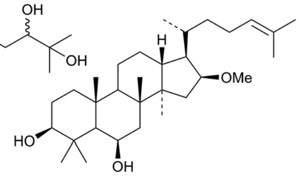
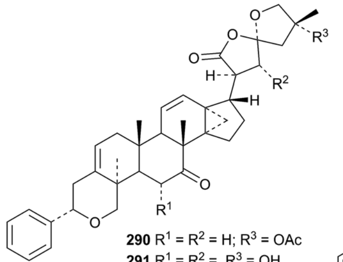
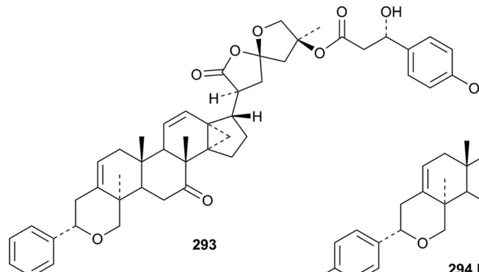

289

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] deacetybrachycarpon-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 suavis*.[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,



290 $R^1 = R^2 = H$; $R^3 = OAc$
291 $R^1 = R^2 = R^3 = OH$
292 $R^1 = H$; $R^2 = R^3 = OH$



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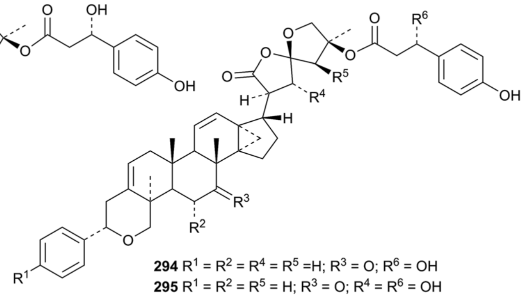
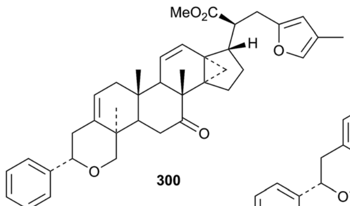


294 $R^1 = R^2 = R^4 = R^5 = H$; $R^3 = O$; $R^6 = OH$
295 $R^1 = R^2 = R^5 = H$; $R^3 = O$; $R^4 = R^6 = OH$
296 $R^1 = OMe$; $R^2 = R^4 = R^6 = H$; $R^3 = O$; $R^5 = OH$
297 $R^1 = R^5 = H$; $R^3 = O$; $R^2 = R^4 = R^6 = OH$
298 $R^1 = OMe$; $R^2 = R^4 = R^5 = H$; $R^3 = O$; $R^6 = OH$
299 $R^1 = R^2 = R^4 = R^6 = H$; $R^3 = \alpha OH, H$; $R^5 = OH$



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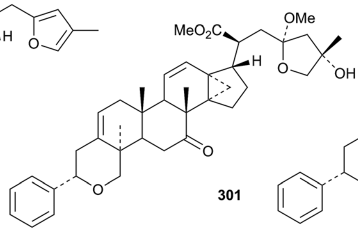

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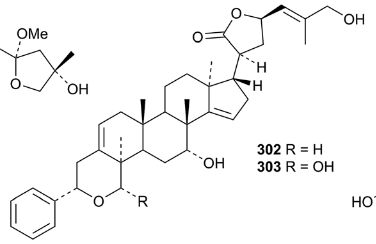
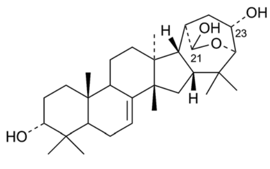
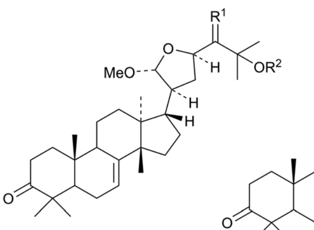


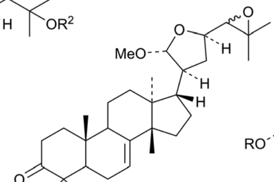
302 R = H
303 R = OH



304
305 21,23-diepimer



306 $R^1 = \beta OAc, H$; $R^2 = H$
307 $R^1 = O$; $R^2 = H$
308 $R^1 = O$; $R^2 = Me$



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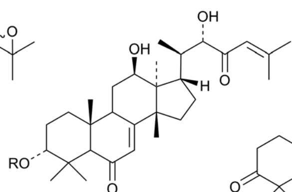
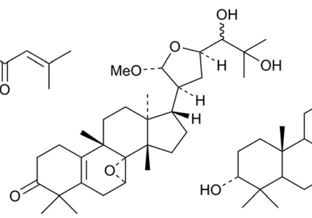


310 R = H
311 R = Ac



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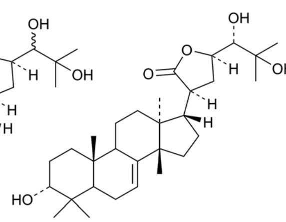

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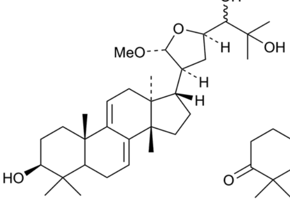

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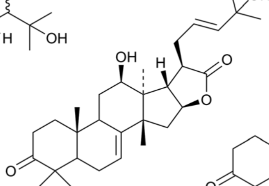

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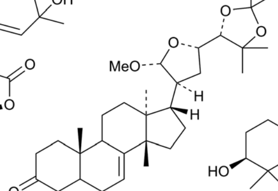

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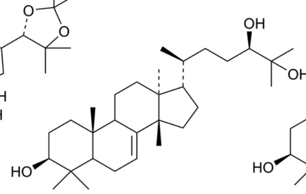

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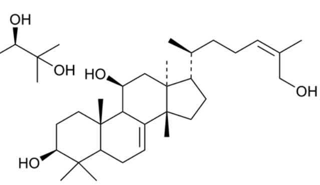

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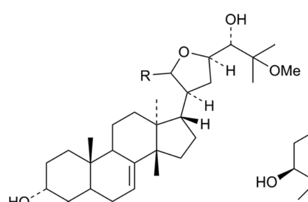
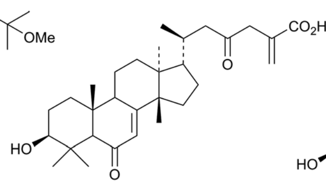


319 R = βOMe
320 R = αOMe



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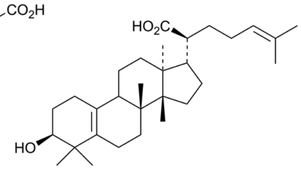

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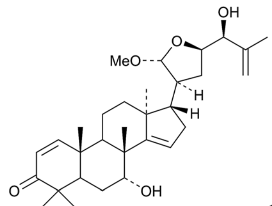
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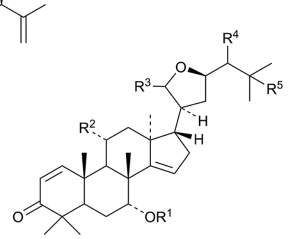
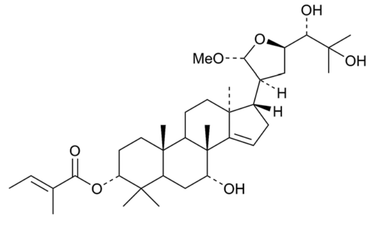

324 R^1 = Ac; R^2 = H; R^3 = αOMe; R^4 = βOH; R^5 = OH
325 R^1 = R^2 = H; R^3 = αOMe; R^4 = αOAc; R^5 = OH
326 R^1 = R^2 = H; R^3 = αOMe; R^4 = βOH; R^5 = OMe
327 R^1 = H; R^2 = OAc; R^3 = αOMe; R^4 = αOH; R^5 = OMe
329 R^1 =Ac; R^2 = H; R^3 = βOMe; R^4 = αOH; R^5 = OH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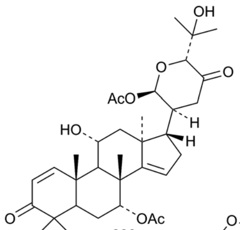
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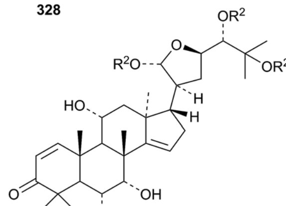
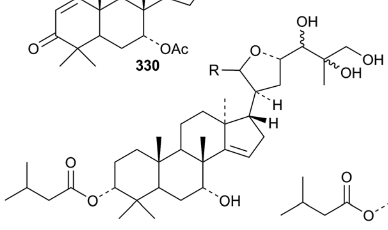
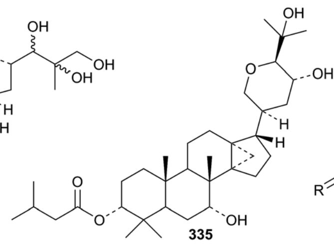

331 R^1 = OH; R^2 = Ac
332 R^1 = R^2 = H


333 R = βOMe
334 R = αOMe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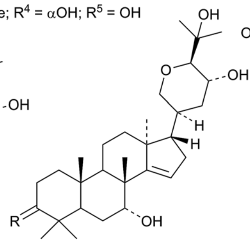
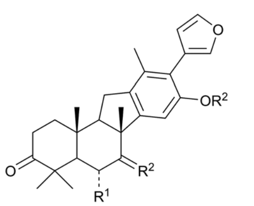
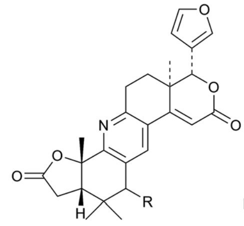
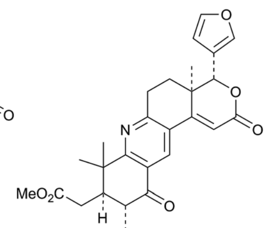

336 R = O
337 R = Otigloyl, H


338 R^1 = H; R^2 = αOH, H; R^3 = Me
339 R^1 = H; R^2 = O; R^3 = Me
340 R^1 = H; R^2 = αOAc, H; R^3 = Me
341 R^1 = R^3 = H; R^2 = αOAc, H
342 R^1 = OH; R^2 = αOAc, H; R^3 = Me
343 R^1 = OH; R^2 = αOAc, H; R^3 = H
344 R^1 = OH; R^2 = αOAc, H; R^3 = Me; 1,2-didehydro
345 R^1 = OAc; R^2 = αOH, H; R^3 = Me; 1,2-didehydro
346 R^1 = OH; R^2 = αOAc, H; R^3 = H; 1,2-didehydro


354 R = βOMe
357 R = αOH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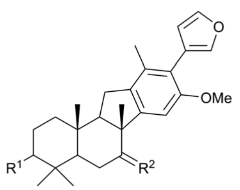
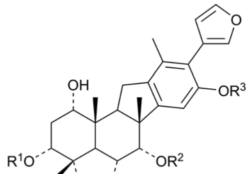
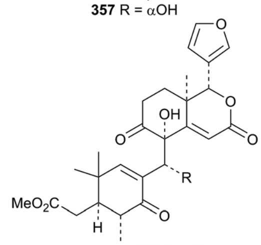
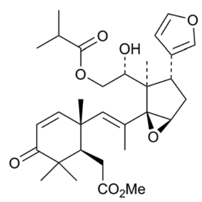

347 R^1 = αOH; R^2 = αOH, H
348 R^1 = βOH; R^2 = αOH, H
349 R^1 = βOH; R^2 = O


350 R^1 = 2-methylbutanoyl; R^2 = H; R^3 = Me
351 R^1 = 2-methylbutanoyl; R^2 = R^3 = H
352 R^1 = tigloyl; R^2 = H; R^3 = Me
353 R^1 = tigloyl; R^2 = Val^i; R^3 = H


356 R = H
358 R = OAc


359

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**, 6α-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 29α-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]

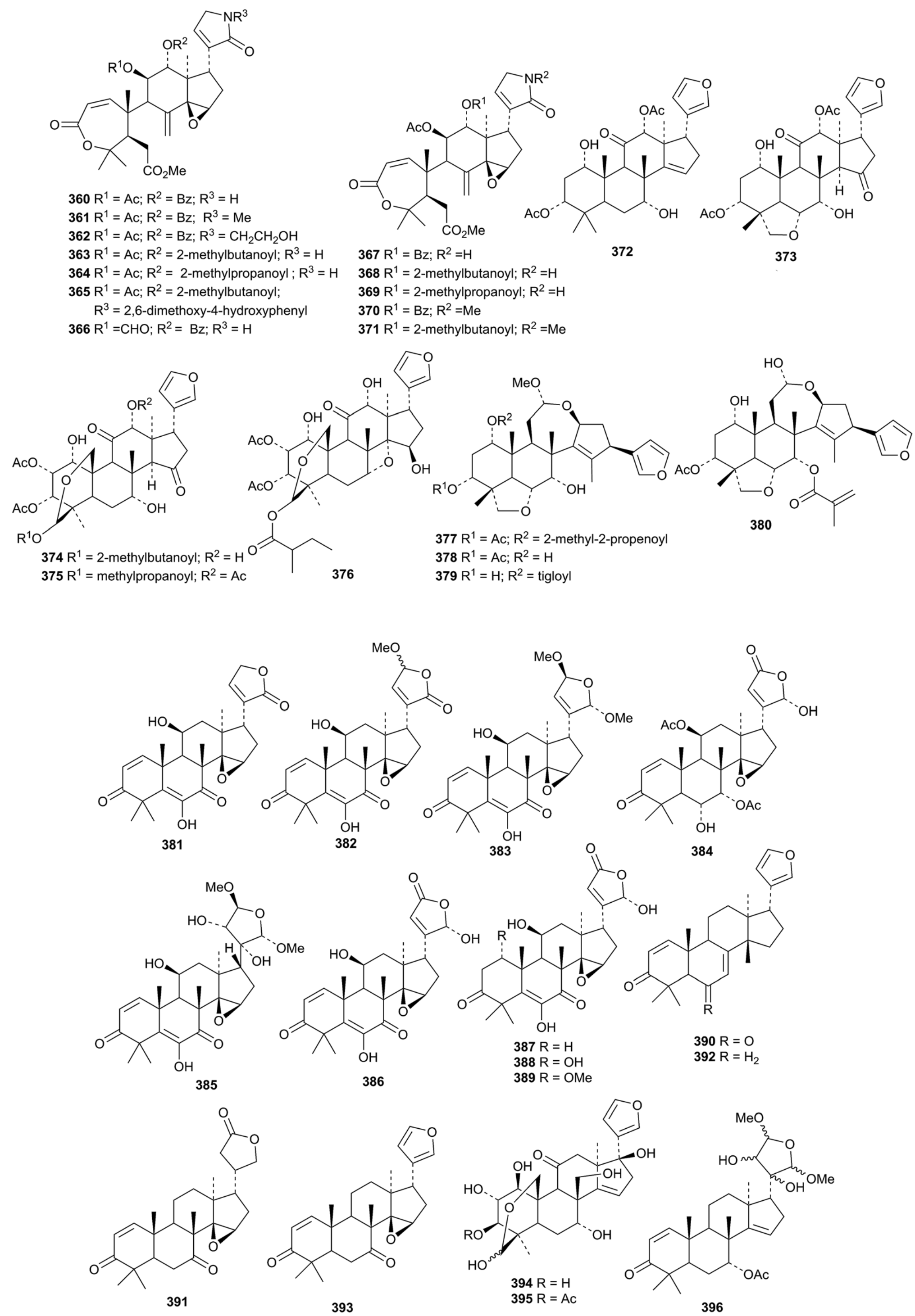
Other new tirucallane derivatives include the acetals **306**–**309** from *Dysoxylum binectariferum*,[143] trichostemonol **310** and the corresponding 3-acetate **311**, trichostemonate, from the stem bark of *Walsura trichostemon*,[144,145] indicalilacols A **312**–D **315** from the fruits of *Azadirachta 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 dysoxylumin A **321** (duplicate name) from *Dysoxylum densiflorum*.[150] The unusual structure **322** has been ascribed to a constituent of *Melia azedarach*.[151]

Xylogranatumines 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

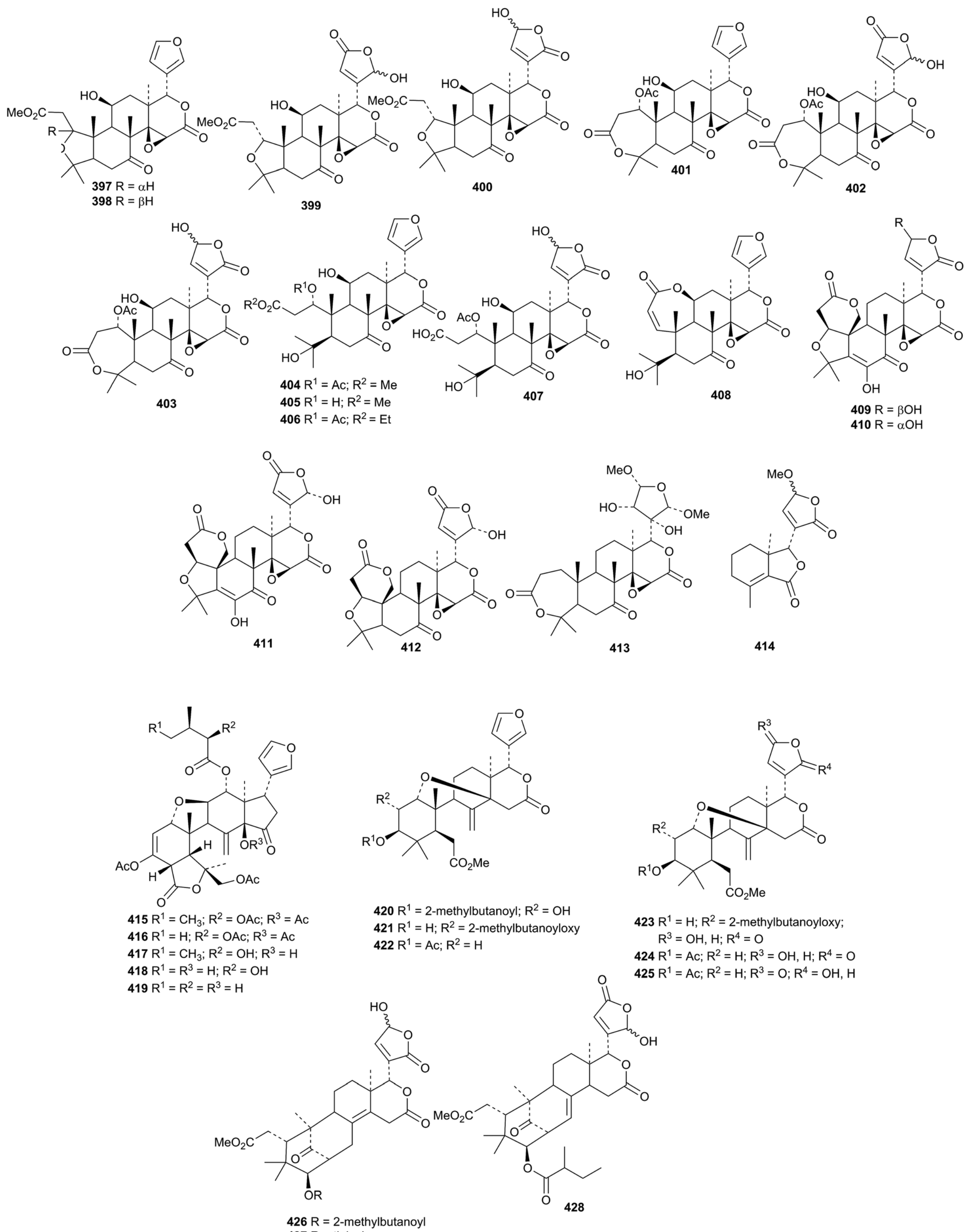
There is a strong interest in the biological activities of limonoids.[157–160] Anticancer[161,162] and pesticidal[163] activities of limonoids have also been highlighted. The publication of new



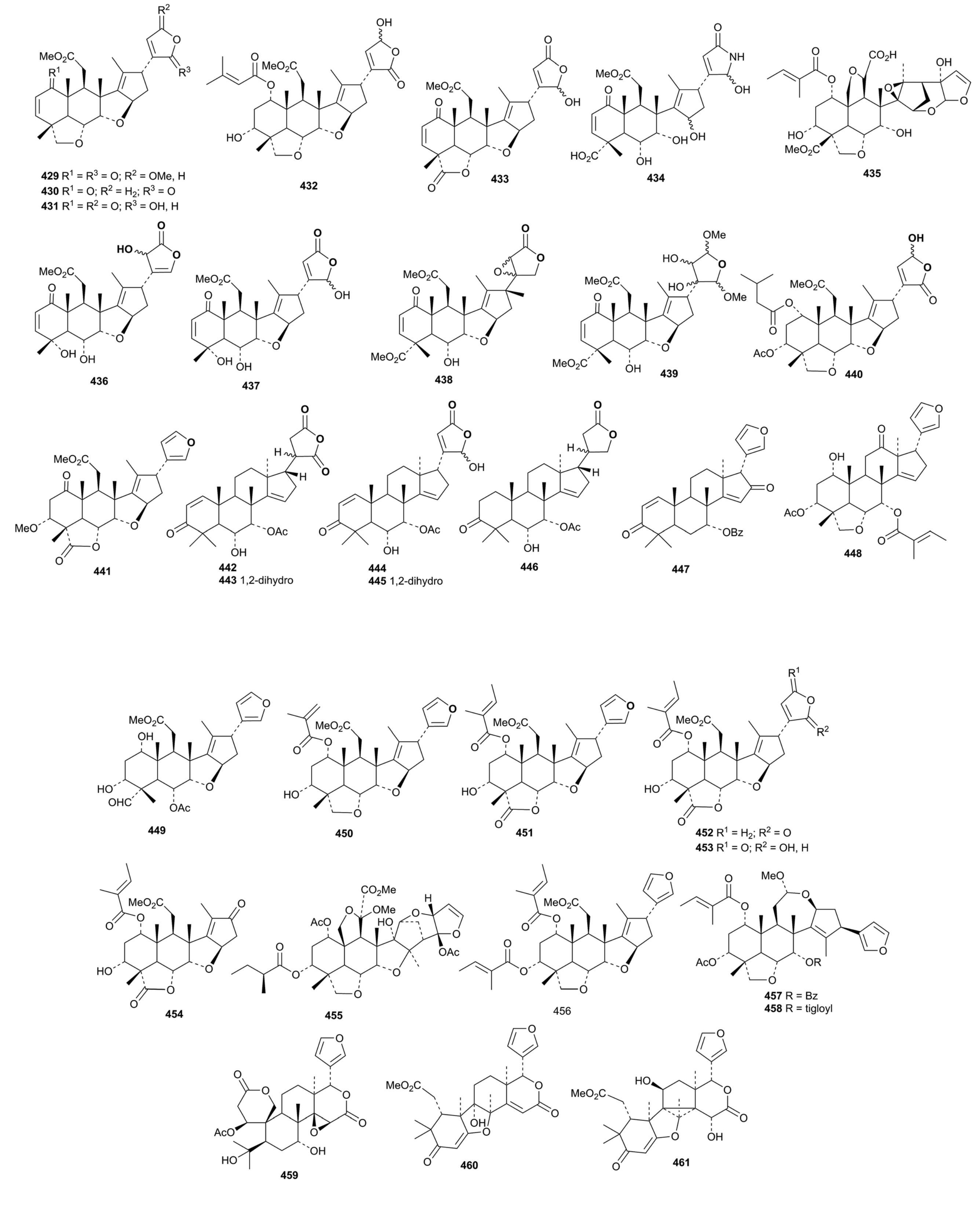
members of this class continues unabated. Walsucochinoids C **338**–R **353**, from *Walsura cochinchinensis*, form an interesting group of rearranged derivatives.[164] The structures of walsuchinoids C **338** and L **347** were confirmed by X-ray analyses.

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 be isolated from *Melia azedarach* together with **380**.[169]



Nine new cedrelone derivatives, walsuranolide B **381**, 11β-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*

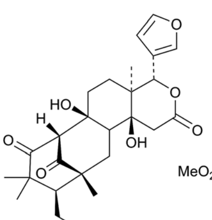


flexuosus[170] and compound **396** from the flowers of *Azadirachta indica* var. *siamensis*.[171]

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*-Methyldasylactone 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-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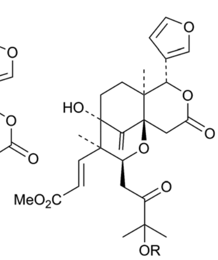
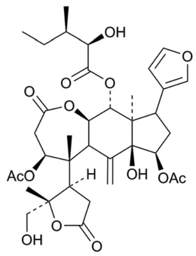

463 R = Ac
464 R = H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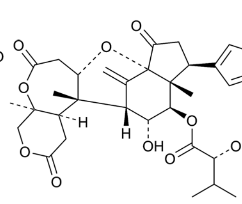
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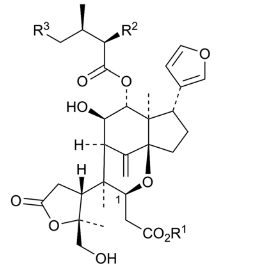
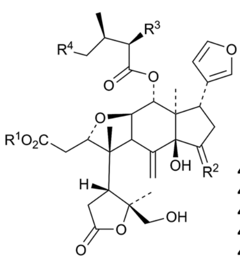
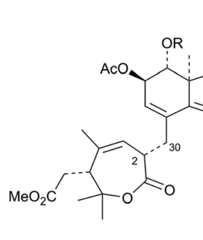
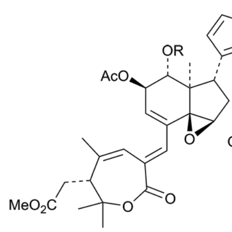
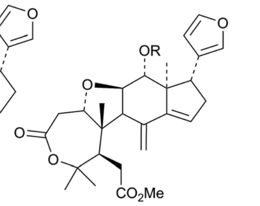
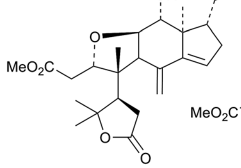

467 R^1 = Me; R^2 = OH; R^3 = CH_3
468 R^1 = Et; R^2 = OH; R^3 = CH_3
469 R^1 = H; R^2 = OH; R^3 = CH_3; 1-epimer
470 R^1 = Et; R^2 = OH; R^3 = CH_3; 1-epimer
471 R^1 = H; R^2 = OH; R^3 = CH_3
472 R^1 = Me; R^2 = OH; R^3 = CH_3
473 R^1 = Et; R^2 = OH; R^3 = CH_3
474 R^1 = R^3 = H; R^2 = OH; 1-epimer
475 R^1 = Et; R^2 = OH; R^3 = H; 1-epimer
476 R^1 = R^3 = H; R^2 = OH
477 R^1 = Me; R^2 = OH; R^3 = H
478 R^1 = Et; R^2 = OH; R^3 = H
479 R^1 = R^2 = R^3 = H

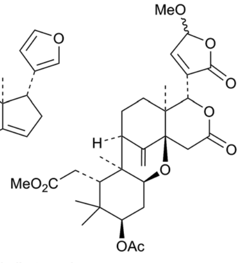

480 R^1 = H; R^2 = O; R^3 = OH; R^4 = CH_3
481 R^1 = Me; R^2 = O; R^3 = OH; R^4 = CH_3
482 R^1 = Me; R^2 = βOAc, H; R^3 = OH; R^4 = CH_3
483 R^1 = Et; R^2 = βOAc, H; R^3 = OH; R^4 = CH_3
484 R^1 = Et; R^2 = βOH, H; R^3 = OH; R^4 = CH_3
485 R^1 = R^4 = H; R^2 = O; R^3 = OH
486 R^1 = Me; R^2 = O; R^3 = OH; R^4 = H
487 R^1 = Et; R^2 = O; R^3 = OH; R^4 = H
488 R^1 = R^3 = R^4 = H; R^2 = O
489 R^1 = Me; R^2 = O;R^3 = R^4 = H


490a R = Ac
490b R = tigloyl
491 R = 2-methylbutanoyl
492 R = Ac; 2,30-didehydro (*E*)
493 R = tigloyl; 2,30-didehydro (*E*)
494 R = Ac; 2,30-didehydro (*Z*)


495 R = Ac
496 R = tigloyl


497 R = tigloyl
498 R = 2-methylbutanoyl
499 R - Bz


500 R = tigloyl
501 R = 2-methylbutanoyl
502 R - Bz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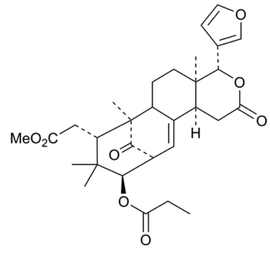
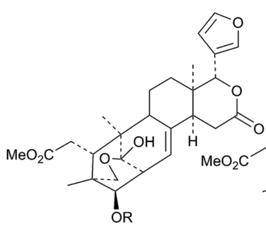
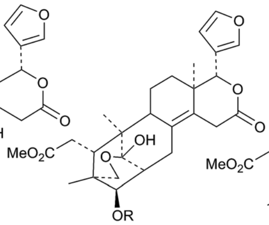

504

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.

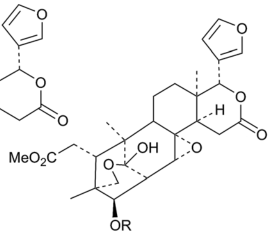
Three new ring C-cleaved derivatives **449–451**, along with a host of known compounds, have been reported from the fruits of *Melia azedarach*.[182] The leaves and bark are the source of the new derivatives **452–454** (ref. 183) while the meliacarpin derivative **455** was found in the leaves.[156]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



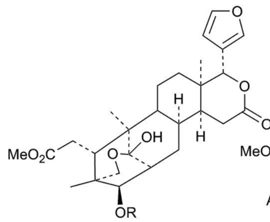
505 R = tigloyl
506 R = 2-methylbutanoyl



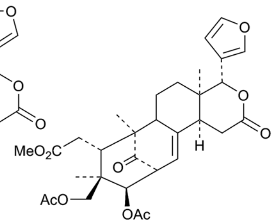
507 R = Ac
508 R = 2-methyl-2-propenoyl



509 R = Ac
510 R = 2-methyl-2-propenoyl



511 R = tigloyl
512 R = 2-methylpropanoyl
513 R = Ac; 8,9,14,15-tetradehydro



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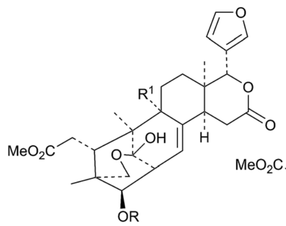

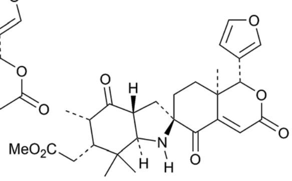

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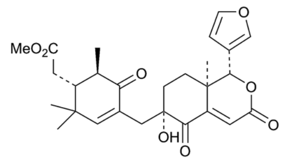

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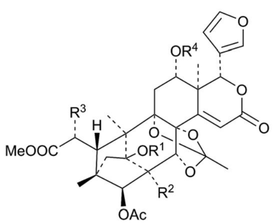
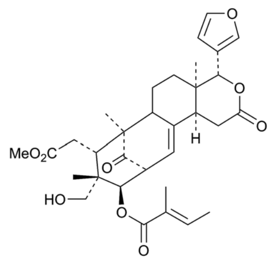


521 $R^1 = R^4$ = H; R^2 = OH; R^3 = OAc
522 $R^1 = R^2 = R^3$ =H; R^4 = Ac
523 $R^1 = R^4$ = Ac; $R^2 = R^3$ =H
524 $R^1 = R^4$ = Ac; R^2 = H; R^3 = OAc



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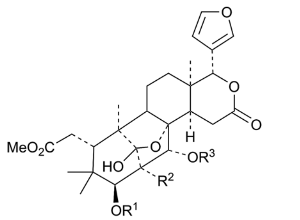
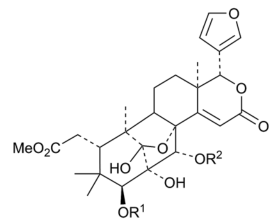
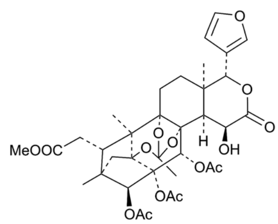


526 $R^1 = R^3$ = 2-methylpropanoyl; R^2 = H
527 R^1 = 2-methylpropanoyl; R^2 = H; R^3 = 2*S*-methylbutanoyl
528 $R^1 = R^3$ = 2*S*-methylbutanoyl; R^2 = OH
529 R^1 = Ac; R^2 = OH; R^3 = 2-methylpropanoyl
532 R^1 = 2-methylpropanoyl; R^2 = OH; R^3 = 2*S*-methylbutanoyl



530 $R^1 = R^2$ = 2*S*-methylbutanoyl
536 R^1 = tigloyl; R^2 = 2*S*-methylbutanoyl
537 R^1 = tigloyl; R^2 = 2-methylpropanoyl



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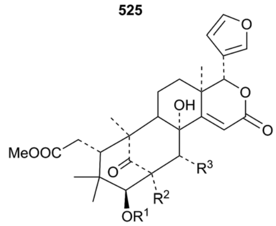
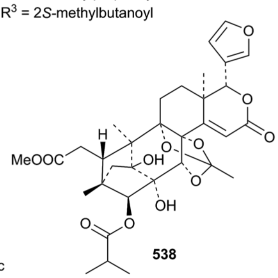


533 R^1 = 2-methylbutanoyl; R^2 = OAc; R^3 = H
534 R^1 = 2-methylbutanoyl; R^2 = OH; R^3 = OAc
535 R^1 = 2-methylpropanoyl; $R^2 = R^3$ = H



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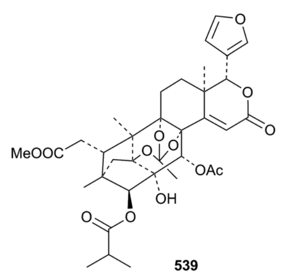

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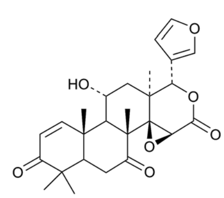

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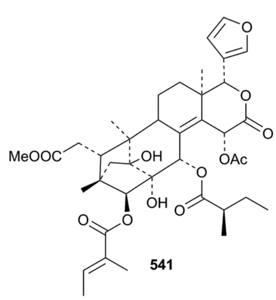

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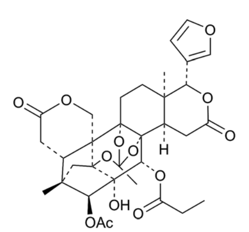


542

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

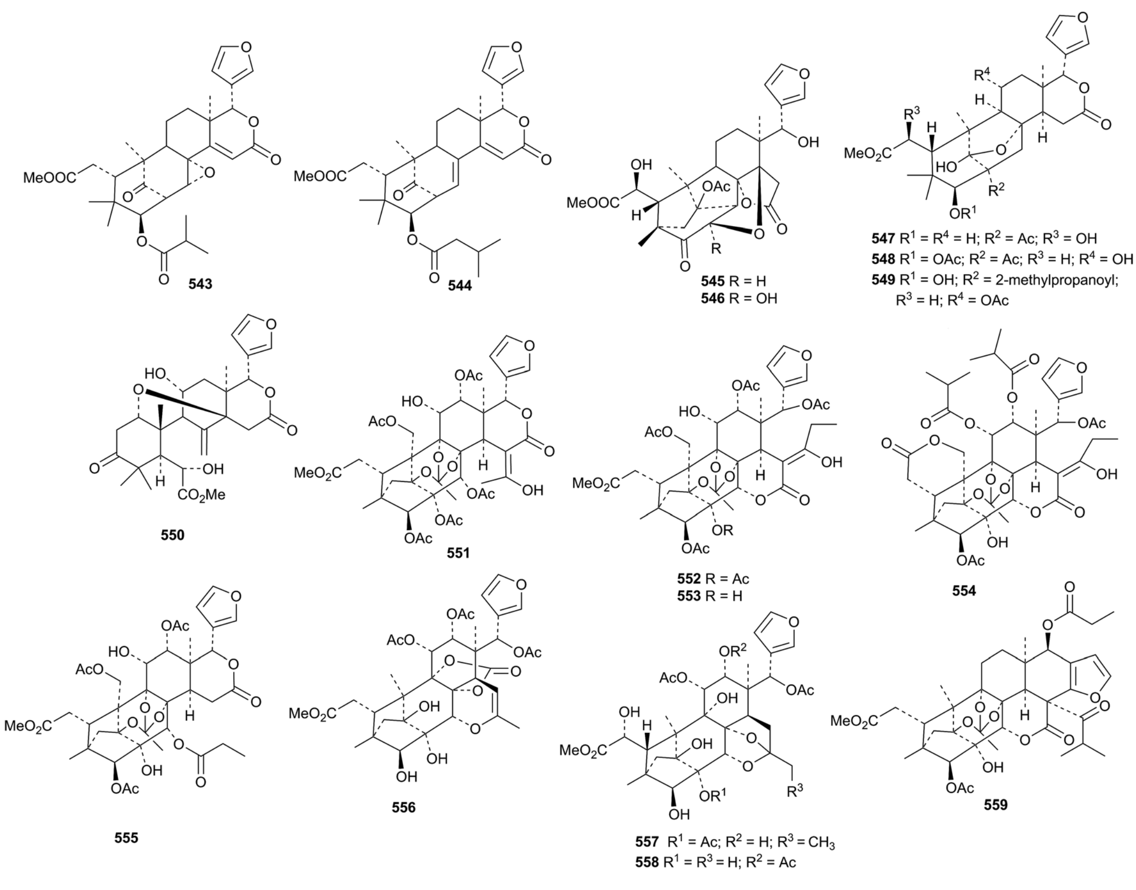
New skeletal variations of rearranged limonoids continue to appear. The structures of trichiconins A **462** and B **463**, from *Trichilia connaroides*, were confirmed by X-ray analyses.[185] They were accompanied by trichiconin C **464**. Zaphaprinins A **465**–Y **489** are modified prieurianin derivatives 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] Cineracipadesin 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.

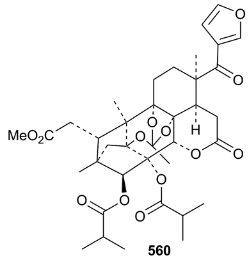
Further investigations of *Khaya ivorensis* have resulted in the isolation of 14,15-didehydroruageanin A **543** and 3-*O*-(3-methylbutanoyl)seneganolide A **544** (ref. 198) and ivorenoids A **545**–F **550**.[199] Velutinasins A **551**–H **558** are phragmalin derivatives from *Chukrasia tabularis*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



Compounds from an Indian *Xylocarpus granatum* include granatumins L **505**–U **514** (ref. 190) and granatumins V **515**–Y **518**.[191] The structures of granatumins L **505** and Y **518** were confirmed by X-ray analyses. Granatumins 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]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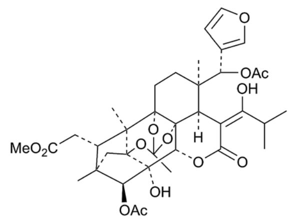
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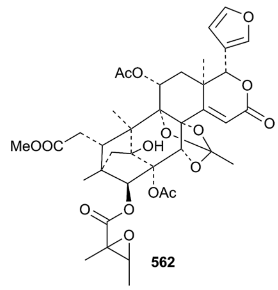
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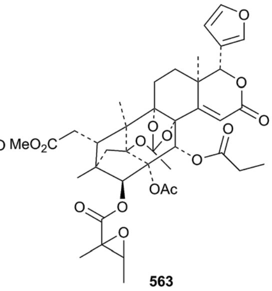
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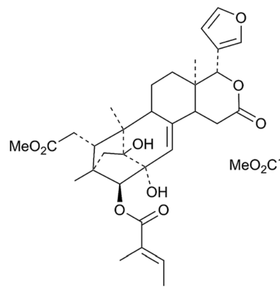
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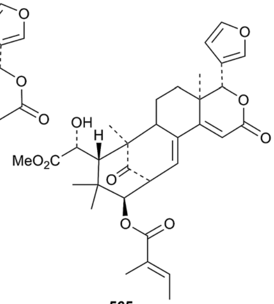
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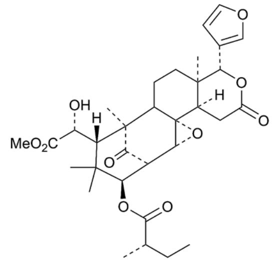
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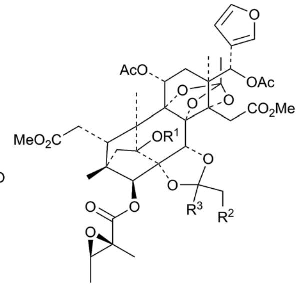
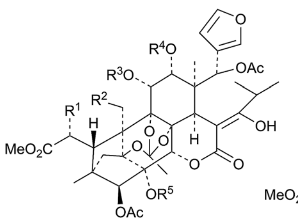
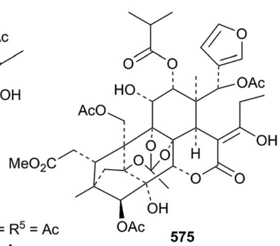

567 R^1 = Ac; R^2 = CH_3; R^3 = βOMe
568 R^1 = Ac; R^2 = CH_3; R^3 = αOMe
569 R^1 = H; R^2 = H; R^3 = αOMe
570 R^1 = Ac; R^2 = H; R^3 = αOMe


571 R^1 = R^3 = H; R^2 = OAc; R^4 = R^5 = Ac
572 R^1 = R^2 = R^3 = H; R^4 = R^5 = Ac
573 R^1 = OAc; R^2 = R^4 = H; R^3 = R^5 = Ac
574 R^1 = R^3 = R^5 = H; R^2 = OAc; R^4 = Ac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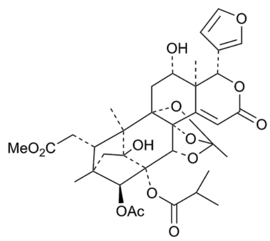
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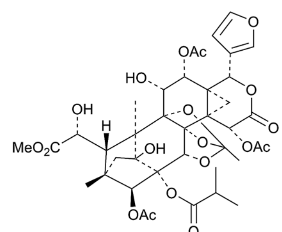
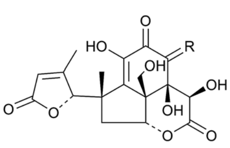

577

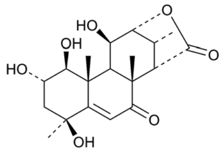
4.2 Quassinoids

Eurylactones E **578**, F **579** and G **580**, eurycomalides D **581**, and E **582** and 13α,18-dihydroeurycomanone **583** are new constituents of the roots of *Eurycoma longifolia*.[207] Other constituents of *Eurycoma longifolia* include Δ^4-14-hydroxyglaucarbol **584**, 5-isoeurycomadilactone **585**, eurycomadilactone **586** and 13-epieurycomadilactone **587** (ref. 208) and eurycomalide C **588**.[209] The structures of Δ^4-14-hydroxyglaucarabol **584** and 5-isoeurycomadilactone **585** were confirmed by X-ray analyses. Shinjulactone 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


578 R = αCH_3, H
579 R = βCH_3, H
580 R = CH_2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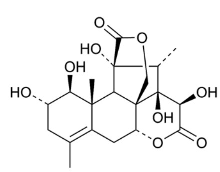
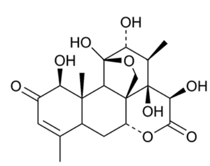

582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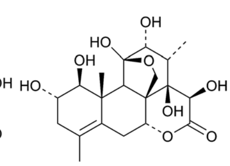
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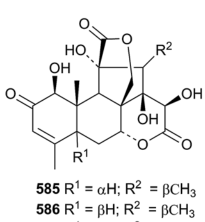
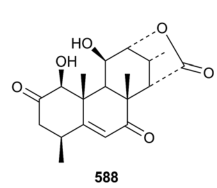

585 R^1 = αH; R^2 = βCH_3
586 R^1 = βH; R^2 = βCH_3
587 R^1 = βH; R^2 = αCH_3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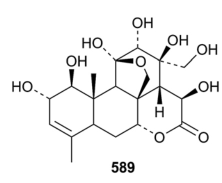
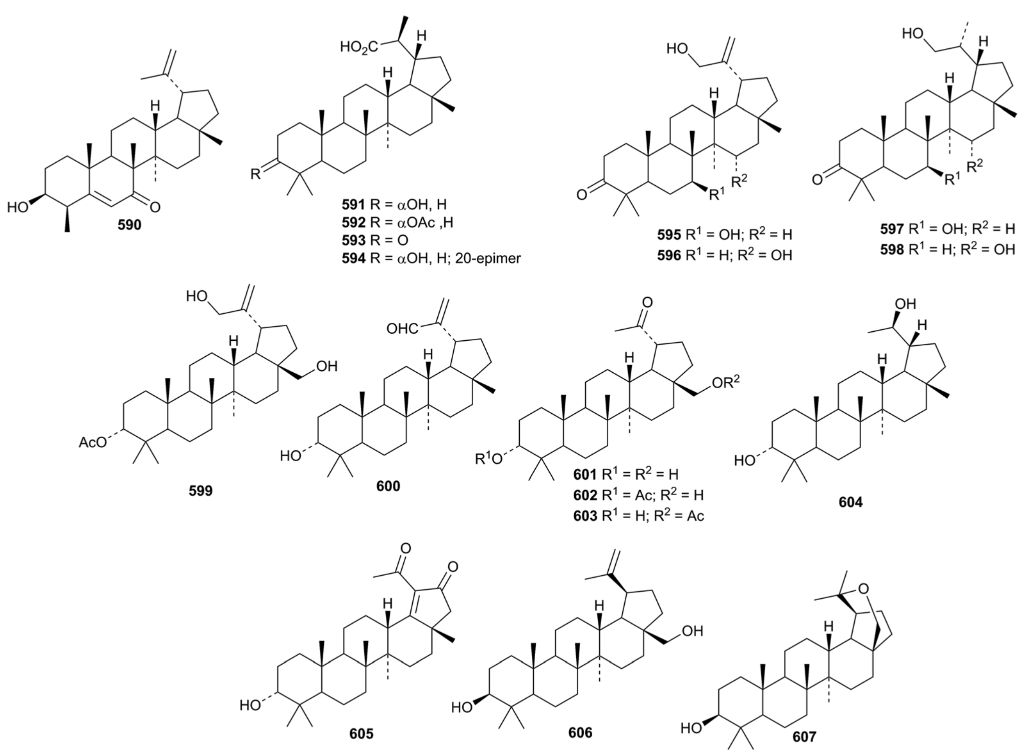

589

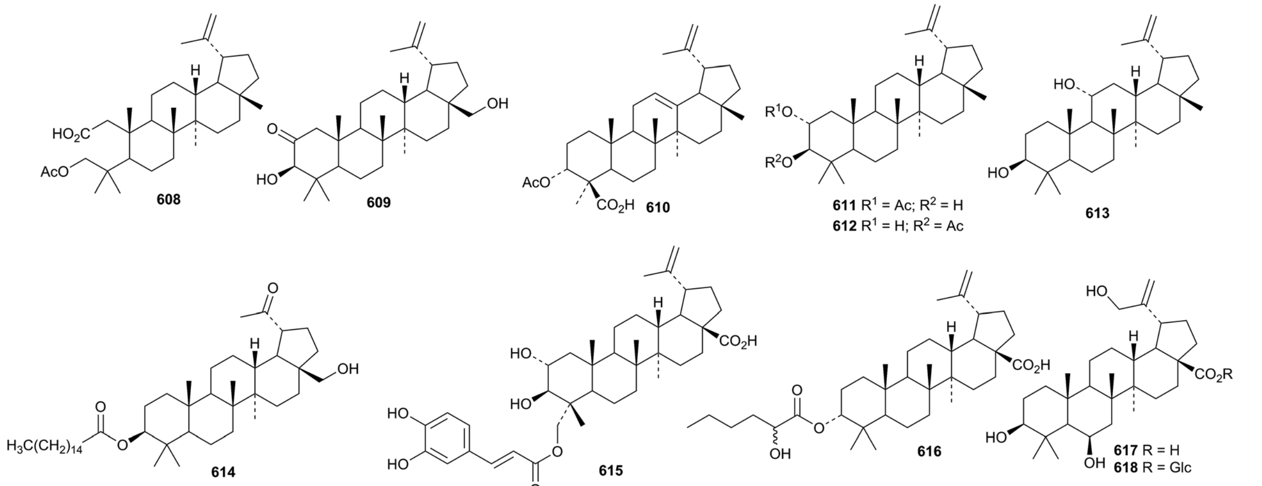
example of a 23-norlupane, 3-hydroxy-23-nor-5,20(29)-lupadien-7-one **590**, has been reported from *Lagerstroemia indica*.[213] *Euonymus carnosus* is a prolific source of lupane triterpenoids. Fifteen new compounds **591–605**, including the 30-nor-derivatives **601–605**, have been isolated.[214] 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-3β,11α-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] 3β,6β,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 acid[232] have been well studied, particularly for their antitumour effects.

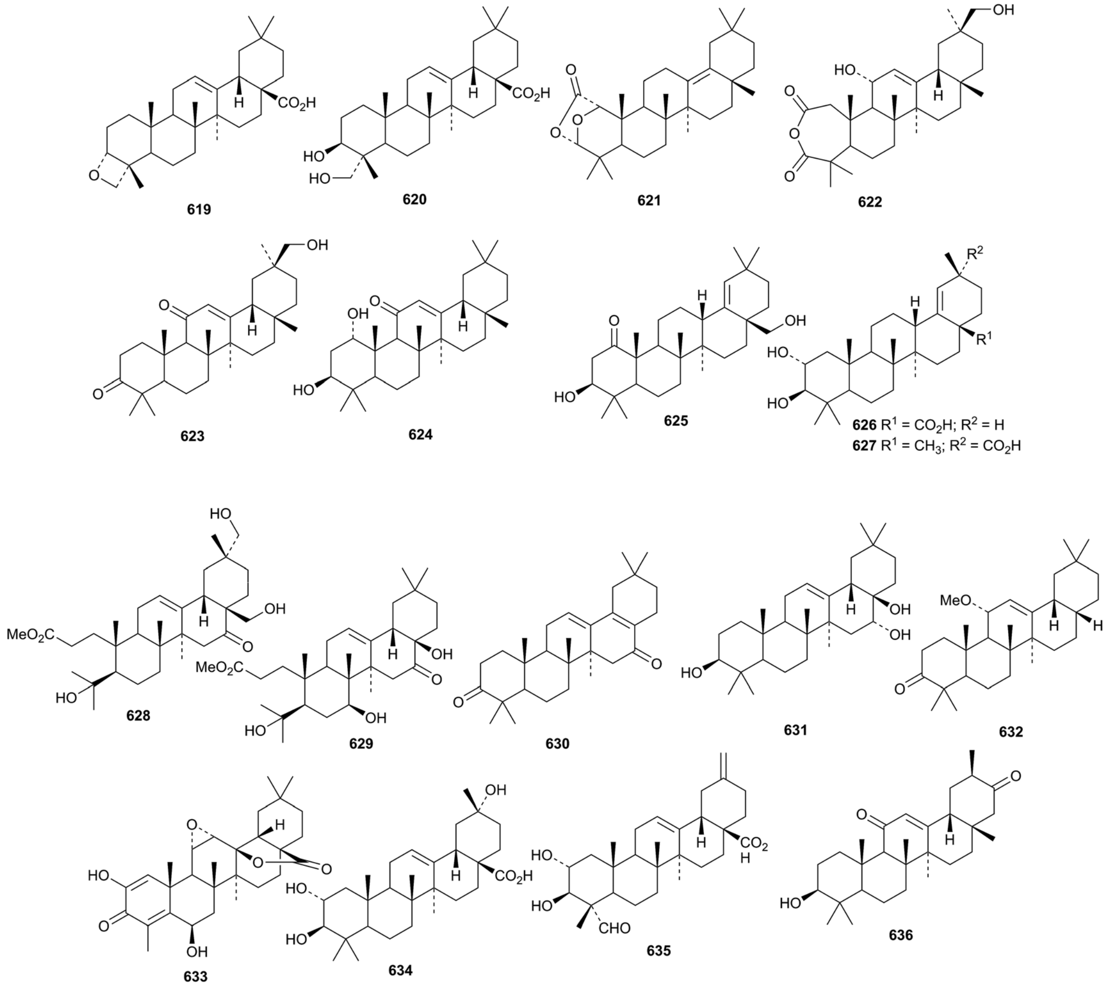
Cyclocaric acid A, from *Cyclocarya paliurus*, was claimed to have the structure **619** with an oxetane ring.[233] Synthesis of the oxetane **619** and re-examination of the original literature report indicates that cyclocaric acid A is identical with hederagenin **620**.[234] The 2,3-seco-derivative **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 2α,3β-dihydroxy-18-oleanen-28-oic acid **626** from *Lawsonia inermis*[237] and the corresponding 29-oic acid **627** from *Mentha suaveolens*.[238]

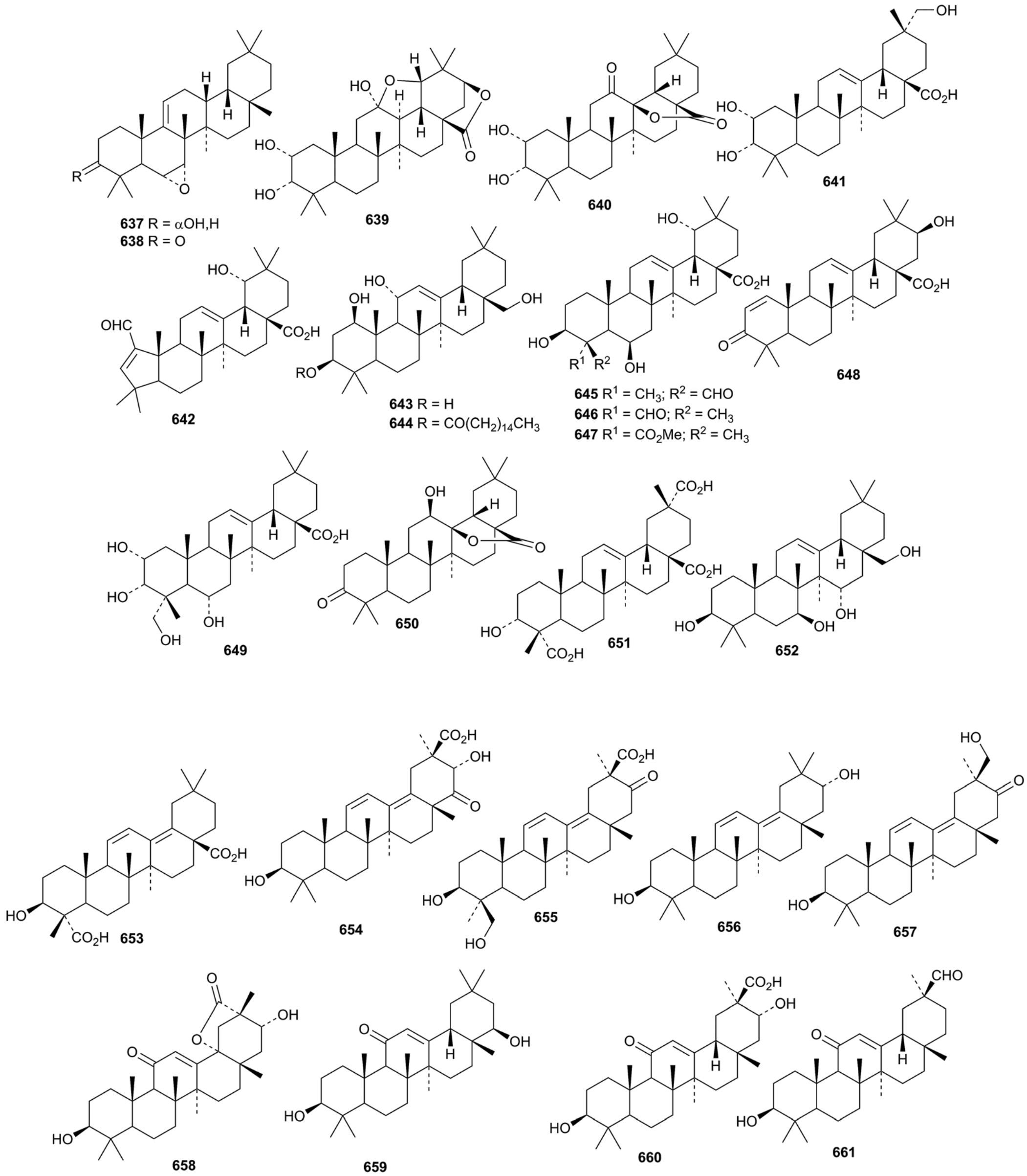
The 3,4-seco-derivatives camelliaoleans A **628** and B **629**, together with the 28-noroleanane derivatives **630** and **631**, have been isolated from *Camellia japonica*.[239] Liquidaformone **632** is another 28-noroleanane from fruits of *Liquidambar formosana*.[240] Asprellol C **633** is a 24-noroleanane 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 ovalifiolata*.[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-1β,3β,11α,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] 3α-hydroxy-12-oleanene-23,28,29-trioic acid **651** from *Acanthopanax gracilistylus*[249] and 12-oleanene-3β,7β,15α,28-tetrol **652** from *Salvia argentea* var. *aurasiaca*.[250]

3β-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, N_1, N_2, 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]

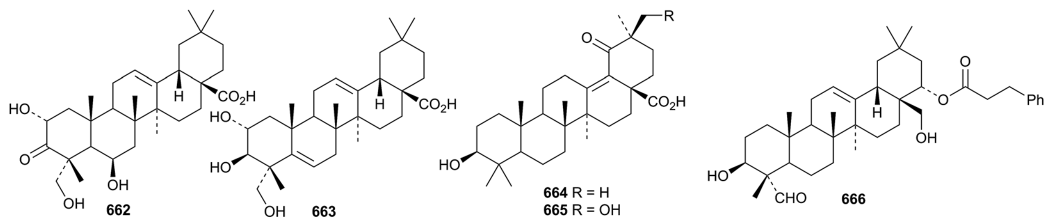
Other oleanane saponins with new genins include centellasaponins E and I, from *Centela asiatica*, with the genins **662** and **663**,[254] hippophosides A–D, from *Hippophae rhamnoides* ssp. *sinensis*, with the genins **664** and **665**,[255] oleiferasaponin B_2, from *Camellia oleifera*, with the 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] *Eclipata prostrata* with the genin 12-oleanene-3β,16β,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.

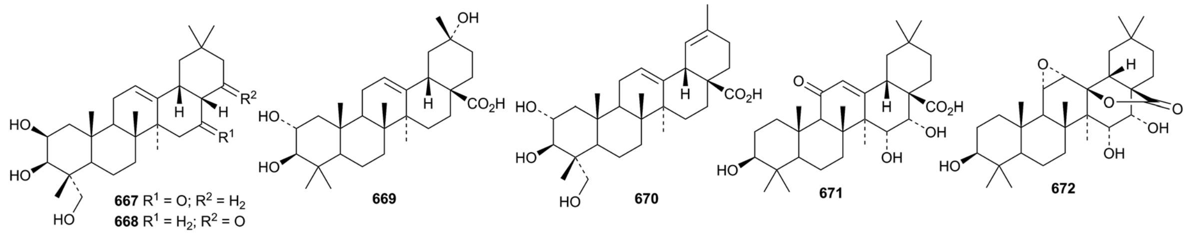
The sources of new oleanane saponins with known genins that have not been assigned trivial names are listed in Table 2.

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 3β,28-dihydroxy-12-oleanen-11-one (procerenone) from *Omphalocarpum procerum*,[317] and the oleoyl ester 12,18-oleanadien-3β-ol.[318] Leonurusoleanolides E **692**–J **697**, from *Leonurus japonicus*, are further esters of the 19(18→17)-*abeo*-28-noroleanane phlomistetraol B.[319]

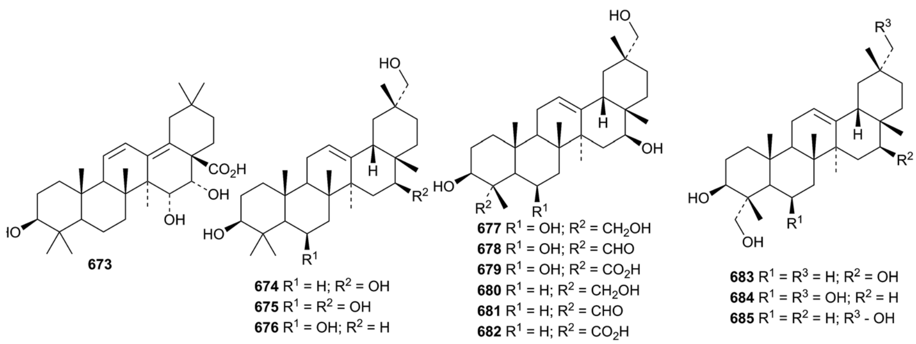
Malaytaxerate **698**, from *Sapium baccatum*, is a ring-E contracted nortaraxerane derivative.[320] *Davidia involucrata* is the



662 663 664 R = H 665 R = OH 666

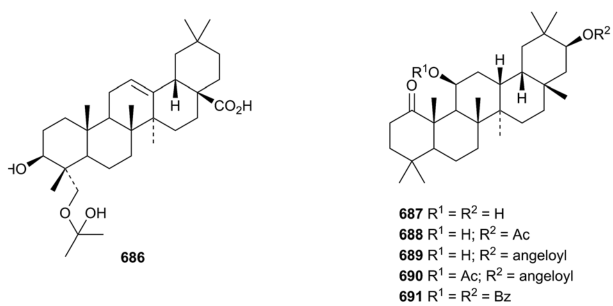


667 R^1 = O; R^2 = H_2
668 R^1 = H_2; R^2 = O
669 670 671 672

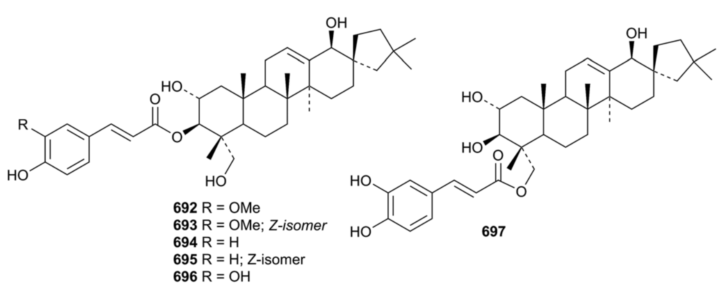


673
674 R^1 = H; R^2 = OH
675 R^1 = R^2 = OH
676 R^1 = OH; R^2 = H
677 R^1 = OH; R^2 = CH_2OH
678 R^1 = OH; R^2 = CHO
679 R^1 = OH; R^2 = CO_2H
680 R^1 = H; R^2 = CH_2OH
681 R^1 = H; R^2 = CHO
682 R^1 = H; R^2 = CO_2H
683 R^1 = R^3 = H; R^2 = OH
684 R^1 = R^3 = OH; R^2 = H
685 R^1 = R^2 = H; R^3 - OH

source of the ring-A contracted nortaraxeranes davinvolunols 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 argentilucida*.[323] The structures of both the multiflorane derivative turranoic 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 klodorol A **710**, from *Kleinia odora*, is 5α-hydroxydebdropanoxide.[326] The authors



686
687 R^1 = R^2 = H
688 R^1 = H; R^2 = Ac
689 R^1 = H; R^2 = angeloyl
690 R^1 = Ac; R^2 = angeloyl
691 R^1 = R^2 = Bz



692 R = OMe
693 R = OMe; *Z-isomer*
694 R = H
695 R = H; Z-isomer
696 R = OH
697

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

Trivial name	Plant species	Reference
Angulasaponins A–D	*Vigna angularis*	261
Aristatosides A–C	*Cephalaria aristata*	262
Bafouoside C	*Cussonia bancoensis*	263
Caspicaosides E–K	*Gliditsia caspica*	264
Celosins H–J (celosin I is a duplicate name)	*Celosia argentea*	265
Clematiunicinosides A–H	*Clematis uncinata*	266
Comastomasaponins A–H	*Comastoma pedunculatum*	267
Conyzasaponins R, S	*Conyza japonica*	268
Conyzasaponins T, U	*Conyza japonica*	269
Davisianosides A, B	*Cephalaria davisiana*	270
Flaccidosides V–VII	*Anemone flaccida*	271
Grindeliosides A–C	*Grindelia argentina*	272
Ilexasprellanosides D–F	*Ilex asprella*	273
Ilexpublesnin R	*Ilex pubescens*	274
Leptocarposide	*Ludwigia leptocarpa*	275
Licorice-saponin O4	*Glycyrrhiza glabra*	252
Lobeliodosides A–D	*Lysimachia lobelioides*	276
Lonicerosides F–J	*Lonicera japonica*	277
Officinoterpenoside D	*Rosmarinus officinalis*	278
Oleiferosides A–H	*Camellia oleifera*	279
Oleiferoside B_1	*Camellia oleifera*	256
Paradoxosides A–E	*Vitellaria paradoxa*	280
Pittangretosides N, O, P	*Pittosporum angustifolium*	281
Pittangretosides A_1, B_1, J, K, M, Q–Z	*Pittosporum angustifolium*	282
Potentillanoside F	*Potentilla anserina*	283
Salbiges A, B	*Salicornia herbacea*	284
Sarconepaside C	*Sarcopyramis nepalensis*	285
Schefflesides A–H	*Schefflera kwangsiensis*	286
Schefflesides I–L	*Schefflera kwangsiensis*	287
Sieboldiisaponin B	*Stachys sieboldii*	288
Simenoside A	*Gypsophila simonii*	289
Schekwangsiensides A–E	*Schefflera kwangsiensis*	223
Uralsaponins M, N, O, U, V, Y	*Glycyrrhiza uralensis*	253
Yemuosides YM_{36}, YM_{37}	*Stauntonia chinensis*	290
Yunganoside E_3	*Glycyrrhiza yunnanensis*	243

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]

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

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

7. The ursane group

The antitumour activity of ursolic acid has been highlighted.[334,335] The unusual 9,25-cyclo-12-ursen-3β-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 20α*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-2α,3β,19α-triol **732**, from *Terminalia arjuna*, has been named torment.[338]

Other simple ursane derivatives include cymosic acid **733** from *Rosa cymosa*,[339] elatumic 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-2α,3α,19α,24,28-pentol **738** from *Meyna* (*Vangueria*) *spinosa*,[342] uncarinic acids H **739** and I **740** from *Uncaria rhynchophylla*,[246] 3α,6β,19α-trihydroxyurs-12-en-28-oic acid **741** from *Mitragyna diversifolia*,[343] 3β,20β-dihydroxyursan-28-oic acid **742** from *Malus domestica*,[344] 3α,11β-dihydroxyurs-12-en-28-oic acid **743** from *Gentiana veitchiorum*,[345] three compounds **744–746** from *Zizyphus jujuba*,[346] three compounds **747–749** from *Microtropis fokienensis*[236] and nine ursanes **750–758** from *Salvia argentea* var. *aurasiaca*.[250]

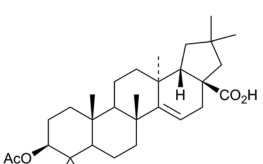
Centrellasaponin J, from *Cenrella asiatica*, has the new ursane genin **759**.[254] Further new ursane genins include **760** from *Callicarpa nudiflora*,[293] **761** from *Clematis argentilucida*,[323] **762** and **763** from *Panax ginseng*[61] and **764–766** from *Schefflera heptaphylla*.[347]

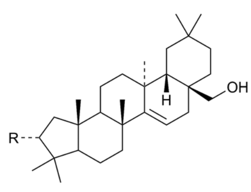
Named ursane saponins with known genins include fagonoside A from *Fagonia cretica*,[348] grandoside from *Syzygium grande*,[349] ilexsaponins G and H from *Ilex pubescens*,[350] ilexasprellanosides A–C from *Ilex asprella*,[273] ilexpublesnins N–Q (Q is the same as zygoeichwaloside H isolated in 2007(ref. 351)) from *Ilex pubescens*,[274] officinoterpenoside C from *Rosmarinus officinalis*,[278] potentillanosides A–E[283] and G[352] from *Potentilla anserina*, sieboldiisaponins A[353] and C[288] from *Stachys sieboldii*, and zygofaboside C from *Zygophyllum 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]

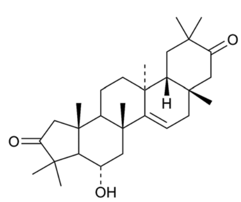
Further ursane esters include the acetate **767** from *Boswellia sacra*,[217] the acetate **768** from *Mentha suaveolens*,[238] ferulates **769** and **770** from *Ampelopsis japonica*.[359] and the palmitate **771** from *Inula cappa*.[360] Flaccidoside IV is a taraxastane saponin with a known genin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

8. The hopane group

The 2,3-seco-21α*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 C_{35} 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]


698


699 R = H
700 R = OH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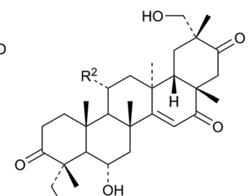
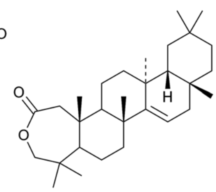

702 R¹ = H; R² = OH
703 R¹ = OH; R² = H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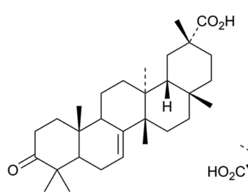
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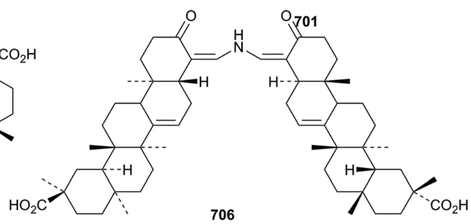
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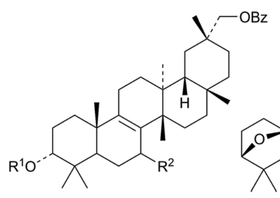
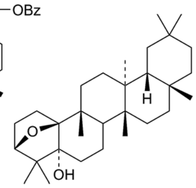
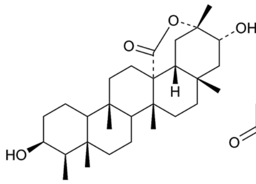
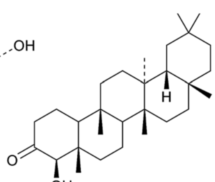
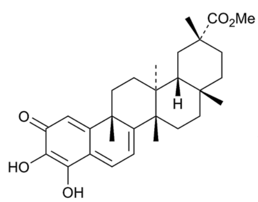
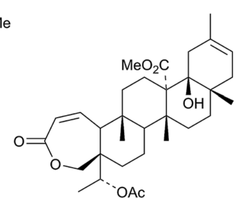

707 R¹ = Ac; R² = αOH
708 R¹ = Bz; R² = αOMe
709 R¹ = Bz; R² = βOMe

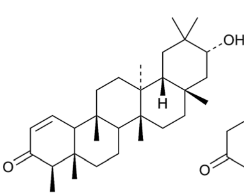

710

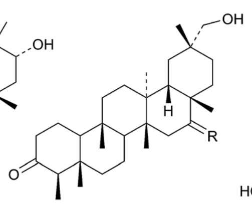

711

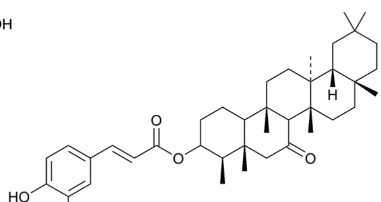

712

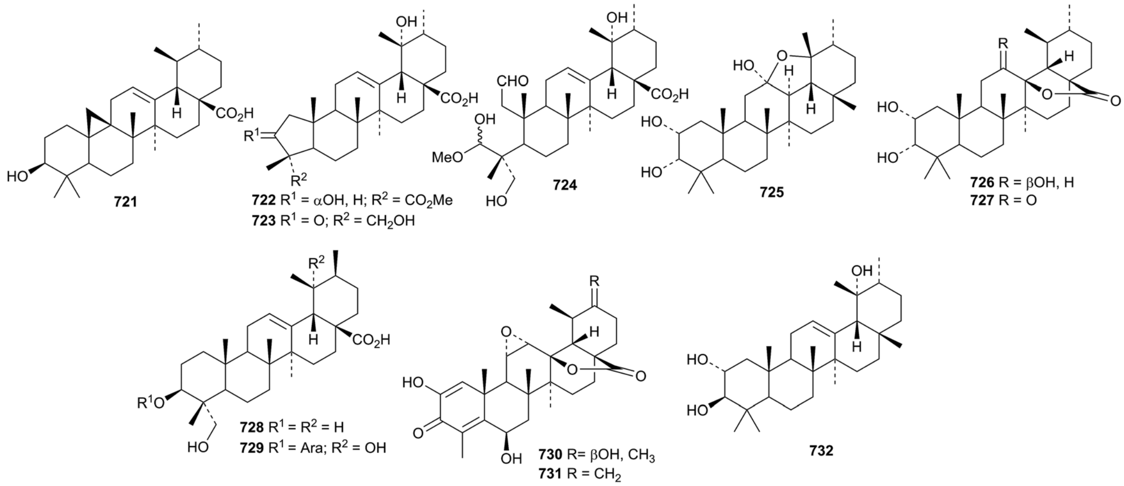

713

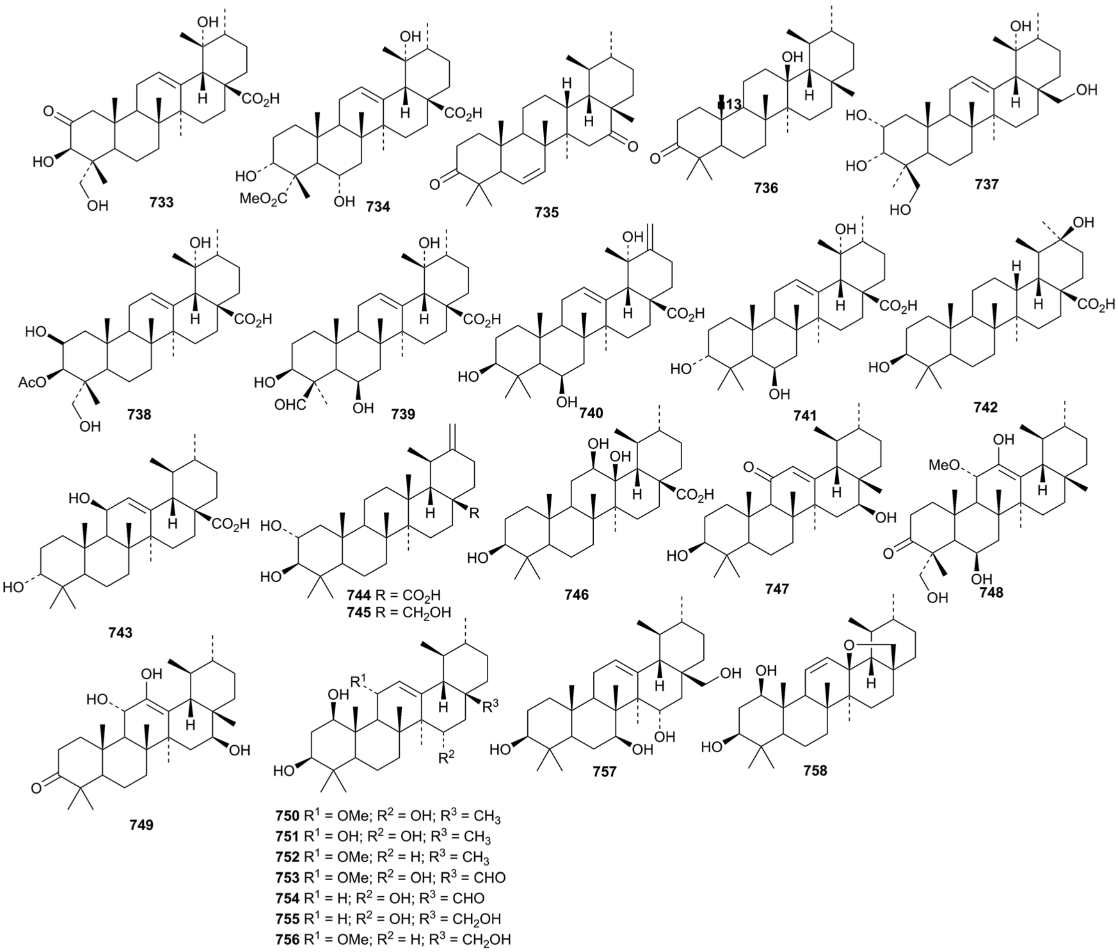

714
715 $\Delta^{20(29)}$-isomer


716


717 R = O
718 R = βOH, H

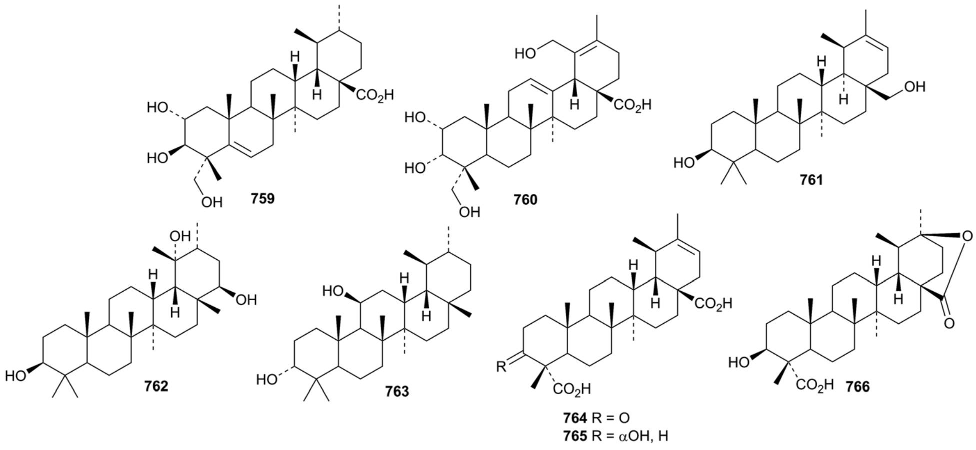

719 R = H
720 R = OH

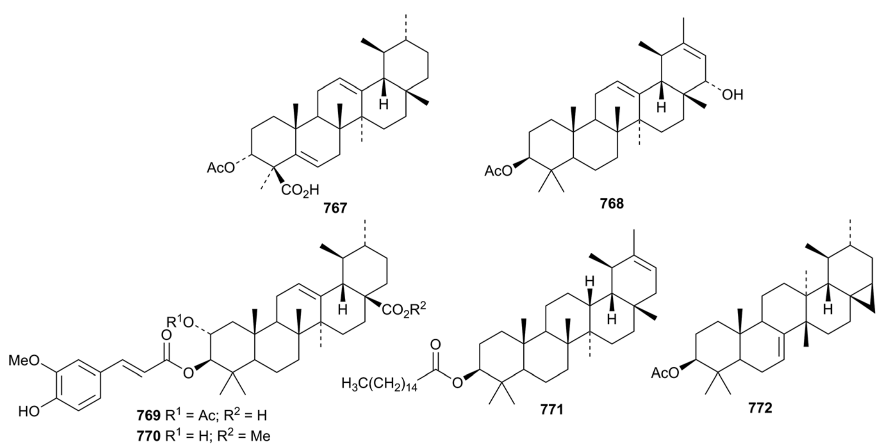


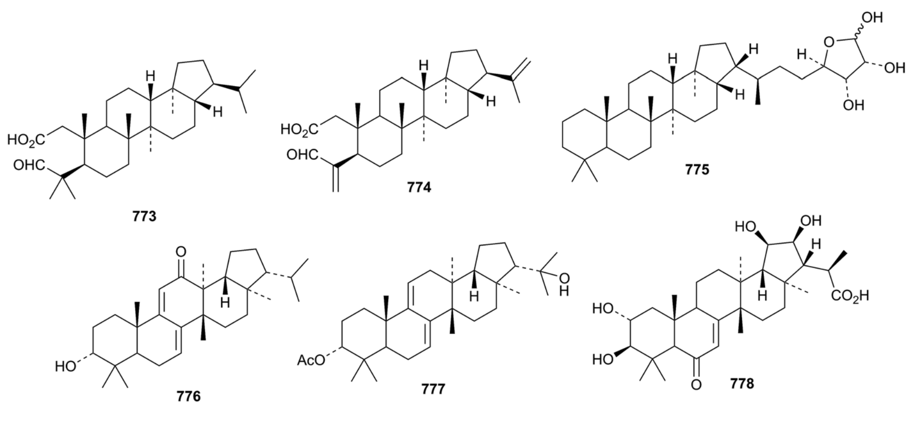


9. Miscellaneous compounds

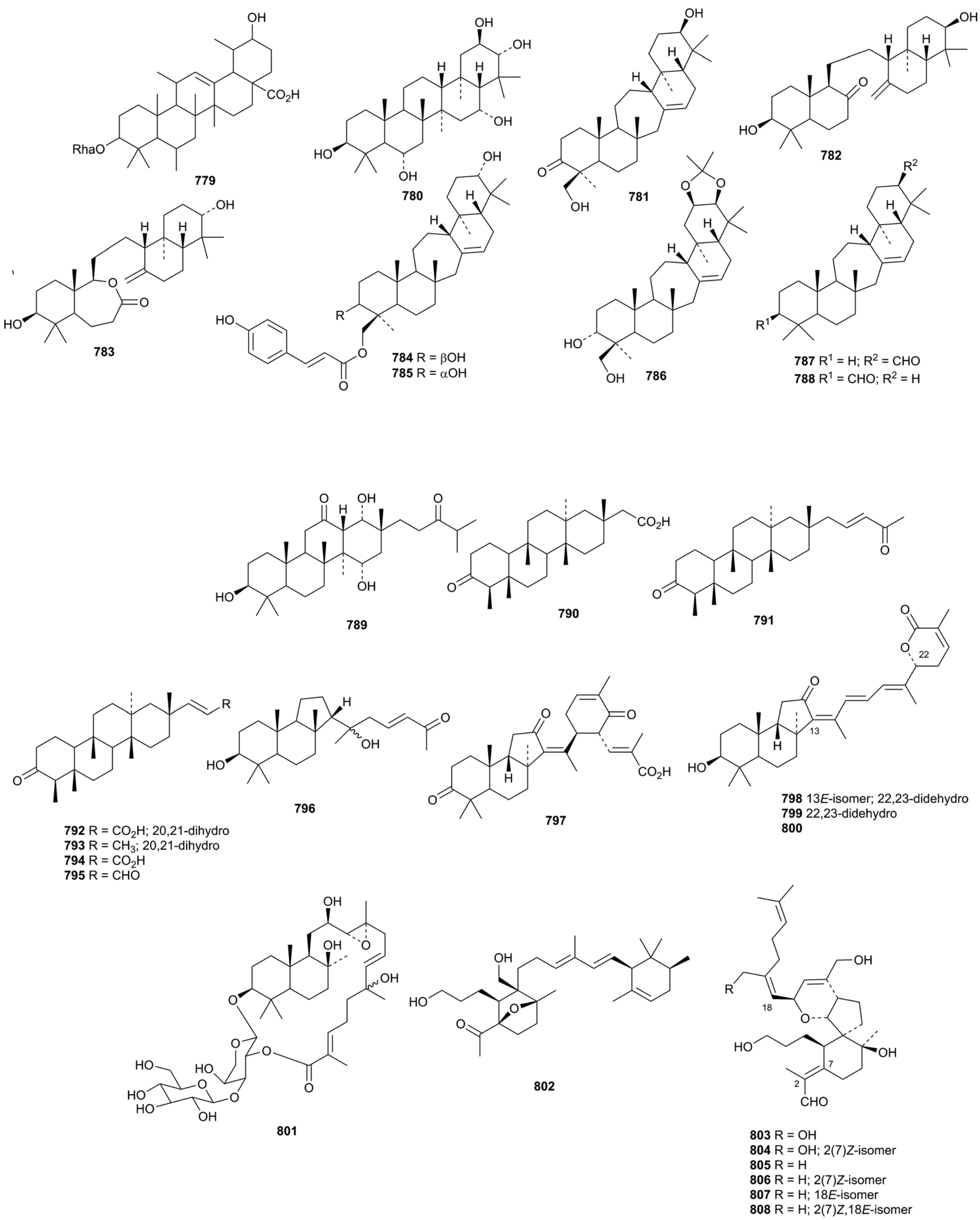
The unlikely structure **779** has been assigned to a triterpene rhamnoside from *Sesbania aculeata*.[366] Three gammacerane saponins, from *Spergula fallax*, have the new genin **780**.[365] *Lycopodium japonicum* is the source of the serratane derivatives lycojaponicuminols A **781**–F **786** (ref. 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**–F **795** were also isolated. Opaciniol A **796**, from *Garcinia opaca*, is a hexnormalabaracane derivative.[48] Further isomalabaricane derivatives, jaspiferins C **797**–F **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 spirioiridotectals A **803**–F **808** from *Iris tectorum*.[374]

10. Conflicts of interest

There are no conflicts of interest.

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