




## Triterpenoids

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

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### 1. Introduction

The interest in the pharmacological activities of triterpenoids continues to be very important.<sup>1</sup> Several reviews have covered the anticancer effects of triterpenoids.<sup>2–9</sup> Other activities that have been highlighted include anti-HIV,<sup>10–12</sup> antiinflammatory,<sup>13</sup> antiviral<sup>6</sup> and against neurodegenerative disorders.<sup>14</sup> As many of the active compounds are saponins there has been an interest in their synthesis<sup>15</sup> and biosynthesis.<sup>16</sup> Reviews have also appeared covering triterpenoids found in *Astragalus* species,<sup>17</sup> *Gymnema sylvestre*,<sup>18</sup> *Panax* species,<sup>19,20</sup> *Sapindus* species<sup>21</sup> and *Siraitia grosvenorii*<sup>22</sup> and plants of the Schisandraceae.<sup>23–25</sup> Triterpenoid biosynthesis in plants<sup>26</sup> and the mechanisms of oxidosqualene cyclases<sup>27</sup> 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*.<sup>28</sup> 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.<sup>29</sup>

### 3. The lanostane group

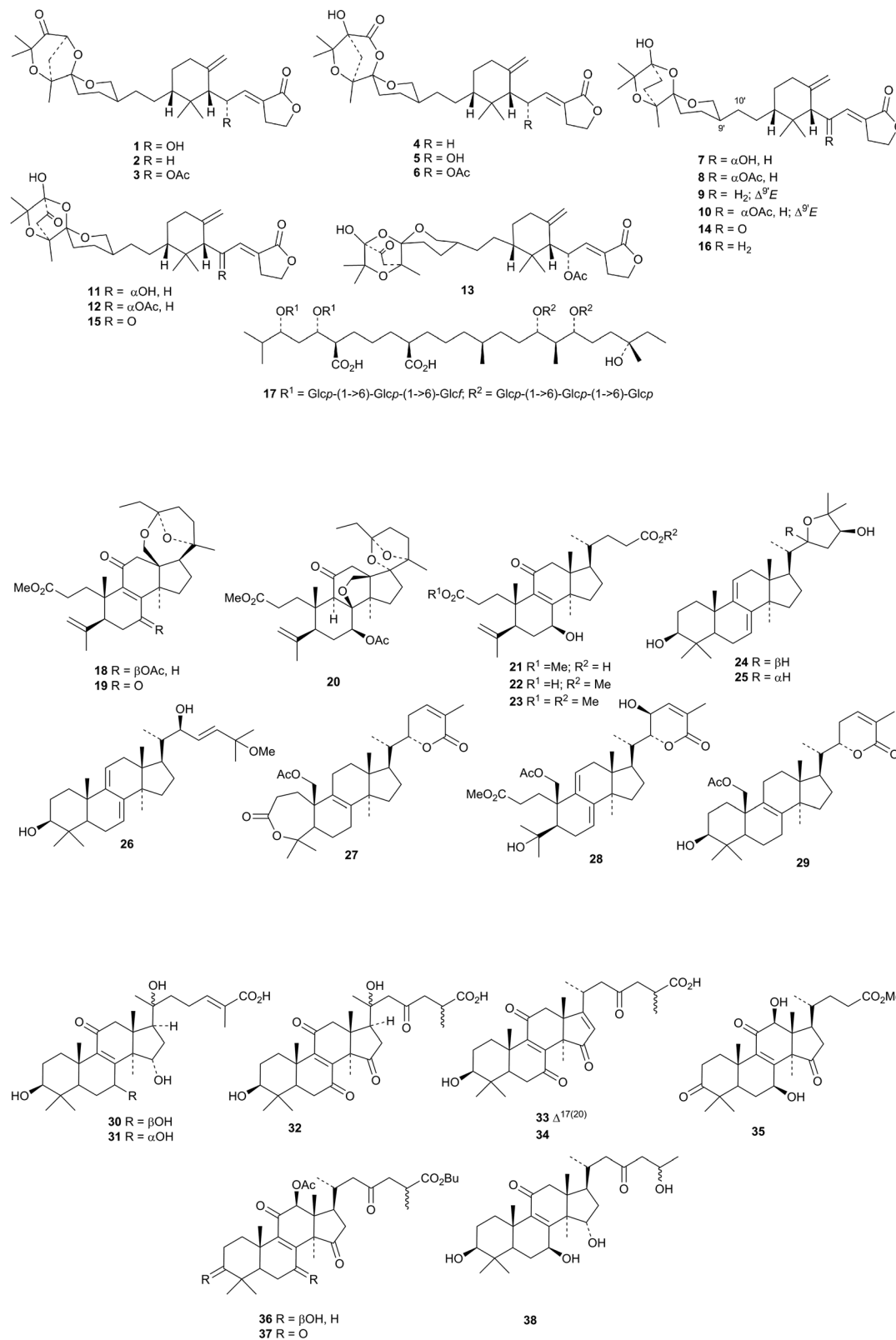
The flow of *Ganoderma* lanostanes continues.<sup>30</sup> *Ganoderma boninense* is the source of ganoboninketals A 18, B 19 and C 20.<sup>31</sup> Fornicatin D 21, E 22 and F 23 and ganodercochlearins A 24, B 25 and C 26 are constituents of *Ganoderma cochlear*.<sup>32</sup> The structure of ganodercochlearin 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.<sup>33</sup> 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*,<sup>34</sup> however the pmr and cmr spectra for rings A and B are not in agreement.

Other *Ganoderma* lanostanes include ganoderic acids XL<sub>1</sub> 30 and XL<sub>2</sub> 31, 20-hydroxyganoderic acid AM<sub>1</sub> 32, ganoderenic acid AM<sub>1</sub> 33 and ganoderesin C 34 from *Ganoderma theaeccolum*,<sup>35</sup> 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*.<sup>38</sup> The biological and pharmacological activities of ganoderic acid and lucidenic acid have been covered in a review.<sup>39</sup>

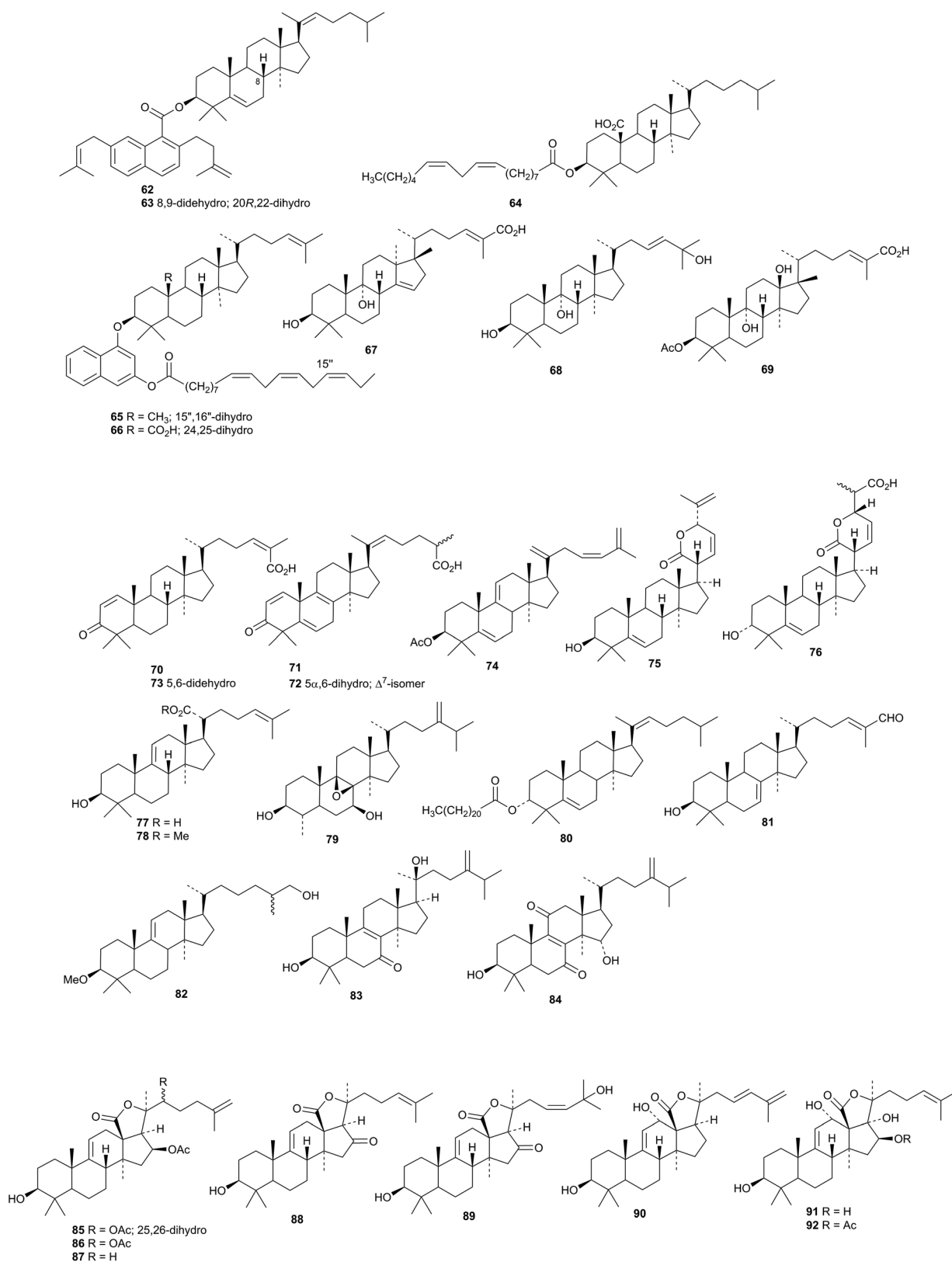
The mushroom *Inonotus obliquus* is a rich source of the 21,24-cyclolanostanes inonotusols A 39–E 43.<sup>40</sup> They are accompanied by inonotusols F 44 and G 45. Inonotusols B 40, D 42 and E 43 have unusual configurations at C17 and inonotusol F 44 has an unusual configuration at C20 and methylation at C24. Further C24-methylated metabolites of *Inonotus obliquus* include inotolactones A 46 and B 47.<sup>41</sup> Hexatenuins A 48, B 49

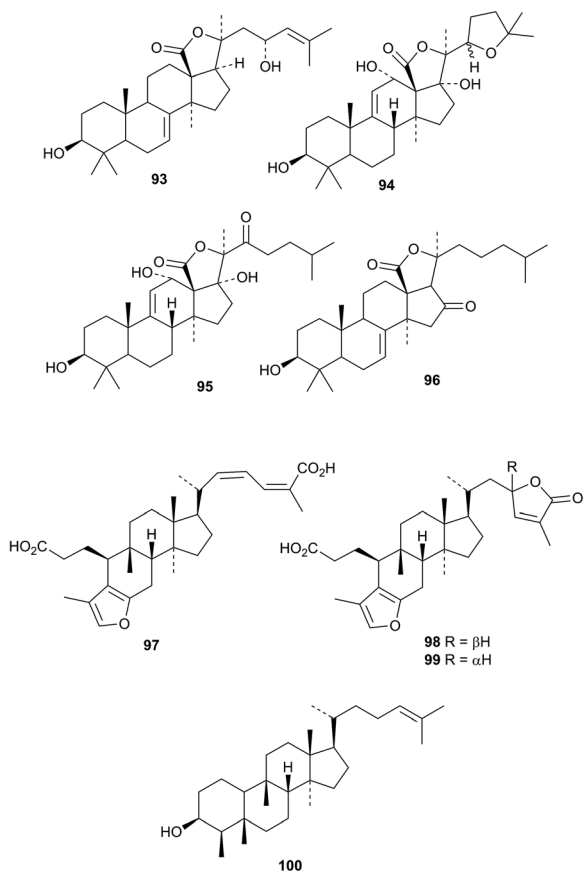
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with holothurinosides Y and Z with known genins.<sup>68</sup> The new genin **96** has been reported for pseudocnoside A from *Pseudocnus dubiosus leoninus*.<sup>69</sup> Holostane saponins with known genins include cucumariosides F<sub>1</sub> and F<sub>2</sub> from *Eupentacta*

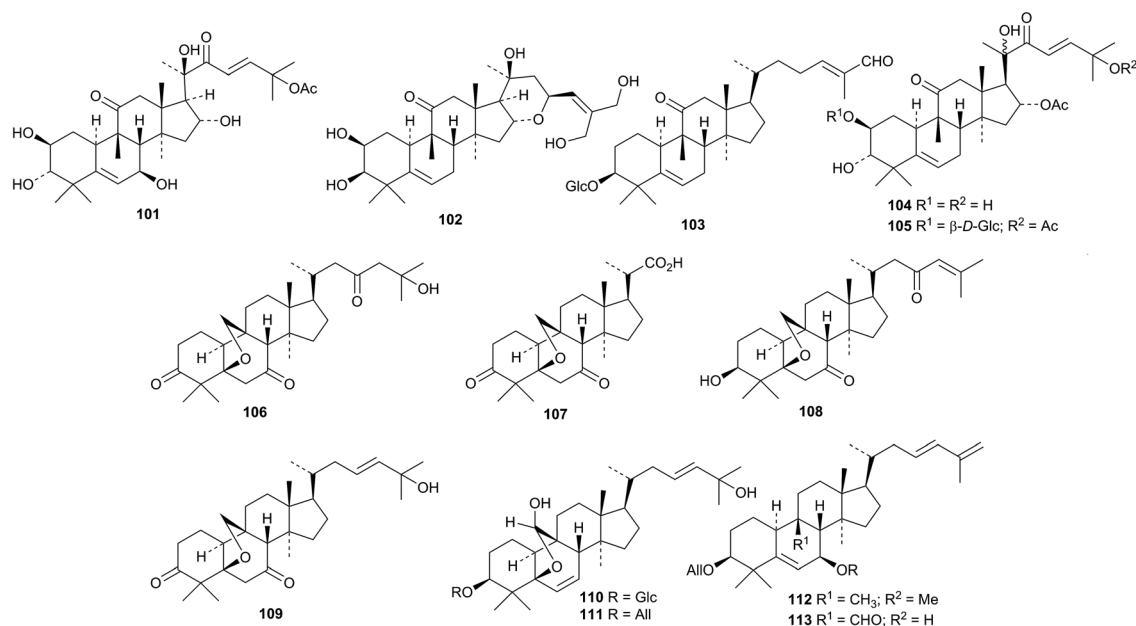
*fraudatrix*,<sup>70</sup> kolgaosides A and B from *Kolga hyalina*,<sup>71</sup> stichloroside F from *Stichopus chloronotus*<sup>72</sup> and violaceosides C, D, E and G from *Pseudocolochirus violaceus*.<sup>73</sup>

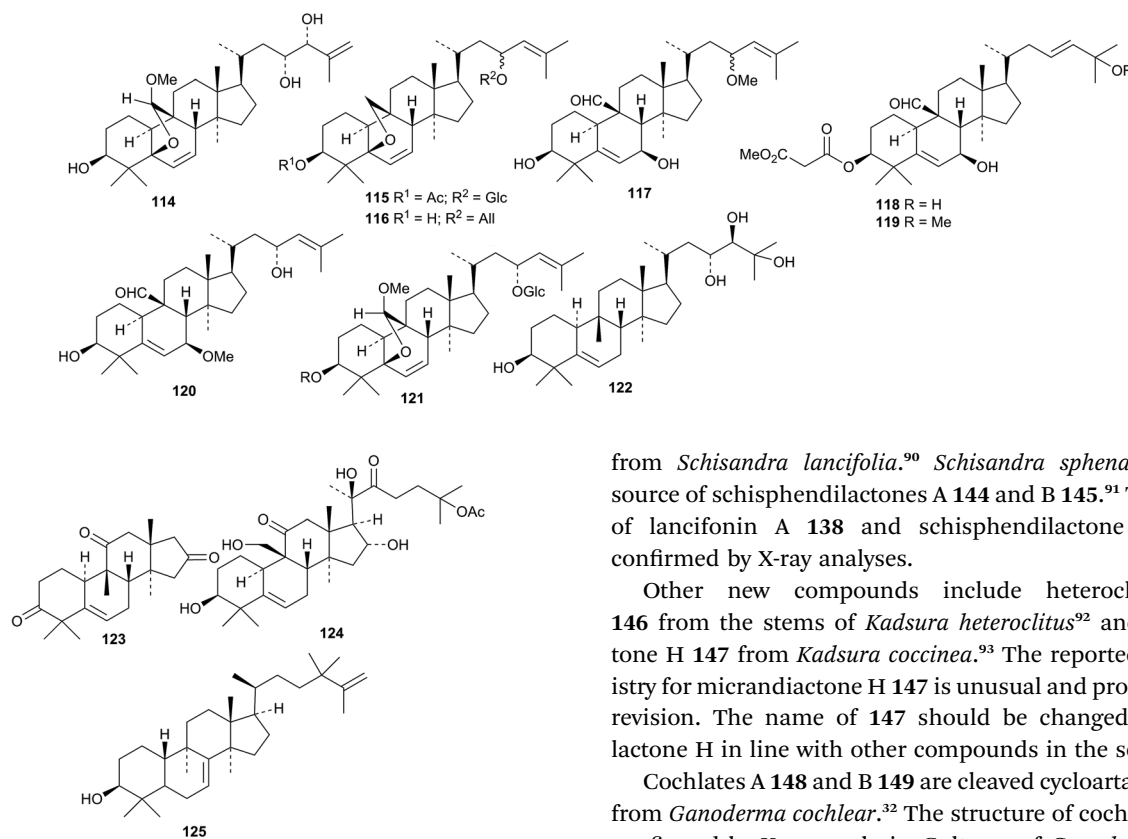
Cucurbitane triterpenoids of mushroom origin have been covered in a review.<sup>74</sup> Three interesting furanoid cucurbitane derivatives, roseic acid **97** and roseolactones A **98** and B **99**, have been isolated from *Russula aurora* and *Russula minutula*.<sup>75</sup> *Empetrum nigrum* var.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

New cucurbitane derivatives isolated from *Hemsleya* species include **101** and **102** from *Hemsleya amabilis*<sup>77</sup> 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*.<sup>78</sup> New cucurbitanes are still being found in the various parts of *Momordica charantia*.<sup>79</sup> The fruit is the source of kuguacins T **106**–**W** **109** (ref. 80) and charantosides D **110**–**G** **113**.<sup>81</sup> 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**.<sup>82</sup> A separate investigation of the leaves led to the isolation of compounds **120** and **121**.<sup>83</sup> Two new glycosides were reported from the seeds, one with the new genin **122**.<sup>84</sup>

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



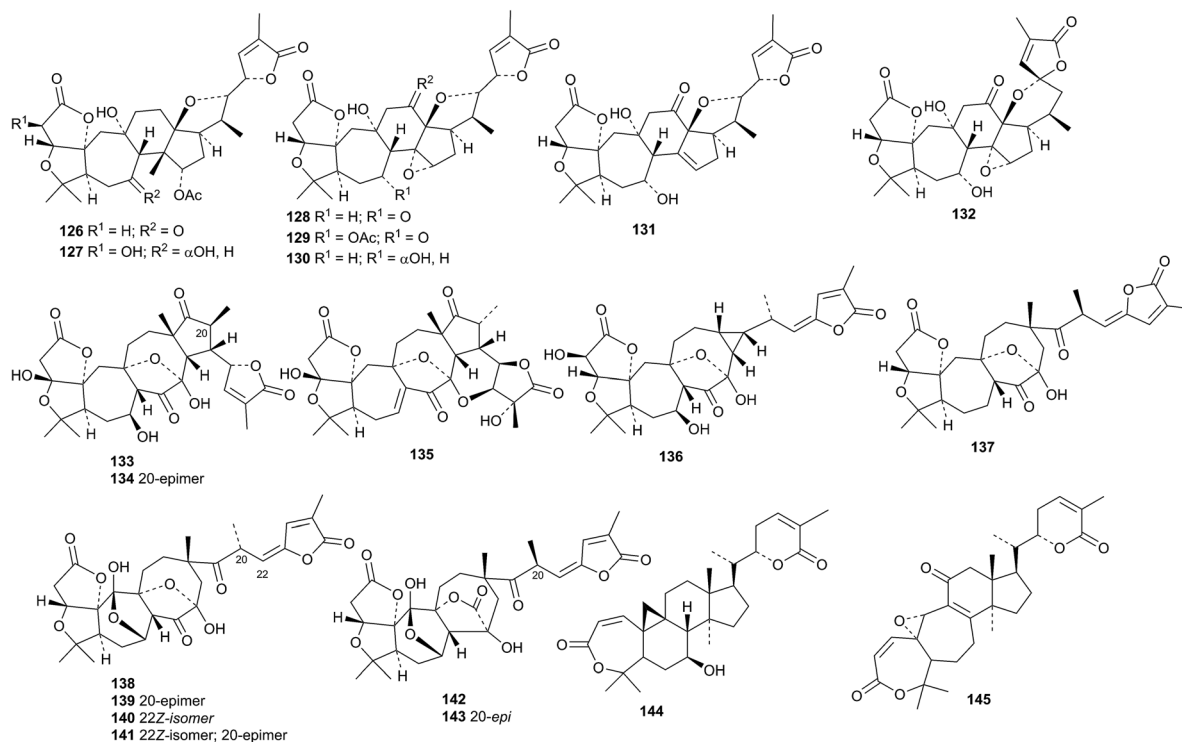


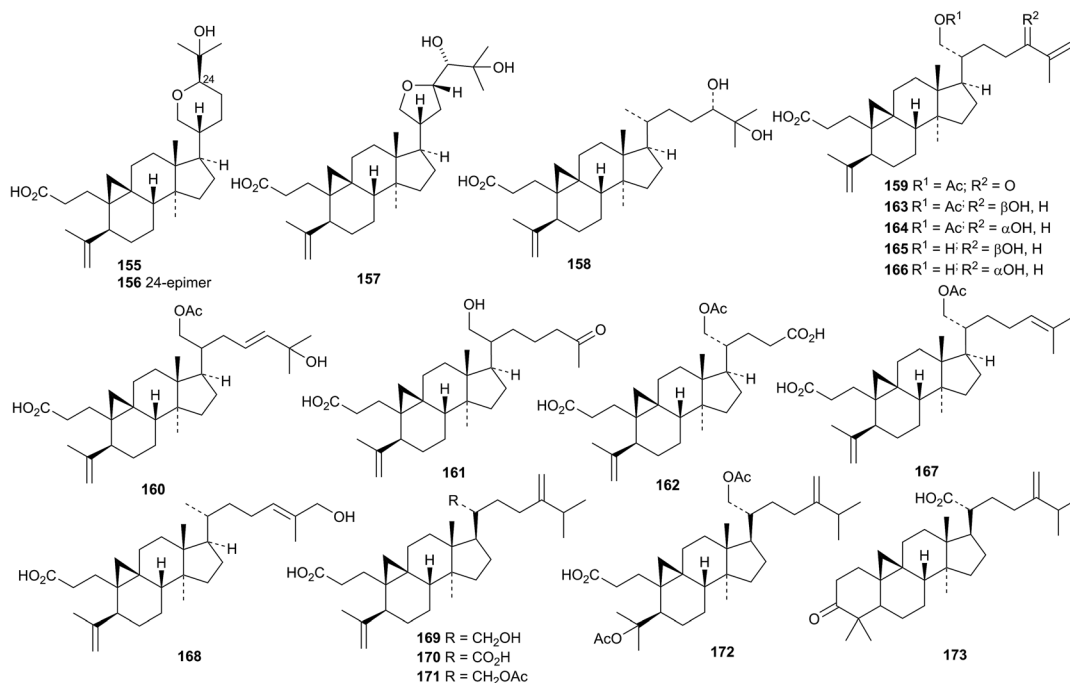
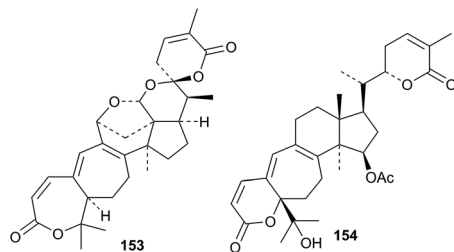
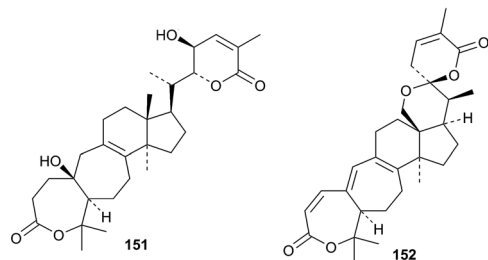
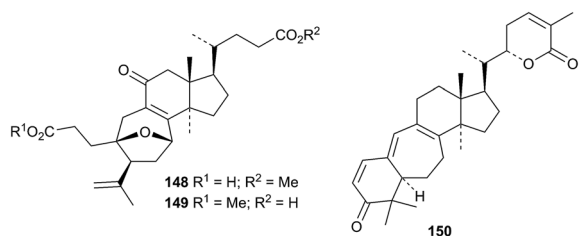
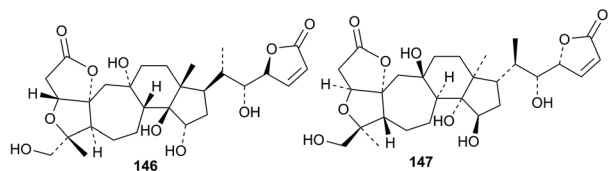
An impressive list of new compounds from *Schisandra chinensis* includes wuweizidilactones J 126–P 132, schindilactones I 133, J 134 and K 135, preschisanartanin N 136 and schisdilactone J 137.<sup>89</sup> Lancifonins A 138–F 143 are new compounds

from *Schisandra lancifolia*.<sup>90</sup> *Schisandra sphenanthera* is the source of schispendilactones A 144 and B 145.<sup>91</sup> The structures of lancifonin A 138 and schispendilactone A 144 were confirmed by X-ray analyses.

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

Cochlates A 148 and B 149 are cleaved cycloartane derivatives from *Ganoderma cochlear*.<sup>32</sup> 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.<sup>33</sup> The structures of ganodermalactones F 152 and G 153 were confirmed by X-ray analyses. The revised structure 154 has been assigned to colossolactone G, a further metabolite of these cultures.





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

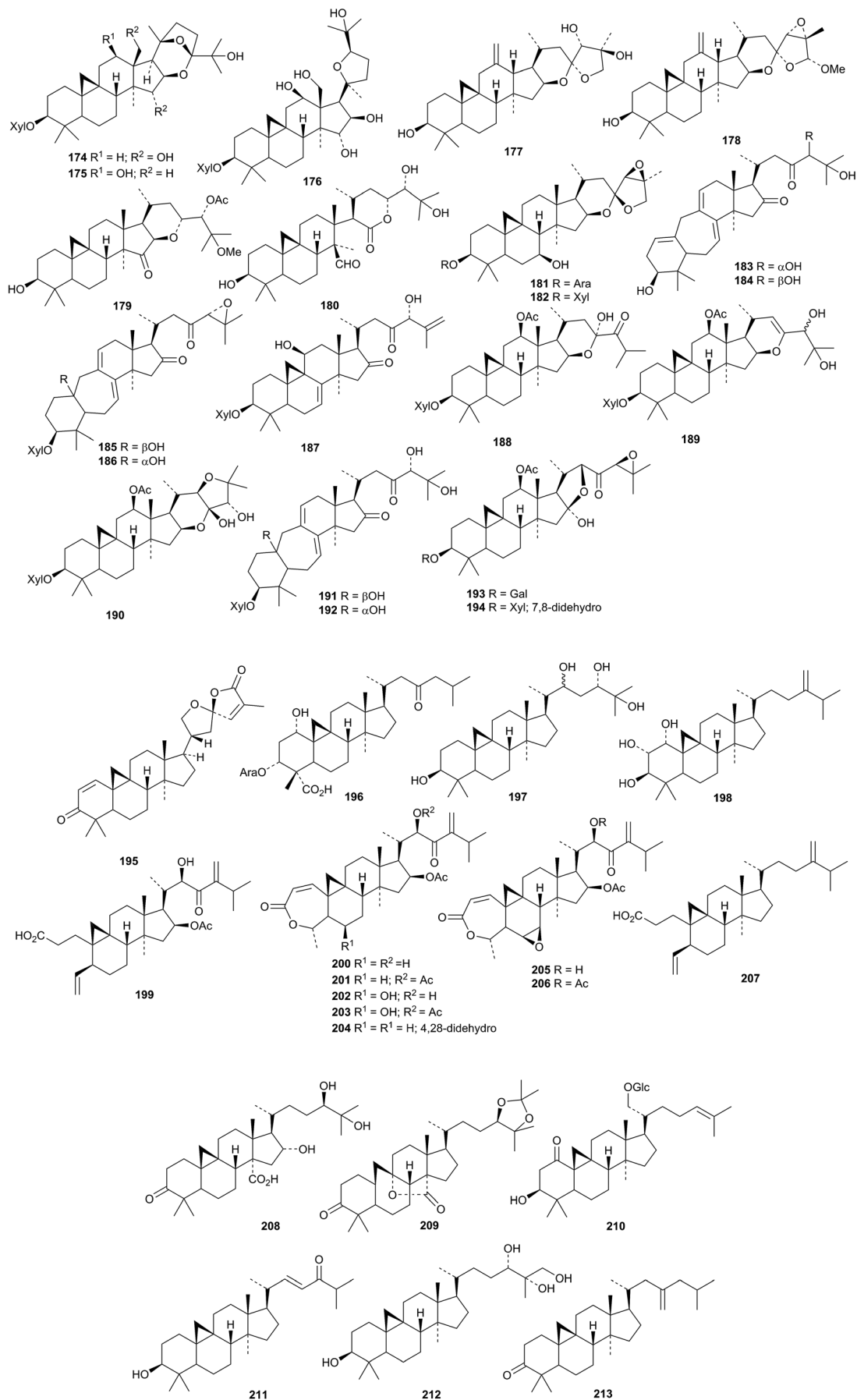
The three cycloartane xylosides 174–176, from *Beesia calthaeifolia*, all have new genins.<sup>96</sup> New compounds from *Cimicifuga* species include the rearranged cycloartanes yunnanterpene G 177 and 12,18-didehydro-26-methoxyacetol 178, isdahurinol 24-acetate 25-methyl ether 179, 15,16-secoshengmanol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

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

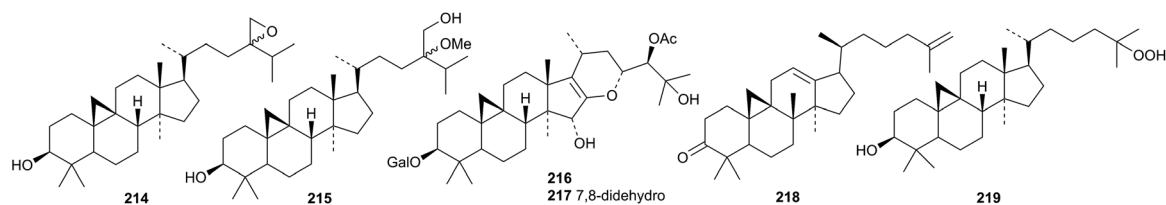
Other new cycloartanes include caloncobic acid C 208 and caloncobalactone C 209 from the leaves of *Caloncoba glauca*,<sup>104</sup> the glucoside rhizostyloside 210, with a new genin, from *Rhizophora stylosa*,<sup>105</sup> compound 211 from *Cassia italica*,<sup>106</sup> and the tetro 212 from the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

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









galactopyranosides but drawn as furanosides.<sup>99</sup> Cycloarta-12,25-dien-3 $\beta$ -ol has been claimed as a constituent of Cameroonian brown propolis but the structure drawn is actually the 9(19)-cyclo dammarane **218**.<sup>110</sup> 25-Hydroperoxycycloartanol **219** is a constituent of *Euphorbia bupleuroides*.<sup>55</sup>

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

## 4. The dammarane group

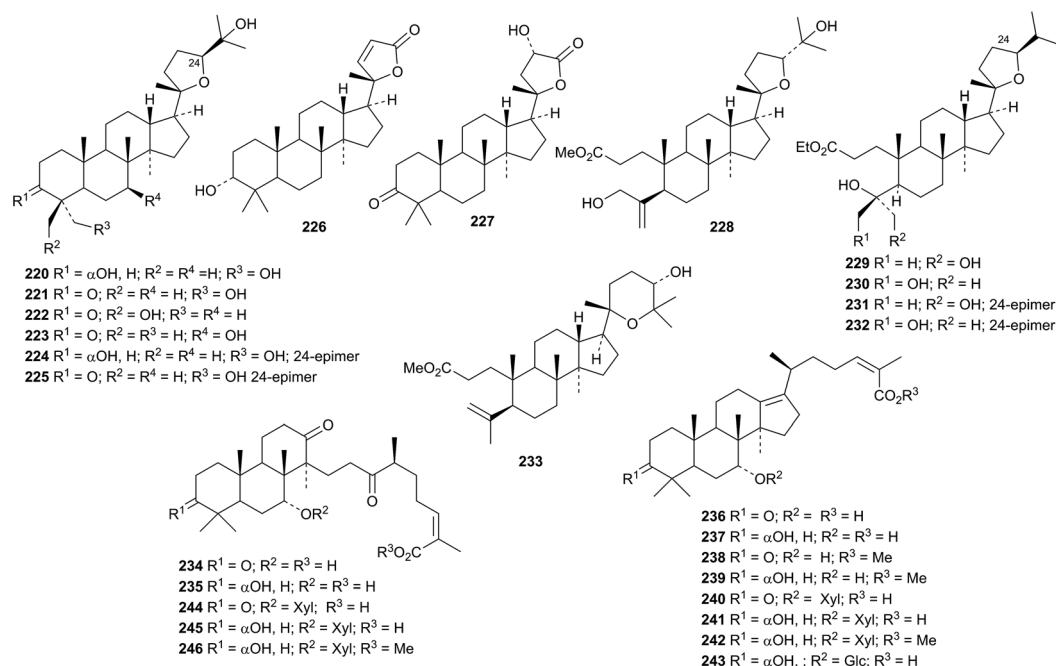
An interesting group of new dammaranes **220–233** has been reported from the stems of *Dysoxylum binectiferum*.<sup>116</sup> Several 13,17-secodammaranes are among the 20-epi-derivatives dysotriflorins A **234–M** **246** from *Dysoxylum densiflorum*.<sup>117</sup> The structure of dysotriflorin I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

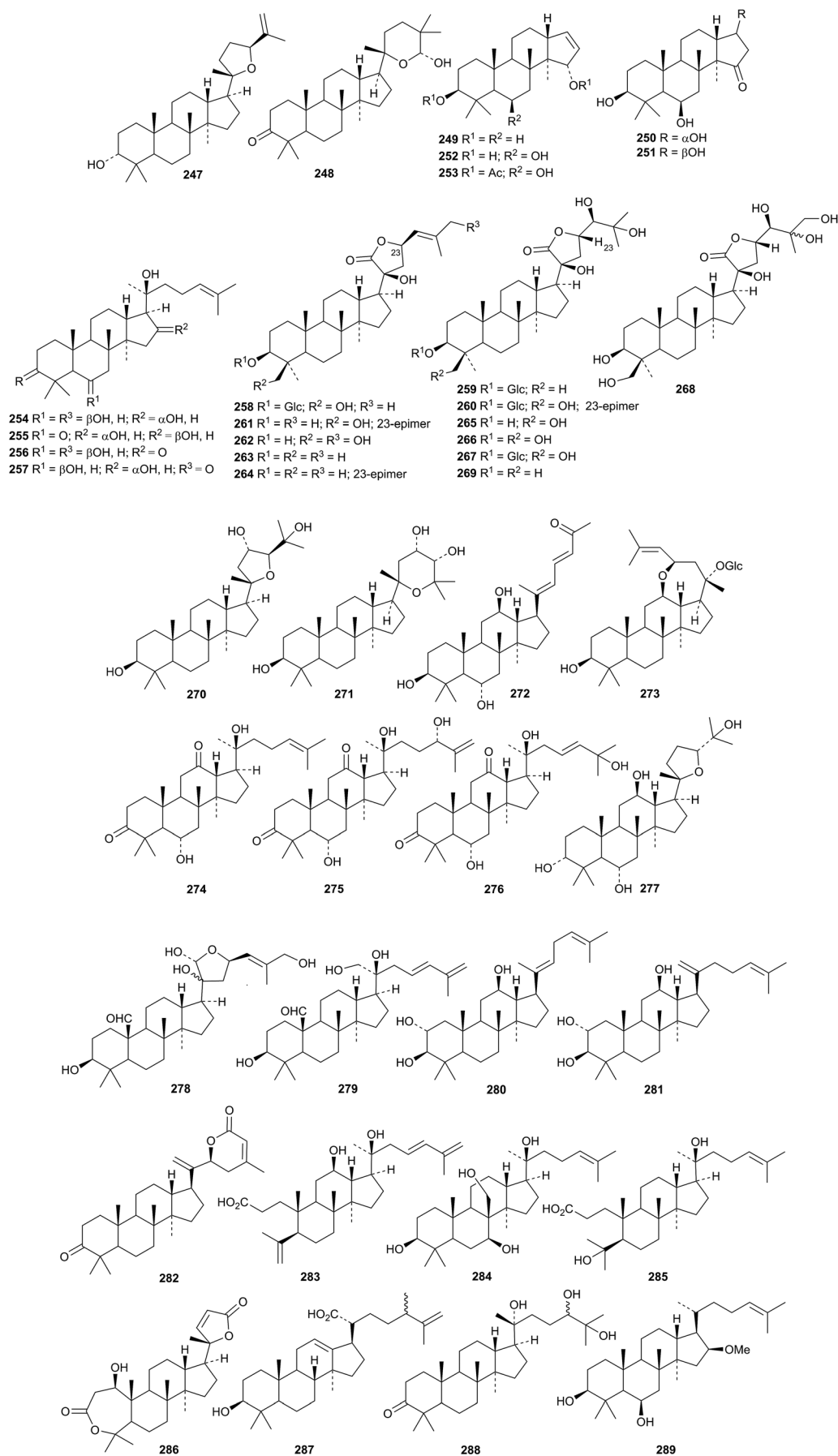
Dysomollisol **247** and dysomollisone **248** are constituents of the fruit of *Dysoxylum mollissimum*.<sup>118</sup> Dysomollisone **248** has been assigned an unusual rearranged side-chain. The octanor-derivative rosanol A **249** has been found in the roots of *Rosa rugosa*.<sup>119</sup> Horipenoids A **250–H** **257**, from *Homonoia riparia*, include several other octanor-derivatives.<sup>120</sup> 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.<sup>121</sup> 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**.<sup>122</sup> The 27-nordammarane **272** and the glucoside **273**, with a known genin, are further constituents of the leaves of *Panax ginseng*.<sup>123</sup> The three 3,12-diketones **274–276** were obtained from the same source.<sup>124</sup> The epoxydammaranetetrol **277** has been isolated from the stems and leaves of American ginseng and given the erroneous name 3 $\alpha$ -ocotillol (ocotillol is an epoxydammaranediol).<sup>125</sup>

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

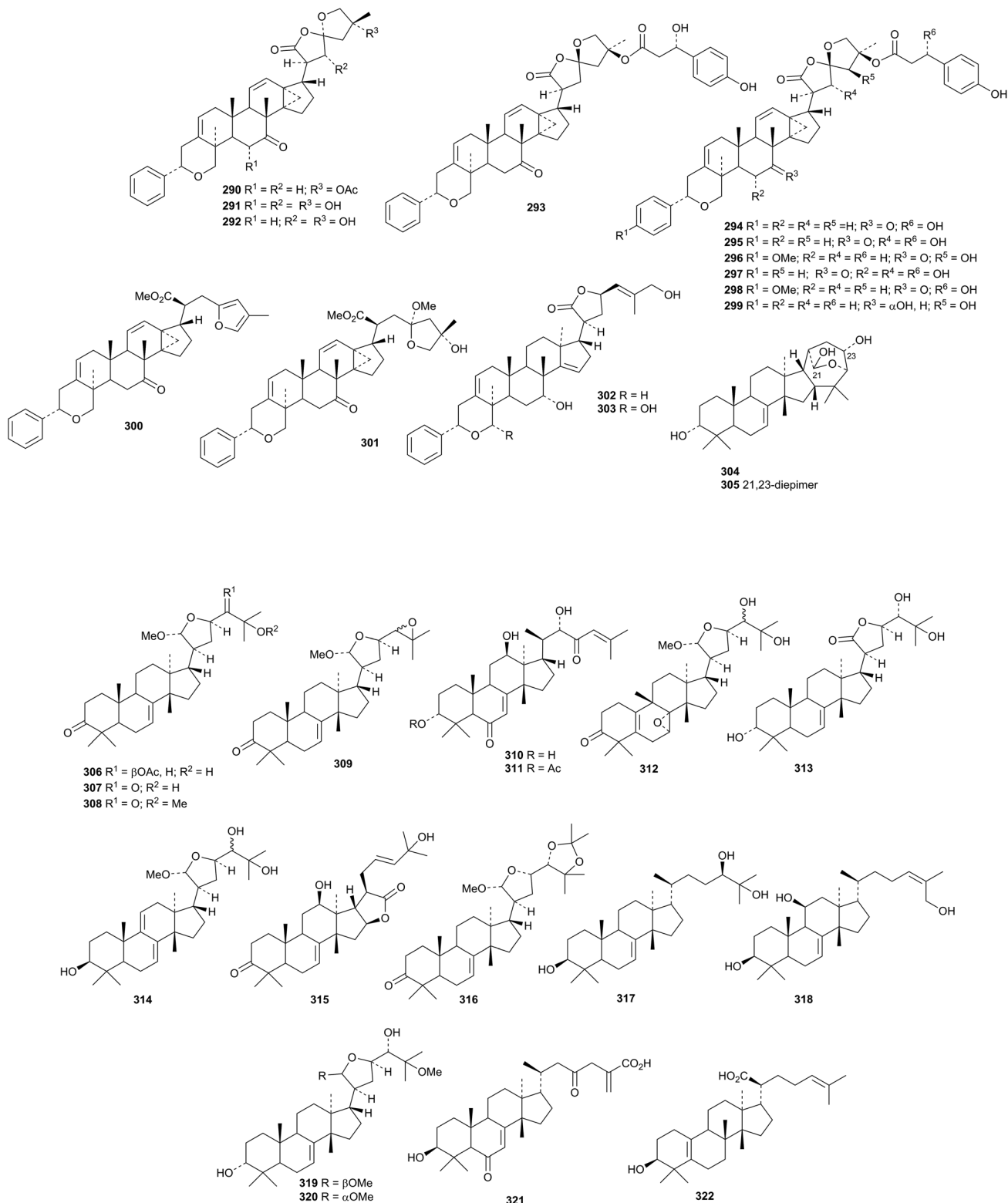


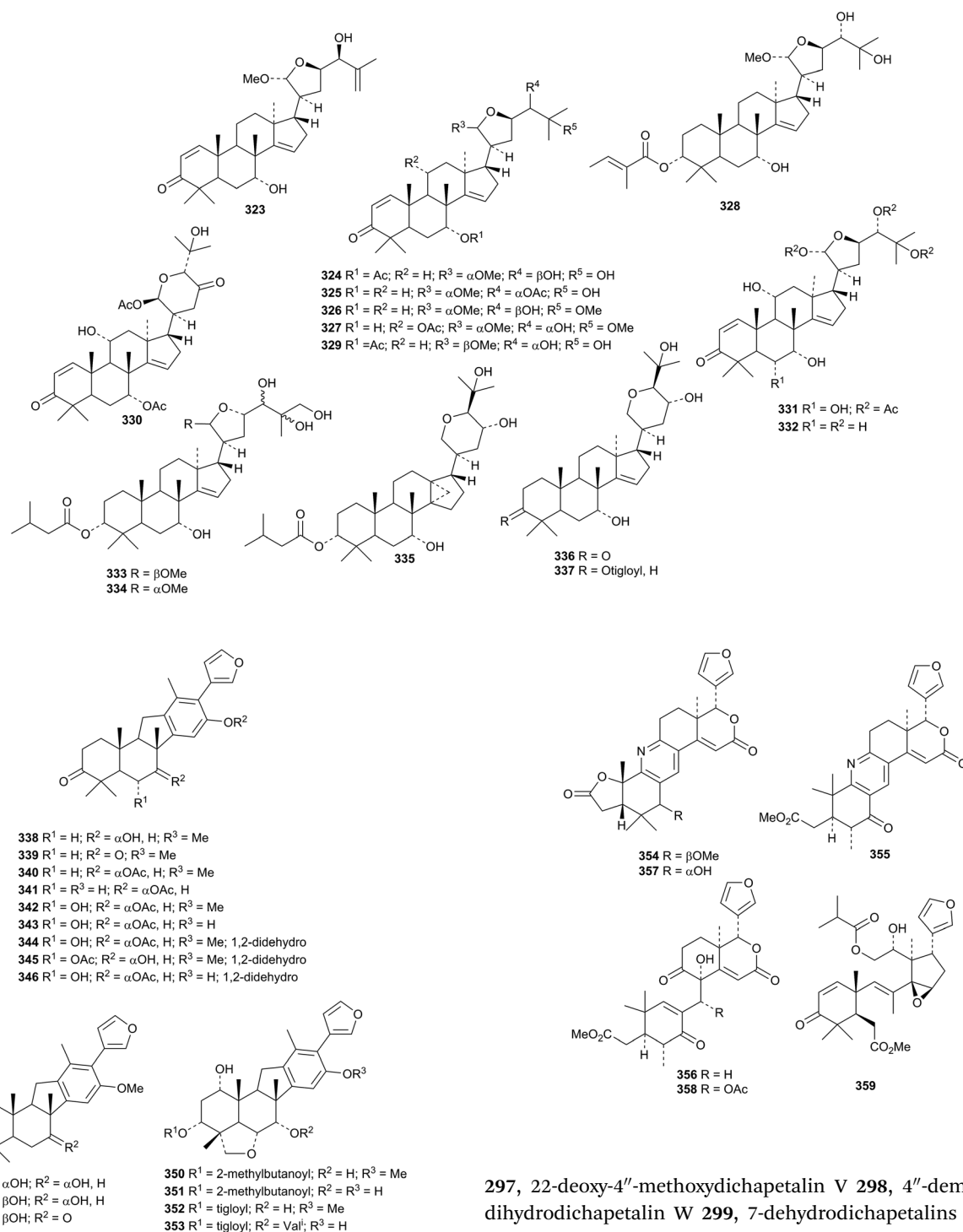


and the keto-lactone **282**.<sup>128</sup> Cyclocarioside K, from *Cyclocarya paliurus*,<sup>129</sup> and tubeimoside C, from *Bolbostemma paniculatum*,<sup>130</sup> also have new genins, **283** and **284**, respectively. Other new dammaranes include the ring A-cleaved derivative **285** from *Aglaia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

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

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





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

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

297, 22-deoxy-4''-methoxydichapetalin V 298, 4''-demethoxy-7-dihydrodichapetalin W 299, 7-dehydrodichapetalins E 300, G 301 and Q 302 and 29 $\alpha$ -hydroxy-21-dehydrodichapetalin Q 303.<sup>141</sup> 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*.<sup>142</sup>

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



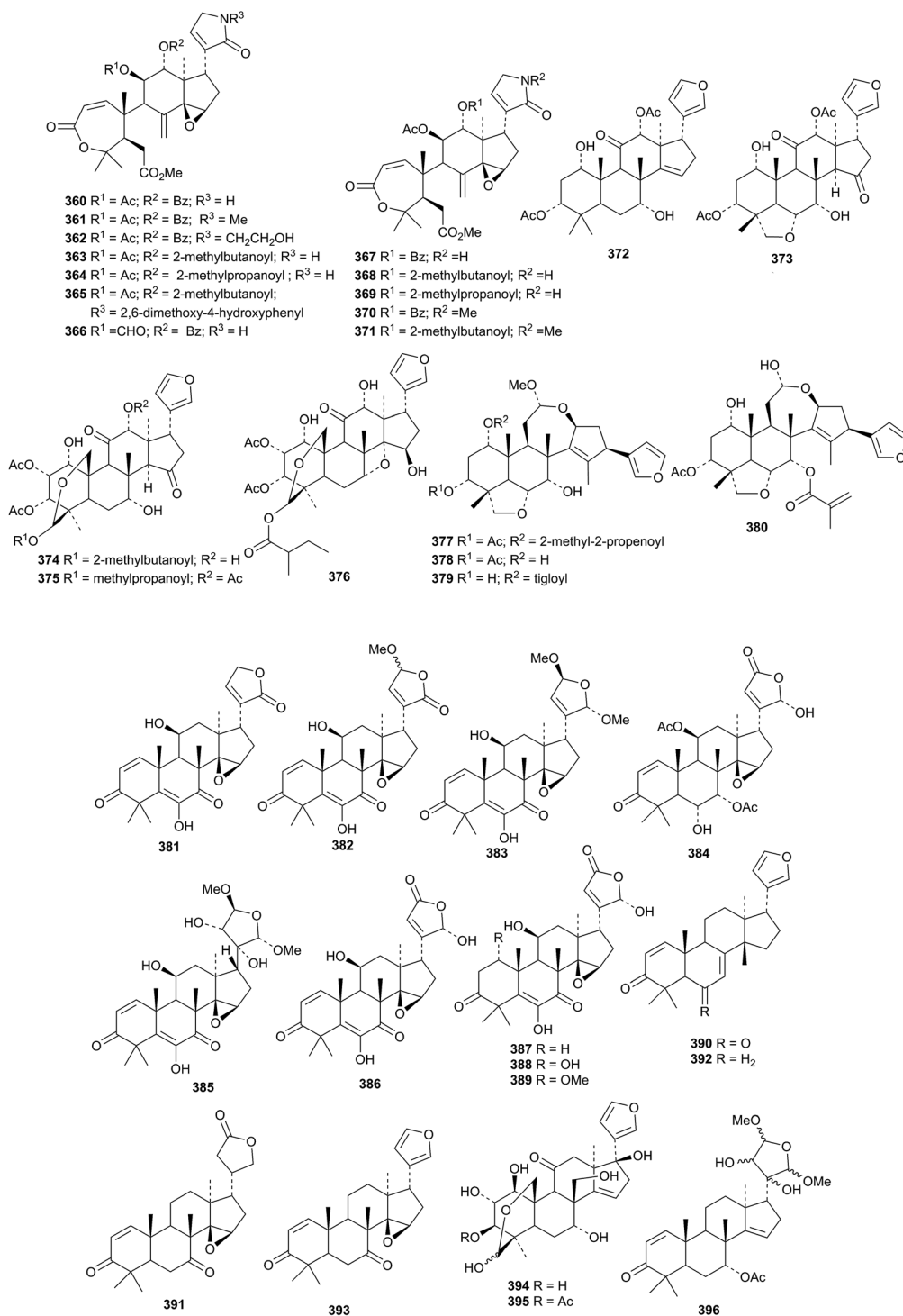
*Celastrus stylosus*,<sup>148</sup> the 21-epimers paramignyols A **319** and B **320** from *Paramignya scandens*<sup>149</sup> and dysoxylum A **321** (duplicate name) from *Dysoxylum densiflorum*.<sup>150</sup> The unusual structure **322** has been ascribed to a constituent of *Melia azedarach*.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

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

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

#### 4.1 Tetranortriterpenoids

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

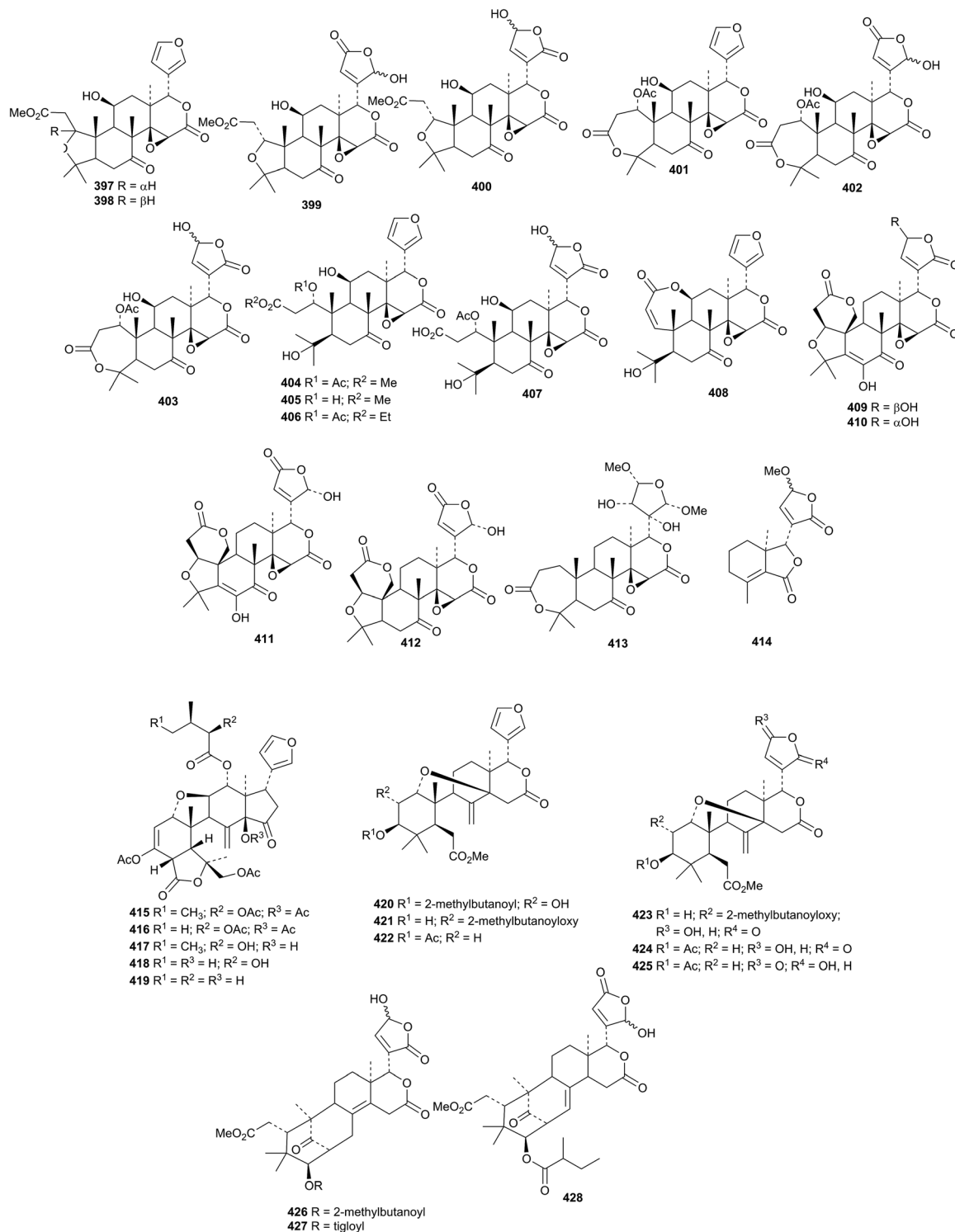


members of this class continues unabated. Walsucochinoids C 338–R 353, from *Walsura cochinchinensis*, form an interesting group of rearranged derivatives.<sup>164</sup> The structures of walsuchinoids C 338 and L 347 were confirmed by X-ray analyses.

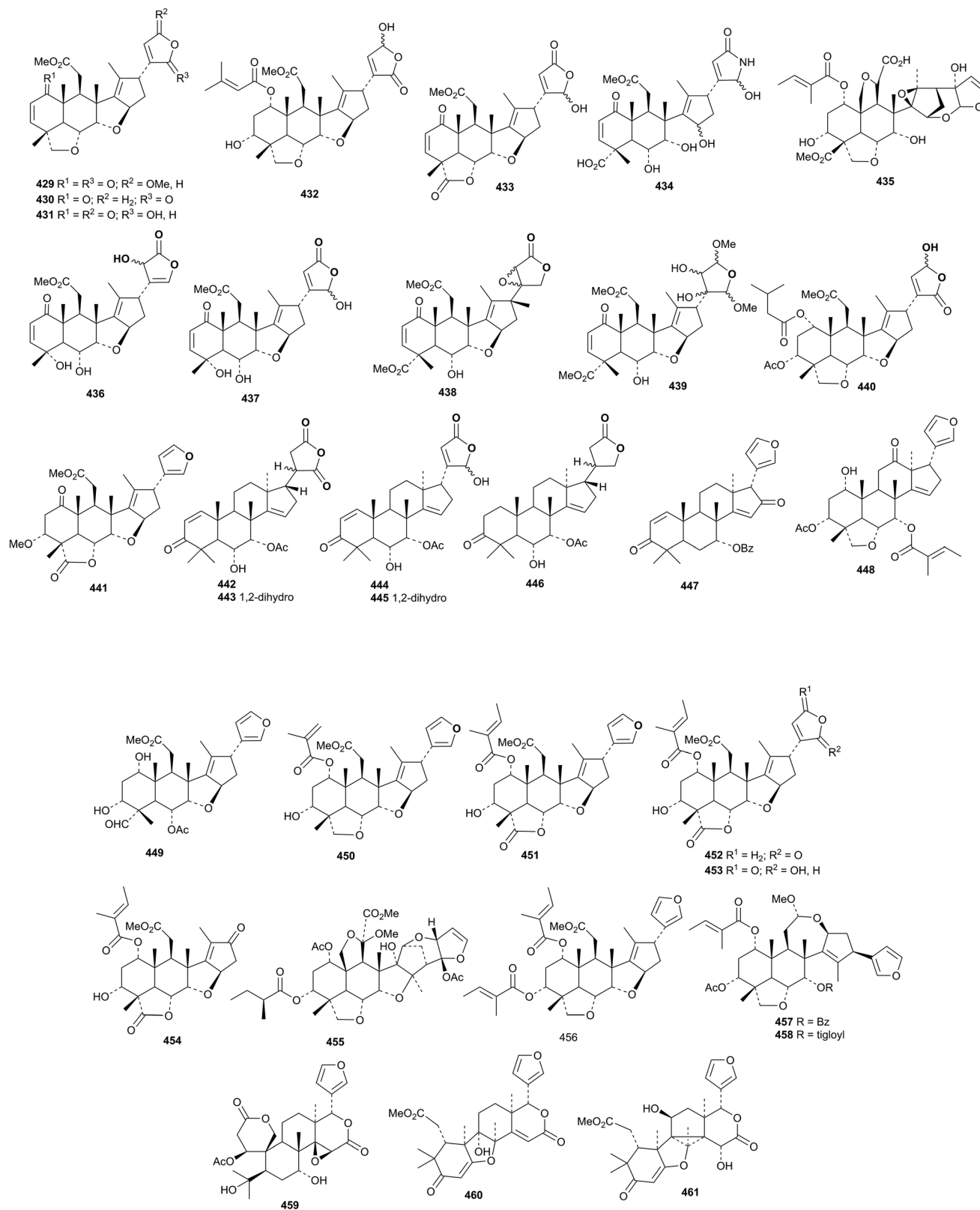
Xylogranatopyridines A 354, B 355 and prexylogranatopyridine 356, from the Chinese mangrove *Xylocarpus granatum*, are closely related to the known xylogranatin F 357 and

hainangranatumin D 358.<sup>165</sup> The unusual 9,11-seco-derivative toonasecone A 359 has been isolated from *Toona ciliata*.<sup>166</sup>

A series of amides, amooramides A 360–L 371, has been reported from the twigs and leaves of *Amoora tsangii*.<sup>167</sup> The highly oxygenated tetranortriterpenoids 372–376, from the fruits of *Melia toosendan*, are accompanied by the ring-C cleaved derivatives 377–379.<sup>168</sup> Compound 378 has also been isolated from *Melia azedarach* together with 380.<sup>169</sup>



Nine new cedrelone derivatives, walsuranolide B **381**, 11 $\beta$ -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*.<sup>107</sup> Dysoxylamins B **390**, C **391** (duplicate names) and compounds **392** and **393** are constituents of *Dysoxylum densiflorum*.<sup>150</sup> Other derivatives with intact skeletons include flexuosoids A **394** and B **395** from *Phyllanthus*

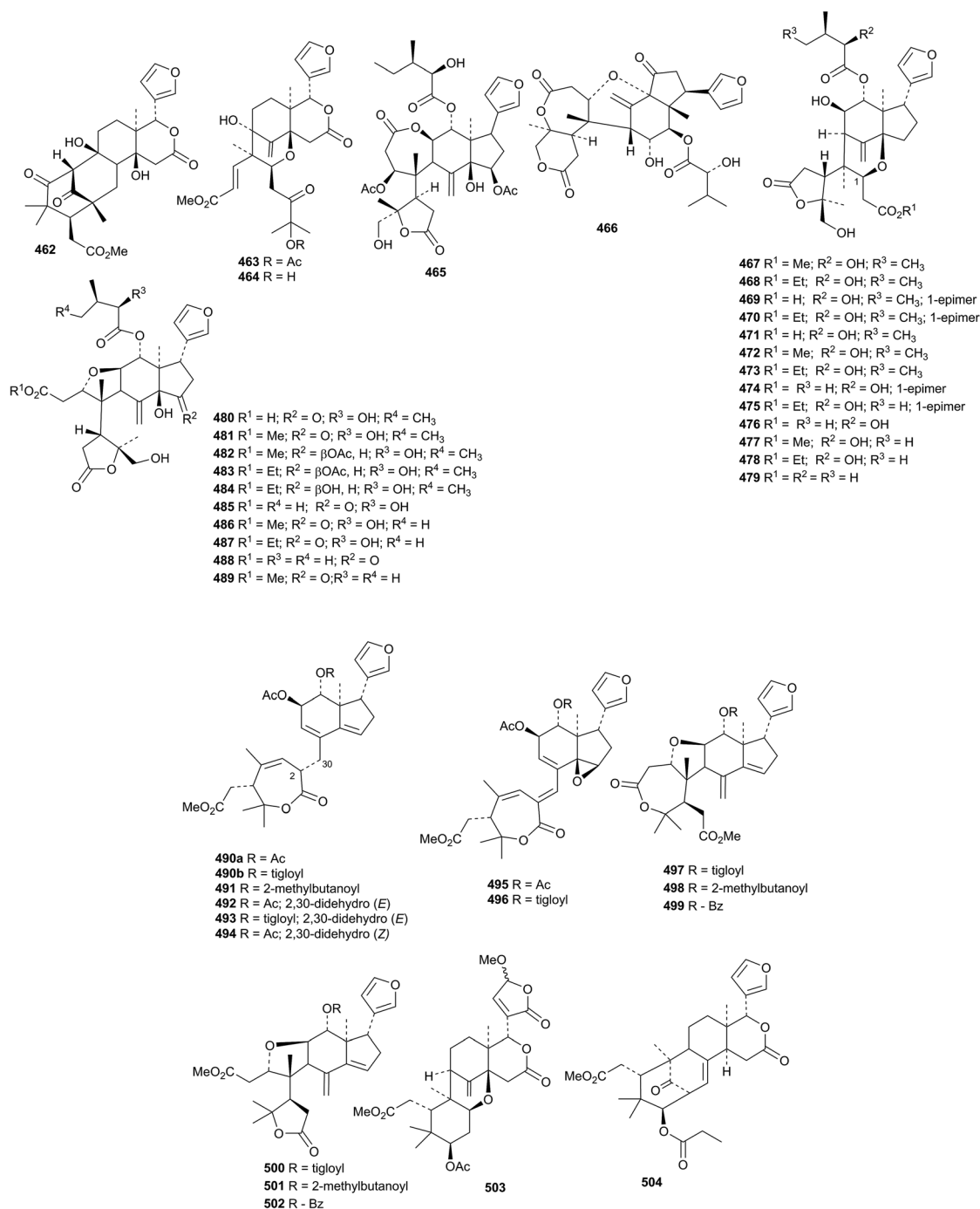


*flexuosus*<sup>170</sup> and compound **396** from the flowers of *Azadirachta indica* var. *siamensis*.<sup>171</sup>

The A,D-seco derivatives clauemargins A **397**–**L 408** have been isolated from the stems of *Clausena emarginata*.<sup>172</sup> 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*<sup>173</sup> and kihadanin C **413** from the root bark of *Dictamnus dasycarpus*.<sup>174</sup> 23-O-Methyl dasylactone B **414** is a further constituent of *Dictamnus dasycarpus*.<sup>174</sup>

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

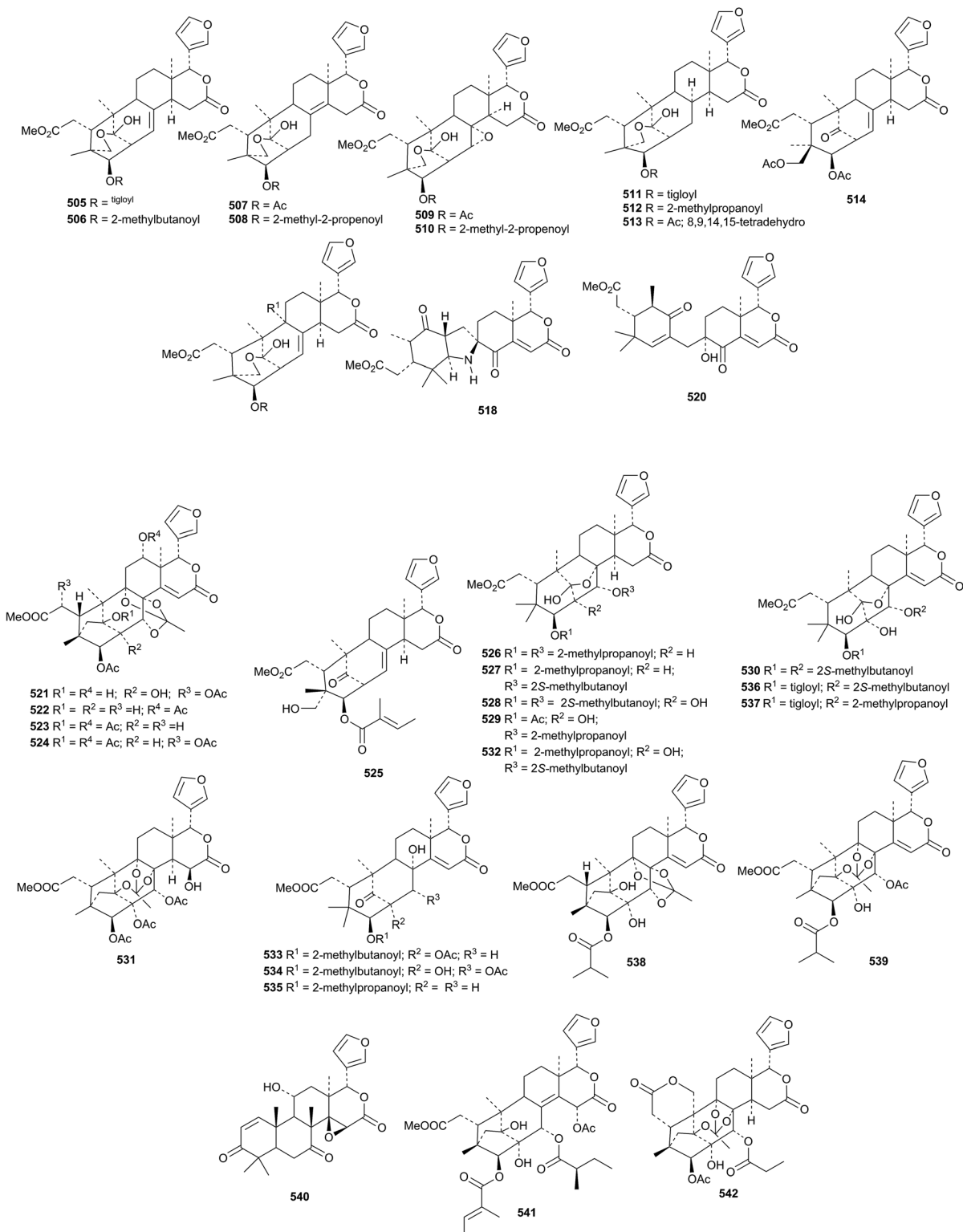
The seemingly endless investigations of the constituents of *Azadirachta indica* have, unsurprisingly, produced more unremarkable ring C-cleaved derivatives. These include the 28-





deoxynimbolide derivative **429**,<sup>177</sup> compounds **430–432**,<sup>178</sup> nimbolide B **433** and nimbic acid B **434** (ref. 179) and compounds **435–437** from *Azadirachta indica*<sup>180</sup> and compounds **438–441** from *Azadirachta indica* var. *siamensis*.<sup>181</sup> 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*.<sup>182</sup> 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.<sup>156</sup> Toosendansins A **456**, B **457** and C **458** are constituents of *Melia toosendan*.<sup>147</sup>



The ichangin derivative **459**, 9 $\alpha$ -hydroxyhortolide **A 460** and 11 $\beta$ -hydroxyhortolide **C 461** were isolated from *Hortia orcadia*.<sup>184</sup>

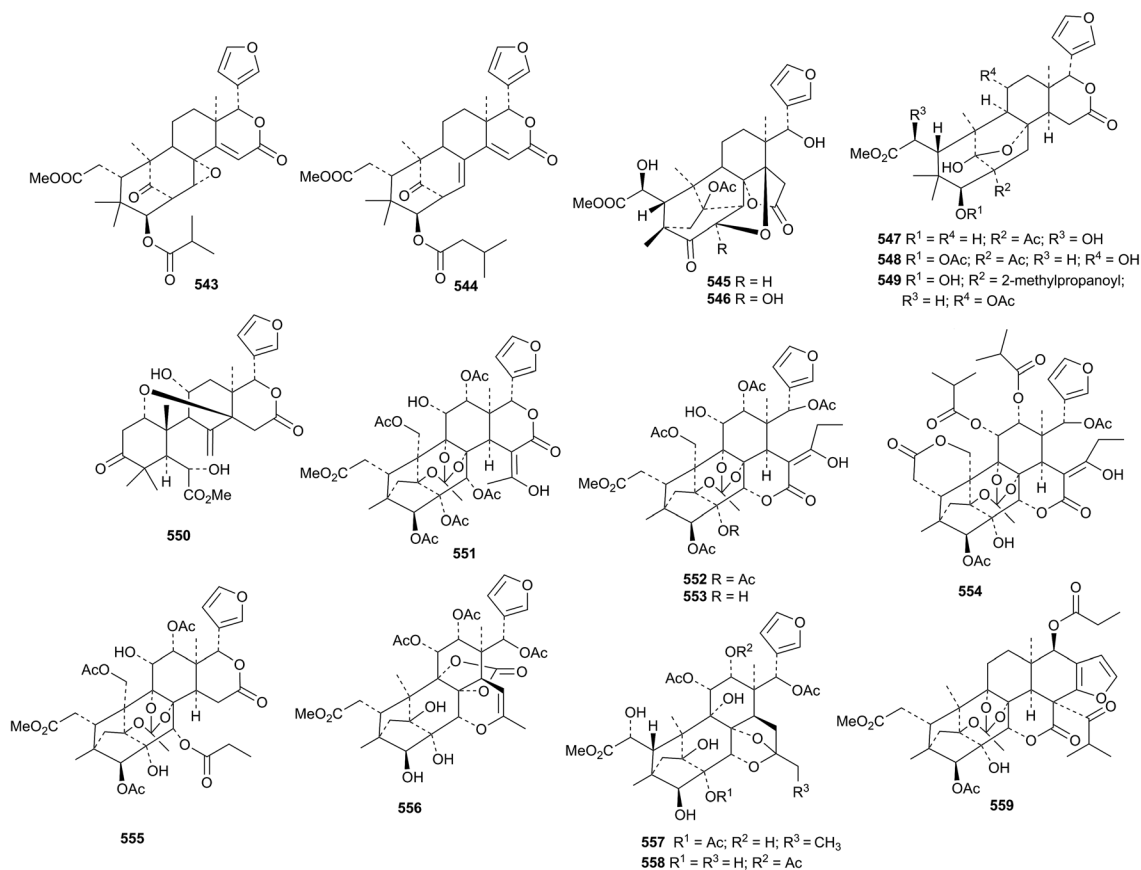
New skeletal variations of rearranged limonoids continue to appear. The structures of trichiconins **A 462** and **B 463**, from *Trichilia connaroides*, were confirmed by X-ray analyses.<sup>185</sup> They were accompanied by trichiconin **C 464**. Zaphraprinins **A 465–Y 489** are modified prieurianin derivatives from the fruits of *Aphanamixis grandifolia*.<sup>186</sup> The structures of zaphraprinins **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*.<sup>187</sup> Cinecicapadesin **G 503** (ref. 188) and the swietenine derivative **504** (ref. 189) are constituents of *Cipadessa cinerascens*.

**525**.<sup>194</sup> Xylorumphins **E 526–J 531** and 2-hydroxyxylorumphin **F 532** are constituents of the seeds of *Xylocarpus rumphii*.<sup>195</sup> 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**.<sup>199</sup> Velutinasins **A 551–H 558** are phragmalin derivatives from *Chukrasia tabularis* var. *velutina*.<sup>200</sup> Velutinalide **C 559** is another new compound from this source.<sup>201</sup>

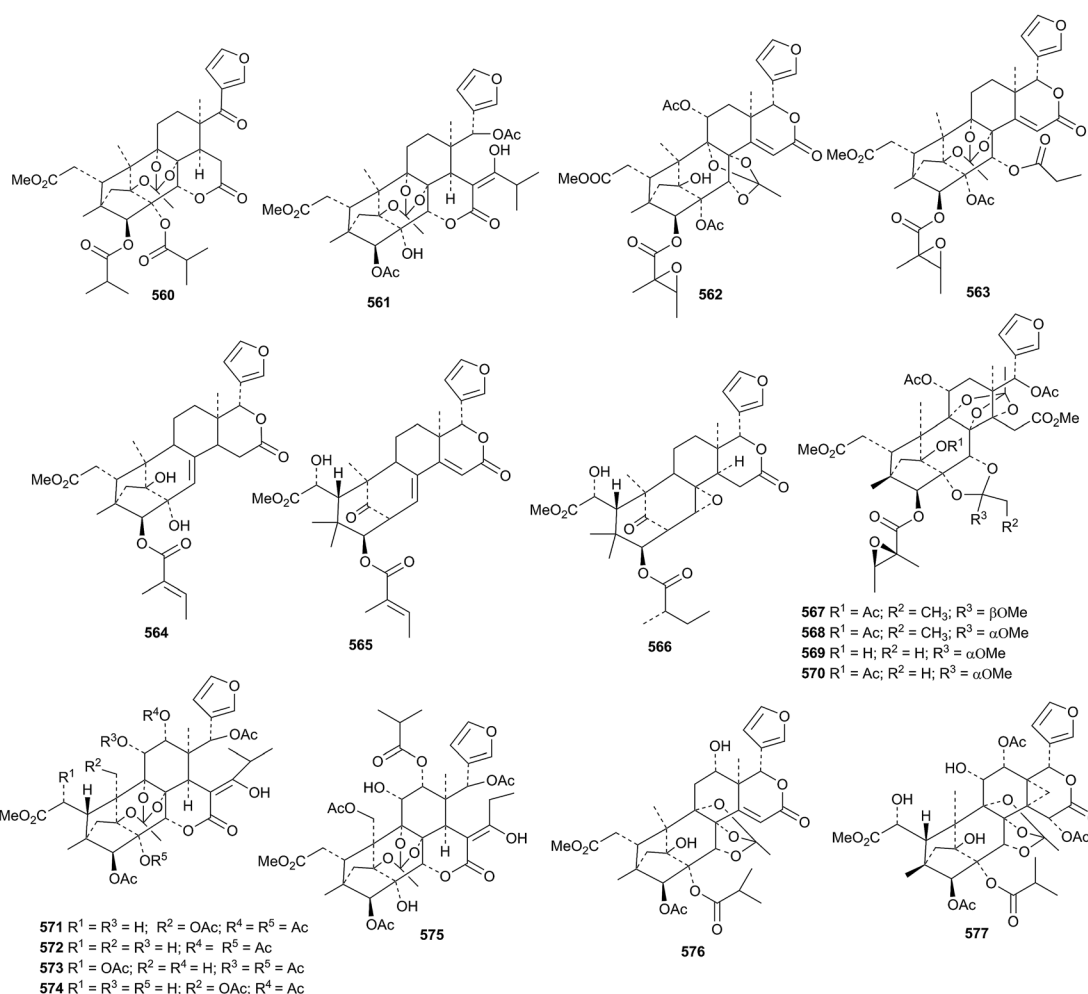


Compounds from an Indian *Xylocarpus granatum* include granatumins **L 505–U 514** (ref. 190) and granatumins **V 515–Y 518**.<sup>191</sup> The structures of granatumins **L 505** and **Y 518** were confirmed by X-ray analyses. Granatumins **M 506** and **V 515** have also been isolated from *Xylocarpus granatum* by another group and named xylomexicanins **H** and **G**, respectively.<sup>192</sup> 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 xylcartin **C**

*Neobeguea mahafalensis* is the source of the phragmalin derivatives libiguin **A 560** and libiguin **B 561** (in equilibrium with its keto tautomer).<sup>202</sup> These compounds are reported to have aphrodisiac properties. 2-Acetylsoymidin **B 562** and soyamidins **D 563** and **E 564** are constituents of *Soymida febrifuga*.<sup>203</sup> Swielimonoids **A 565–F 570** are additional constituents of *Swietenia macrophylla* seeds.<sup>204</sup> Chukvelutilides **I 571–O 577** are further new phragmalin derivatives from the seeds of *Chukrasia tabularis*.<sup>205</sup> Synthetic studies have indicated that the biosynthesis of the 1,8,9-orthoester moiety in phragmalins involves intermediates with an ester at C-1.<sup>206</sup>





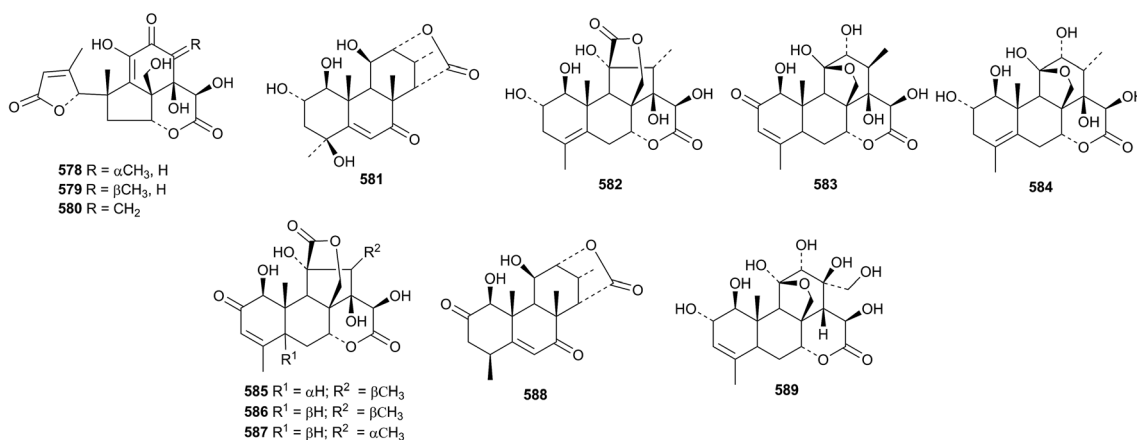
## 4.2 Quassinoids

Eurylactones E 578, F 579 and G 580, eurycomalides D 581, and E 582 and 13 $\alpha$ ,18-dihydroeurycomanone 583 are new constituents of the roots of *Eurycoma longifolia*.<sup>207</sup> Other constituents of *Eurycoma longifolia* include  $\Delta^4$ -14-hydroxyglucarbol 584, 5-isoeurycomadilactone 585, eurycomadilactone 586 and 13-epieurycomadilactone 587 (ref. 208) and eurycomalide C 588.<sup>209</sup> The structures of

$\Delta^4$ -14-hydroxyglucarbol 584 and 5-isoeurycomadilactone 585 were confirmed by X-ray analyses. Shinjulactone O 589 has been isolated from the root bark of *Ailanthus altissima*.<sup>210</sup>

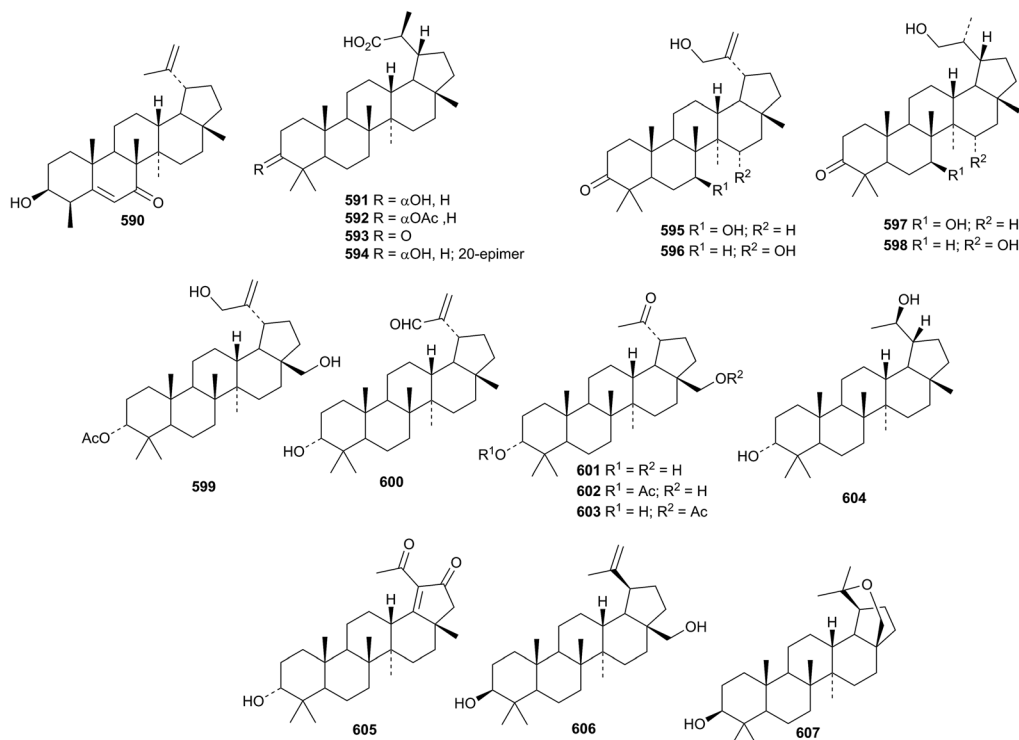
## 5. The lupane group

Betulinic acid has been reported to have a variety of pharmacological activities including antitumour activity.<sup>211,212</sup> The first

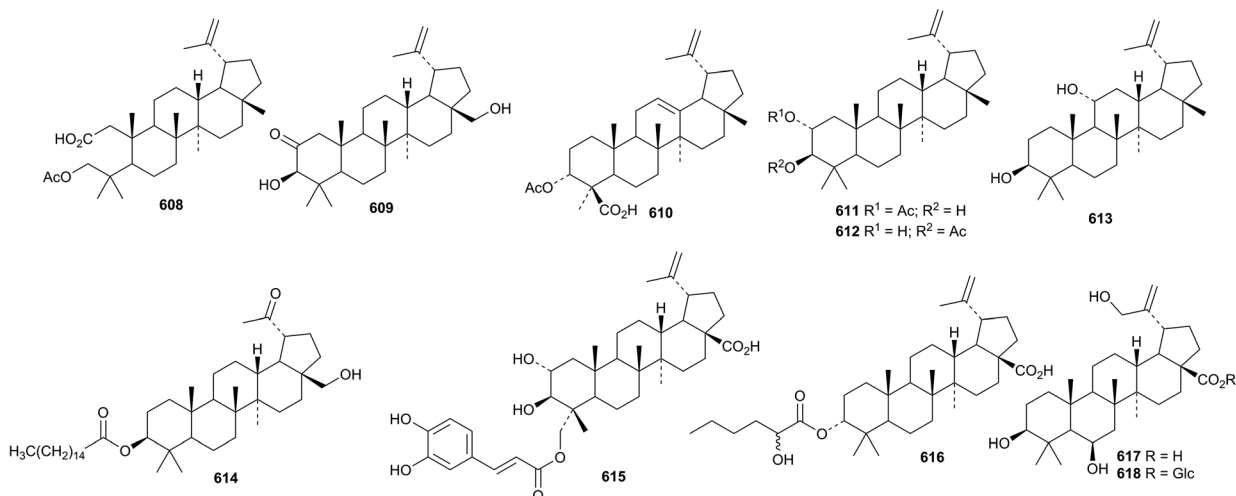


example of a 23-norlupane, 3-hydroxy-23-nor-5,20(29)-lupadien-7-one **590**, has been reported from *Lagerstroemia indica*.<sup>213</sup> *Euonymus carnosus* is a prolific source of lupane triterpenoids. Fifteen new compounds **591–605**, including the 30-nor-derivatives **601–605**, have been isolated.<sup>214</sup> 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*.<sup>215</sup>

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



Other simple lupane derivatives include salacinins A **608** and B **609** from *Salacia hainanensis*,<sup>216</sup> the acetates **610** from *Boswellia sacra*<sup>217</sup> and **611** and **612** from *Salvia viridis*,<sup>218</sup> from *Schefflera kwangsiensis*<sup>223</sup> and saponins from *Eryngium agavifolium*.<sup>224</sup>



## 6. The oleanane group

Oleanane triterpenoids and their saponins have a wide range of pharmacological activities.<sup>225–227</sup> Oleanolic acid<sup>228–231</sup> and maslinic acid<sup>232</sup> have been well studied, particularly for their anti-tumour effects.

Cyclocaric acid A, from *Cyclocarya paliurus*, was claimed to have the structure **619** with an oxetane ring.<sup>233</sup> Synthesis of the oxetane **619** and re-examination of the original literature report indicates that cyclocaric acid A is identical with hederagenin **620**.<sup>234</sup> The 2,3-seco-derivative **621** has been found in *Ligularia przewalskii*,<sup>235</sup> 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**.<sup>236</sup> Further 18-oleanene derivatives include 2 $\alpha$ ,3 $\beta$ -dihydroxy-18-oleanen-28-oic acid **626** from *Lawsonia inermis*<sup>237</sup> and the corresponding 29-oic acid **627** from *Mentha suaveolens*.<sup>238</sup>

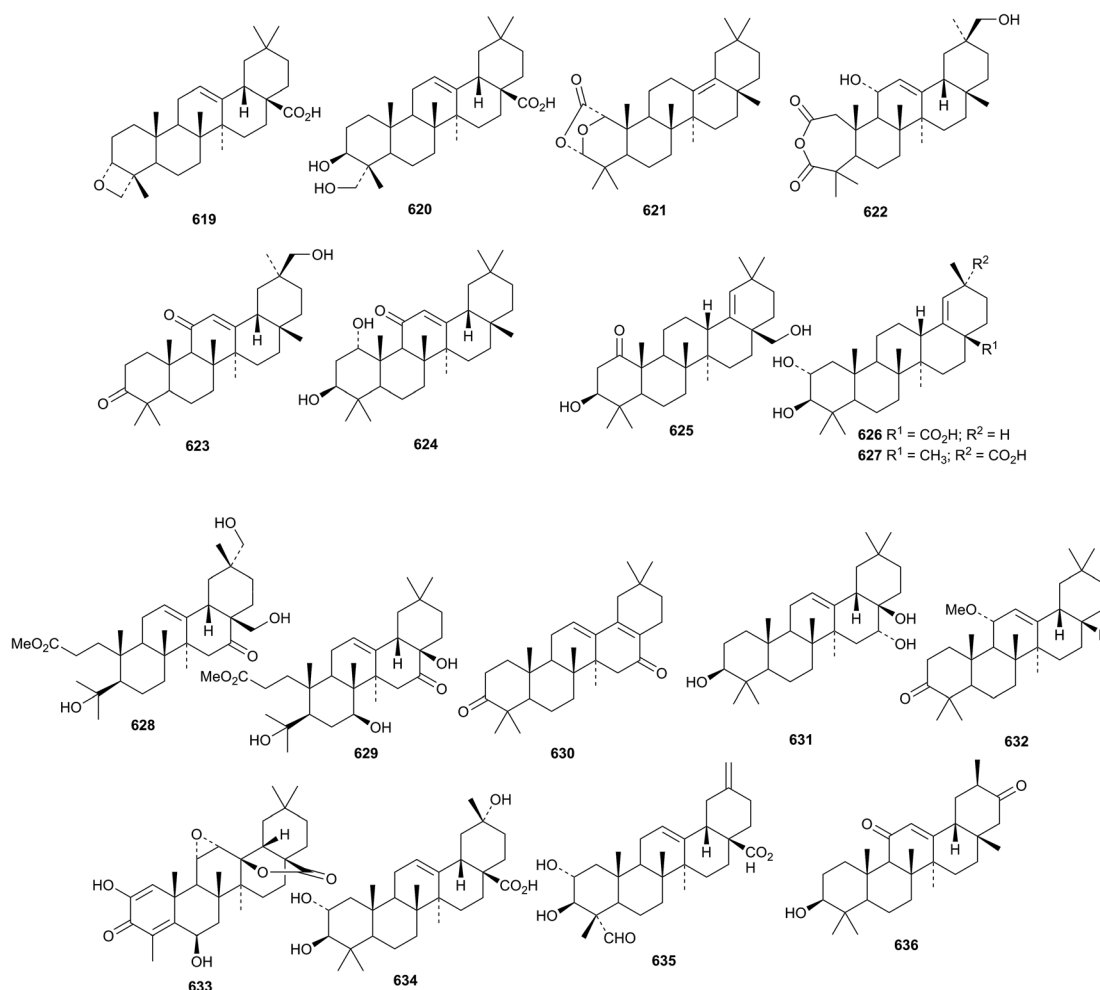
The 3,4-seco-derivatives camelliaoleans A **628** and B **629**, together with the 28-noroleanane derivatives **630** and **631**, have been isolated from *Camellia japonica*.<sup>239</sup> Liquidiformone **632** is another 28-noroleanane from fruits of *Liquidambar formosana*.<sup>240</sup> Asprellol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

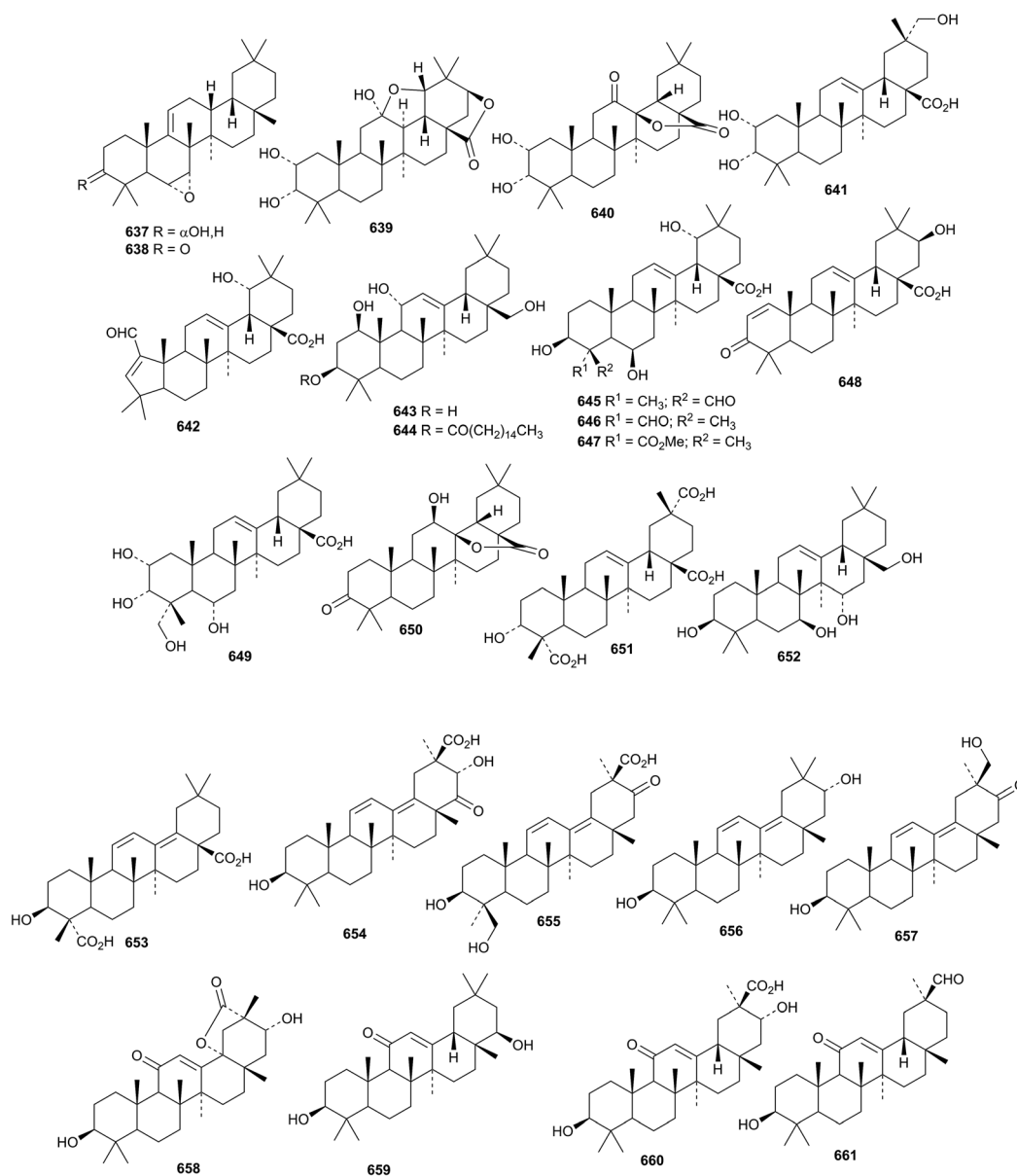
*asprella*,<sup>241</sup> whereas the noroleananes **634** and **635** have been found in *Akebia trifoliata*<sup>242</sup> and glyyunnansapogenin I **636** is from *Glycyrrhiza yunnanensis*.<sup>243</sup>

Two unusual 9(11)-oleanene derivatives **637** and **638**, lacking a ketone at C-12, have been isolated from *Boswellia ovalifoliata*.<sup>244</sup> Cannabifolin A **639**, from *Vitex negundo* var. *cannabifolia*, has unusual *cis*-fused C/D rings.<sup>245</sup> 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.<sup>119</sup>

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

3 $\beta$ -Hydroxy-11,13(18)-oleanadiene-23,28-dioic acid **653**, previously identified as the genin of saponarioside J, has been isolated from *Anoectochilus elwesii*.<sup>251</sup> Yunganosides L, M, N<sub>1</sub>, N<sub>2</sub>, O and P are saponins from *Glycyrrhiza yunnanensis* with the new genins yunganogenins L **654**–P **658**.<sup>243</sup> Licorice-





saponins M3 and N4, from *Glycyrrhiza glabra*, have the new genin **659**.<sup>252</sup> 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.<sup>253</sup>

Other oleanane saponins with new genins include centellasaponins E and I, from *Centela asiatica*, with the genins **662** and **663**,<sup>254</sup> hippophosides A–D, from *Hippophae rhamnoides* ssp. *sinensis*, with the genins **664** and **665**,<sup>255</sup> oleiferasaponin B<sub>2</sub>, from *Camellia oleifera*, with the genin **666**,<sup>256</sup> tubeimosides A and B, from *Bolbostemma paniculatum*, with the genins **667** and **668**,<sup>130</sup> saponins from *Akebia trifoliata* with the noroleanane genins **669** and **670**,<sup>257</sup> *Entada phaseoloides* with the genins **671–673**,<sup>258</sup> *Eclipta prostrata* with the genin 12-oleanene-3 $\beta$ ,16 $\beta$ ,29-triol **674** (ref. 259) and *Silphium asteriscus* also with the genin **674** together with eleven related genins **675–685**.<sup>260</sup>

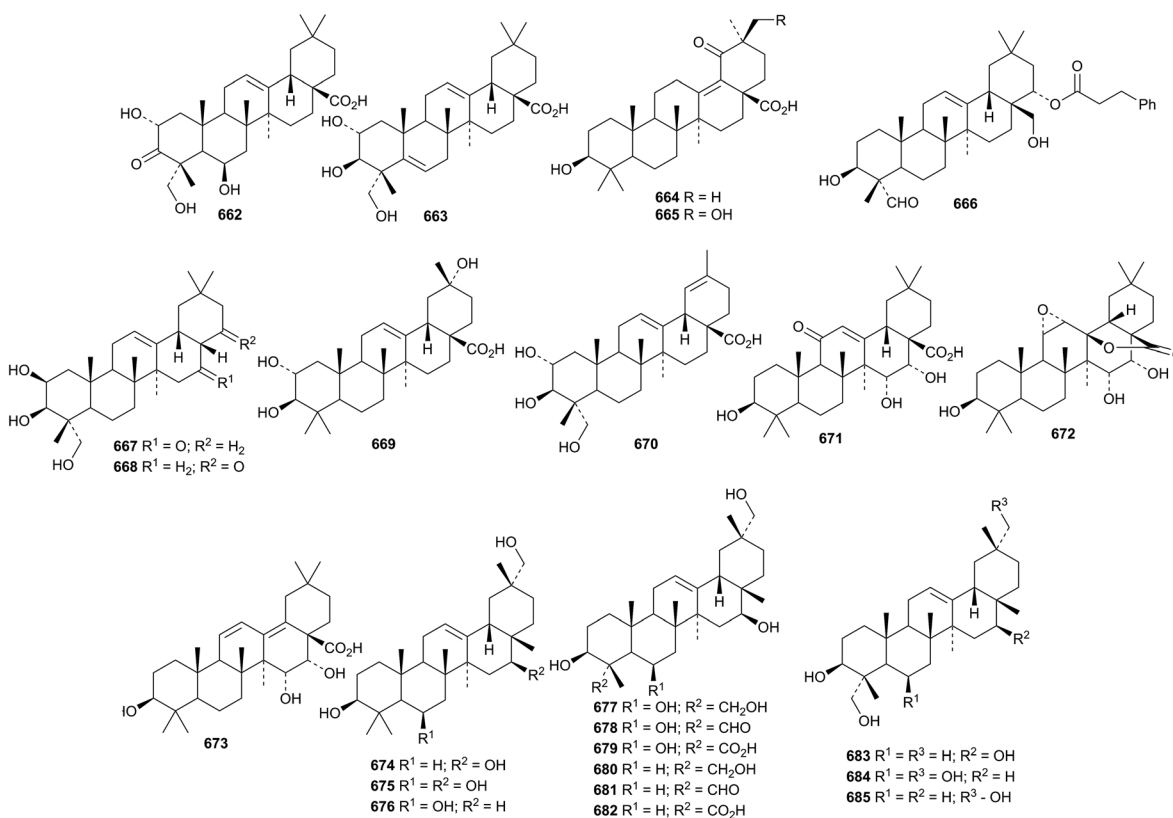
New oleanane saponins with known genins that have been assigned trivial names are listed in Table 1.

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*.<sup>315</sup> 11,21-Dihydroxy-1-oleananone **687** and four esters **688–691** are claimed to be substituents of *Coriandrum sativum*.<sup>316</sup> Other new oleanane esters include the 3-palmitoyl ester of 3 $\beta$ ,28-dihydroxy-12-oleanen-11-one (procerenone) from *Omphalocarpum procerum*,<sup>317</sup> and the oleoyl ester 12,18-oleanadien-3 $\beta$ -ol.<sup>318</sup> Leonurusoleanolides E **692–J** **697**, from *Leonurus japonicus*, are further esters of the 19(18 $\rightarrow$ 17)-abeo-28-noroleanane phlomis-tetraol B.<sup>319</sup>

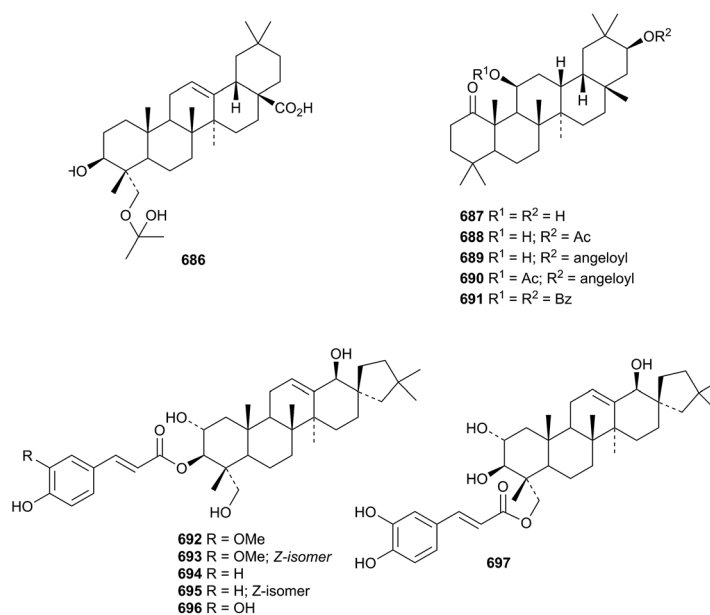
Malaytaxerate **698**, from *Sapium baccatum*, is a ring-E contracted nortaraxerane derivative.<sup>320</sup> *Davidia involucrata* is the





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**.<sup>321</sup> The structure of the 2,3-secotaraxerane pycanocarpine **704**, from *Pleiocarpa pycnantha*, was established by X-ray analysis.<sup>322</sup> A taraxerane saponin with a known genin has been isolated from the roots of *Clematis argenticulida*.<sup>323</sup> The structures of

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



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

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

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

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

## 7. The ursane group

The antitumour activity of ursolic acid has been highlighted.<sup>334,335</sup> The unusual 9,25-cyclo-12-ursen-3 $\beta$ -ol **721** has been reported from Cameroonian brown propolis.<sup>110</sup> The ring-A modified ursanes daivinvolunic acids **A 722**, **B 723** and **C 724** have been isolated from *Davidia involucrata*.<sup>336</sup> 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**.<sup>245</sup> The structure of cannabifolin **A 725** was confirmed by X-ray analysis to have *cis*-fused rings C and D. Two ursane derivatives **728** and **729**, with the unusual 20 $\alpha$ H-configuration, have been identified in *Ilex cornuta*.<sup>337</sup> Asprellols **A 730** and **B 731**, from *Ilex asprella*, are 24-norursane derivatives.<sup>241</sup> Urs-12-ene-2 $\alpha$ ,3 $\beta$ ,19 $\alpha$ -triol **732**, from *Terminalia arjuna*, has been named torment.<sup>338</sup>

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

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

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





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

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

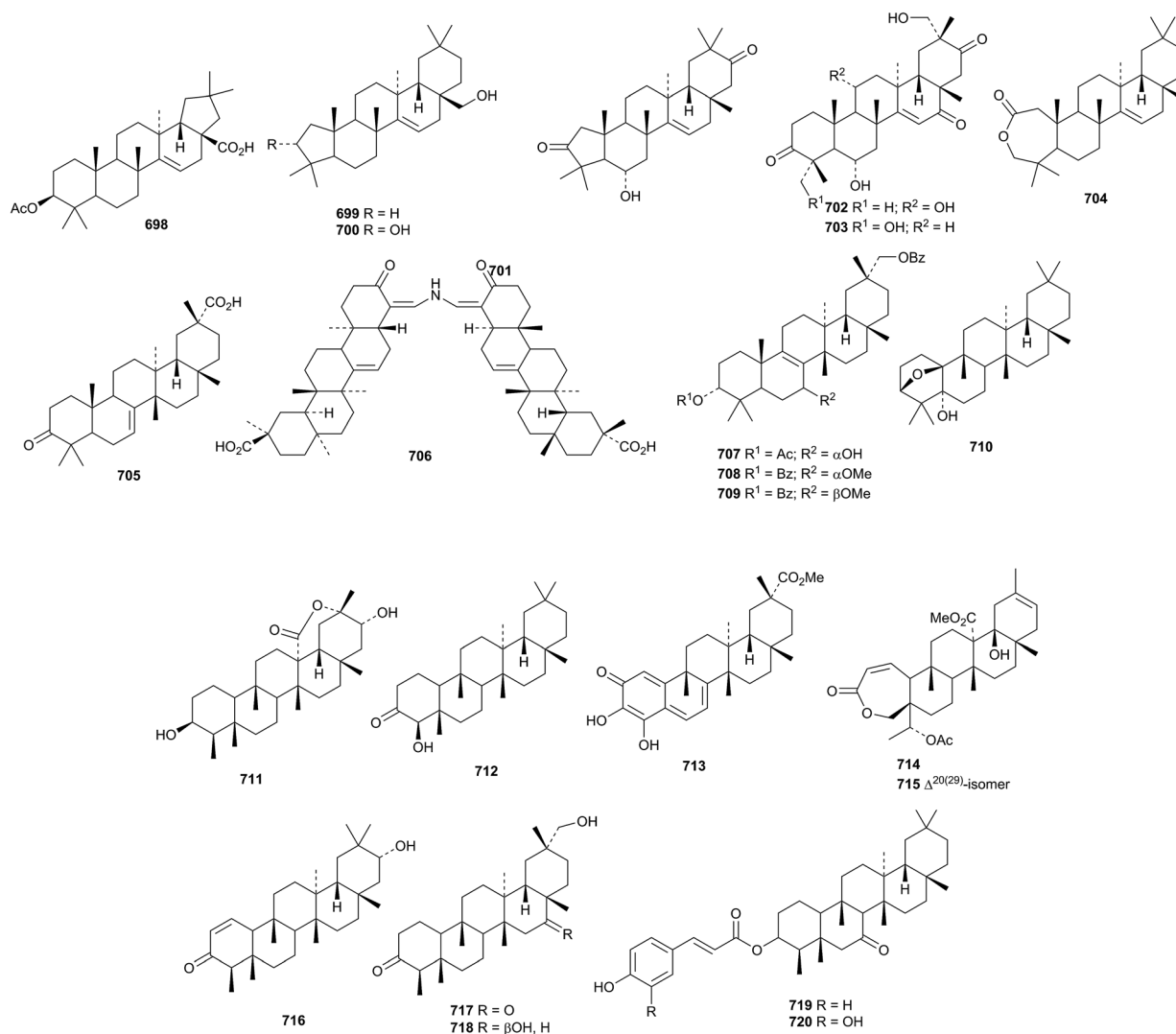
Named ursane saponins with known genins include fagonoside A from *Fagonia cretica*,<sup>348</sup> grandoside from *Syzygium grande*,<sup>349</sup> ilexosaponins G and H from *Ilex pubescens*,<sup>350</sup> ilexasprellanosides A–C from *Ilex asprella*,<sup>273</sup> ilexpubescensins N–Q (Q is the same as zygoeichwaloside H isolated in 2007(ref. 351)) from *Ilex pubescens*,<sup>274</sup> officinoterpenoside C from *Rosmarinus officinalis*,<sup>278</sup> potentillanosides A–E<sup>283</sup> and G<sup>352</sup> from *Potentilla anserina*, sieboldisaponins A<sup>353</sup> and C<sup>288</sup> from *Stachys sieboldii*, and zygofaboside C from *Zygothymum fabago*.<sup>354</sup> Unnamed saponins with known genins have been isolated from *Eucommia ulmoides*,<sup>355</sup> *Ilex*

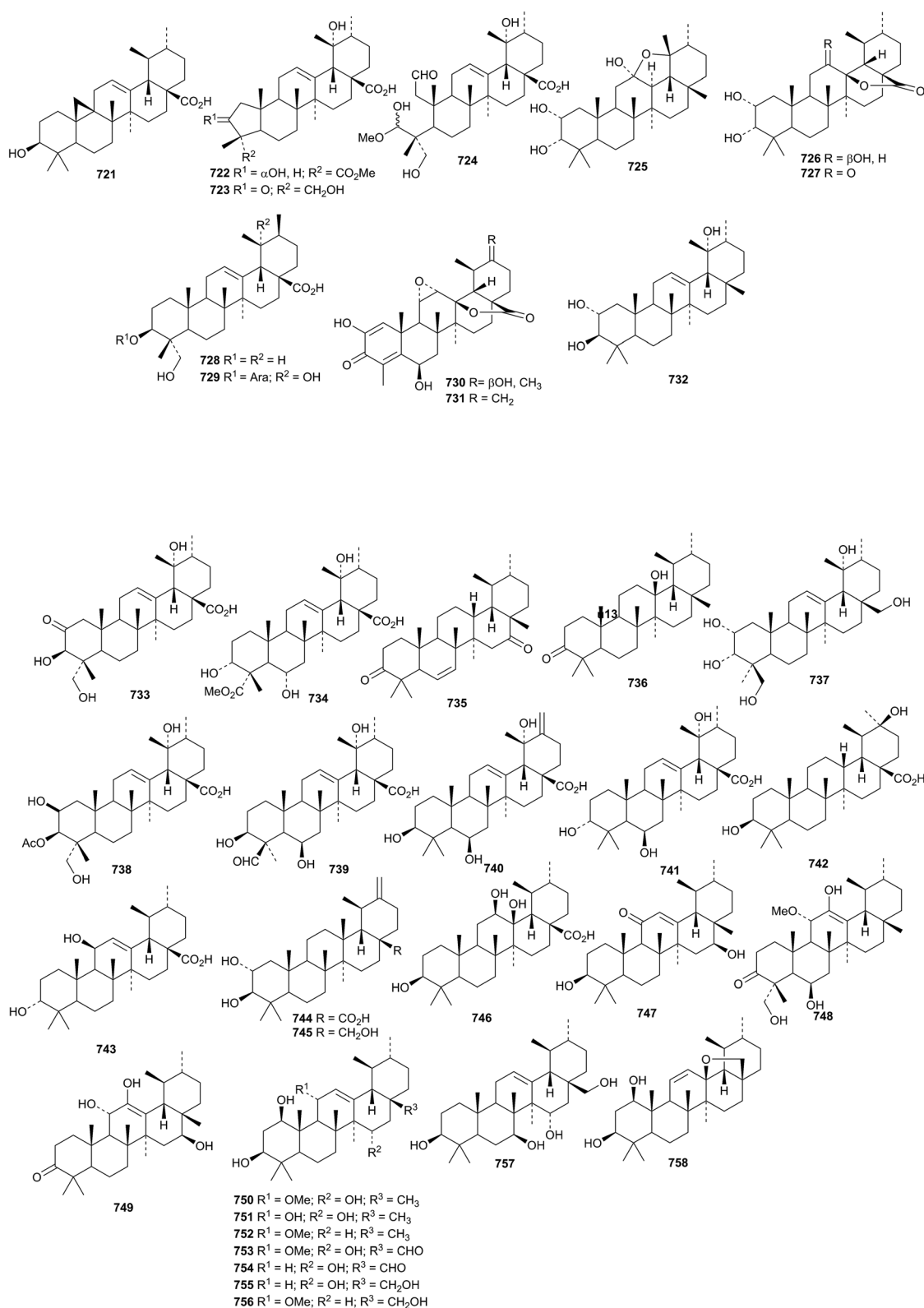
*cornuta*,<sup>356,357</sup> *Melissa officinalis*,<sup>304</sup> *Schefflera heptaphylla*<sup>347</sup> and *Vitex negundo*.<sup>358</sup>

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

## 8. The hopane group

The 2,3-seco-21 $\alpha$ H-hopane derivatives 773 and 774 have been isolated from *Megacodon stylophorus*.<sup>362</sup> The structure of 773 was confirmed by X-ray analysis. Ribosylhopane 775, which has been postulated as a precursor of C<sub>35</sub> bacteriohopanepolyols in *Streptomyces coelicolor*, has now been found in blocked mutants.<sup>363</sup> Two fernane derivatives 776 and 777 have been reported from *Lonicera quinquelocularis* however the structures are drawn lacking C-28 in the reference.<sup>364</sup> A fernane saponin, from *Spergula fallax*, has the new genin 778.<sup>365</sup>



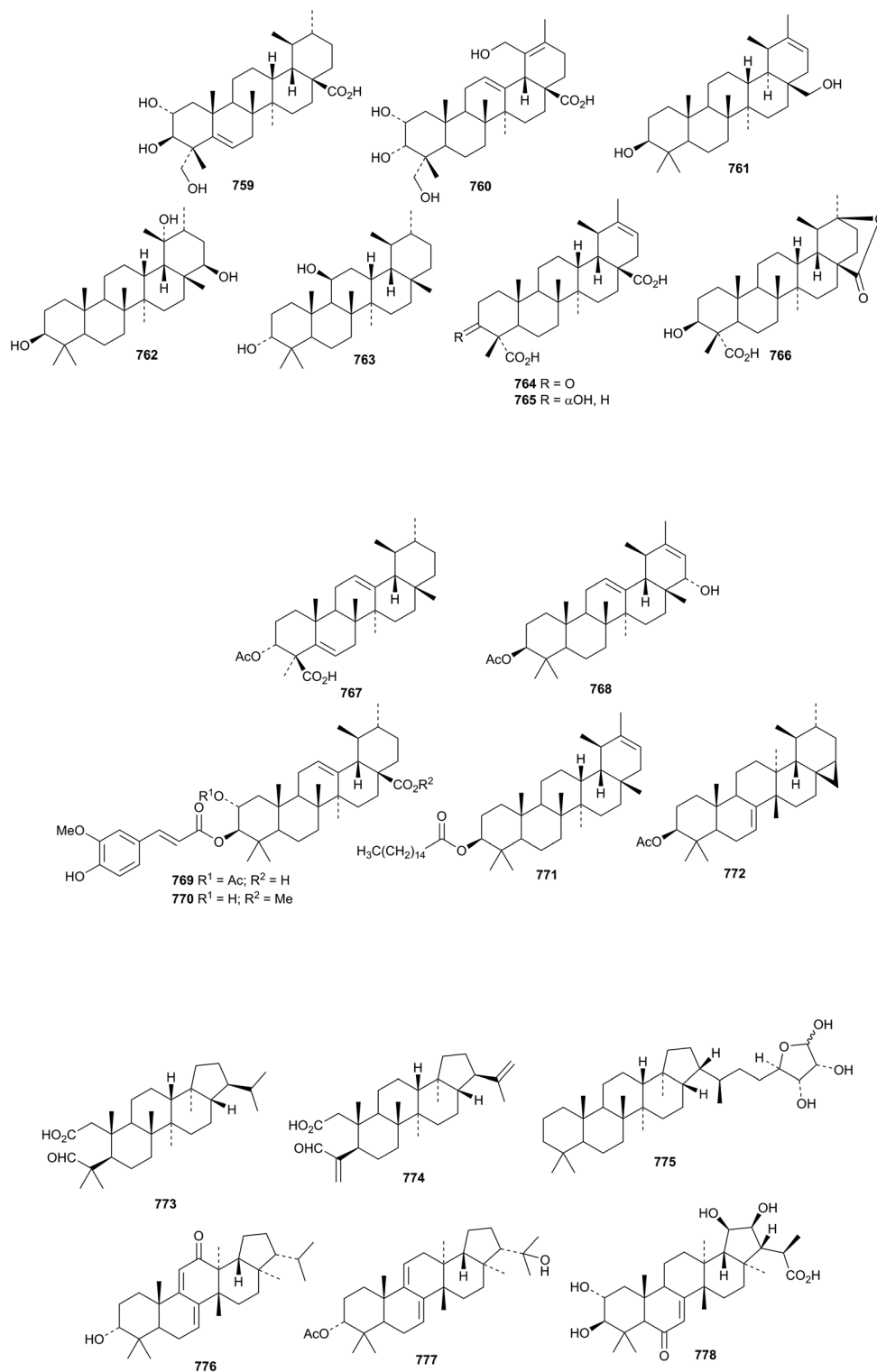


## 9. Miscellaneous compounds

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

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

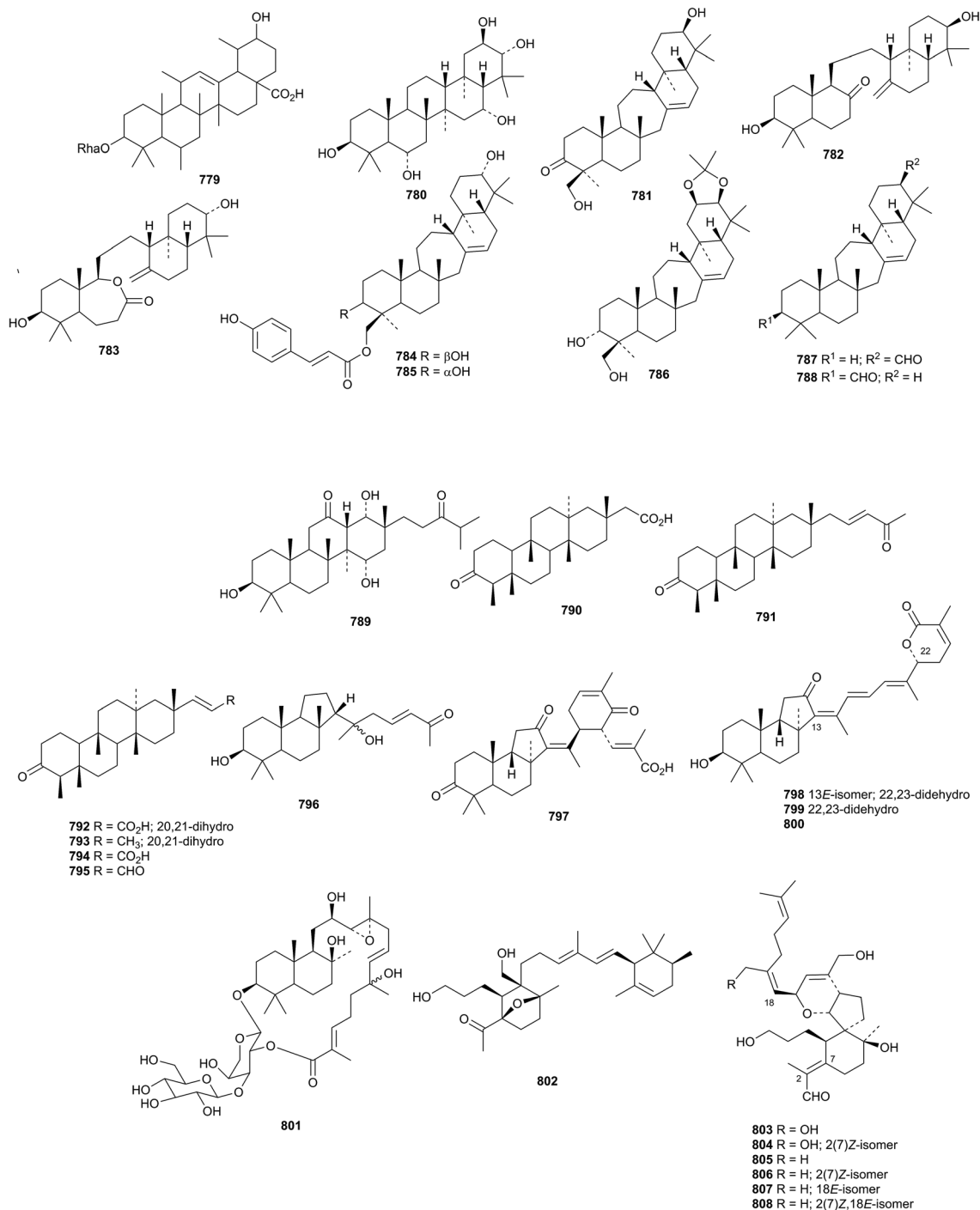




Fatsioside A, from fruit of *Fatsia japonica*, has the new bacchane genin **789**.<sup>369</sup> The structure of the norshionane derivative astershionone A **790**, from *Aster tataricus*, was established by X-ray analysis.<sup>370</sup> The related astershionones B **791–F 795** were

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





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

## 10. Conflicts of interest

There are no conflicts of interest.

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