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Diterpenoids of terrestrial origin

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Covering January to December 2015. Previous review; *Nat. Prod. Rep.*, 2015, 32, 1654–1663.

This review covers the isolation and chemistry of diterpenoids from terrestrial as opposed to marine sources and includes labdanes, clerodanes, abietanes, pimaranes, kauranes, cembranes and their cyclization products. There are 214 references.

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1 Introduction

This report covering the period January to December, 2015, follows the pattern of its predecessors^{1,2} and includes the identification and chemistry of diterpenoids of terrestrial as opposed to marine origin. The latter are covered in the articles on marine natural products.³ Traditional Chinese medicines have continued to be a treasure trove of novel diterpenoids. Many of these warrant a further examination of their structure–biological activity relationships in order to identify the pharmacophores. There are a number of diterpenoids that are sufficiently abundant to provide suitable starting materials for partial synthesis. Several studies in this context have been reported during the year including work on the abietane diterpenoids. This has been reviewed.^{4,5}

Advances in the synthesis of multi-functionalized decalins,⁶ the bicyclo[3,2,1]-octane system of the *ent*-kauranoids,^{7,8} the atisane diterpenoids,⁹ the neodolastanes,¹⁰ the pseudopterosin aglycones,¹¹ and vinigrol,¹² together with the use of dehydrogenation to access diterpenoid degradation products that are found in the environment,¹³ have all been reviewed. Other

articles on the diterpenoid composition of *Pinus sibirica*¹⁴ and various aspects of the diterpene biosynthetic syntheses including their genetics, have appeared.^{15,16} Genetic studies have led to the identification of diterpene gene clusters¹⁷ and of silent pathways that can be activated to produce diterpenoids.¹⁸

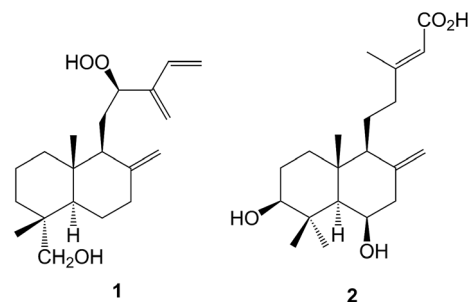
2 Acyclic and related diterpenoids

The syntheses of C-8, C-9 and C-10 deuteriated geranylgeraniols have been reported.¹⁹

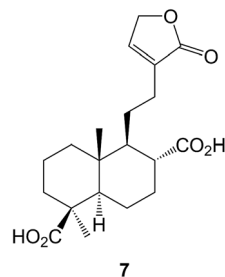
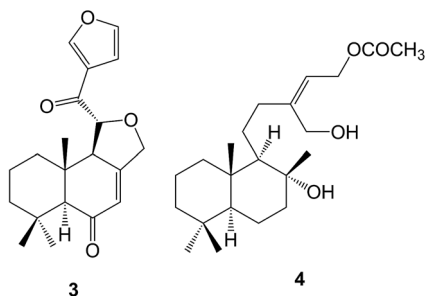
3 Bicyclic diterpenoids

3.1 Labdanes

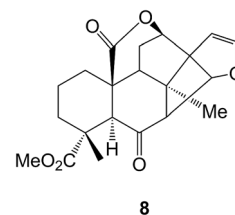
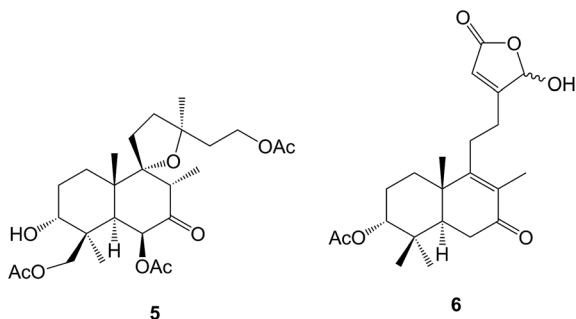
Labdanolic acids have been identified as biomarkers for the botanical origin of French ambers²⁰ whilst copalic acid and its relatives have been associated²¹ with the biological activity of the resins from *Copaifera* species. The lanceolatanols, including some rare hydroperoxides such as the 12-hydroperoxide **1**, have been isolated²² from the Chinese fir, *Cunninghamia lanceolata* (Cupressaceae) which is grown in plantations for timber production. The lanceolatins A–G (*e.g.* A, **2**) are a group of labdanes and abietanes which were obtained²³ from *Cephalotaxus lanceolata* (Cephalotaxaceae). Some of the abietanes described in this paper were formulated without comment, as a dienone tautomer of a phenol.



A number of the labdanes which have been found in members of the Zingiberaceae, e.g. *Alpinia japonica*,²⁴ *Curcuma longa*²⁵ and *Hedychium longipetalum*²⁶ such as the hedy-longnoids A–C (e.g. A, **3**), inhibit the production of nitric oxide. The paraguhenryisins A–D (e.g. C, **4**) which were isolated²⁷ from the capitate glandula trichomes of *Paragutzlaffi henryi* (Acanthaceae), have phytotoxic properties and may provide a defensive measure against other invasive plants. The absolute configuration at C-14 of the labdanes from *Physalis nicandroides* (Solanaceae) has been established.²⁸

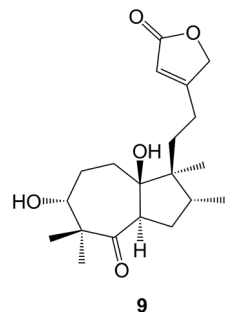


Labdane glycosides have been reported²⁹ as constituents of *Diplopterygium rufopilosum* (Gleicheniaceae) whilst examination of the seeds and leaves of *Colophospermum mopane* [Fabaceae (Leguminosae)]³⁰ and *Leonotis leonurus* (Lamiaceae)³¹ has yielded some further labdanes and clerodanes. Continued examination of *Leonurus japonicus* gave leojaponin D³² whilst the macranthins (e.g. A, **5**) were anti-inflammatory labdanes which were obtained³³ from *L. macranthus*. Further studies on white horehound (*Marrubium vulgare*, Lamiaceae) afforded³⁴ 12(*S*)-hydroxymarrubiin. The structure **6** has been assigned³⁵ to cinereanoid A which was isolated from *Roylea cinerea* (Lamiaceae) whilst the vitexolides A–E were similar anti-bacterial γ -hydroxy- $\alpha\beta$ -unsaturated 15 \rightarrow 16-lactones which were obtained³⁶ from *Vitex vestita* (Lamiaceae).



A large number of labdanes have been detected in Chinese liverworts including the haplomintrins (e.g. A, **8**) from *Haplomitrium minioides*³⁹ in which a cyclobutane ring has been formed by the possible photochemical addition of a side-chain furan across the double bond of a 7,8-en-6-one. Other examples of labdanes which have been isolated include the ptychanthins P and R from *Ptychanthus striatus*⁴⁰ and the scapairrins A–Q from *Scapania irrigua*.⁴¹

Various methods for the recovery of useful compounds from *Stevia rebaudiana* (Asteraceae) have been reviewed.⁴² The fermentation of *S. rebaudiana* with the yeast *Saccharomyces cerevisiae* has led⁴³ to the formation of some modified sterebins arising from the selective epoxidation and hydration of the 14,15-double bond. Examination of the Taiwanese shrub, *Callicarpa randaiensis* (Verbenaceae) in the search for anti-inflammatory agents afforded⁴⁴ the randainins A–D. As an alternative to the biosynthesis suggested in the original paper, their structures (e.g. A, **9**) may arise by the oxidative cleavage of a 5,10-double bond of a halimane followed by aldol condensations of the 5,10-diketone to form the *trans* 7/5 and 5/7 ring systems of these diterpenoids.

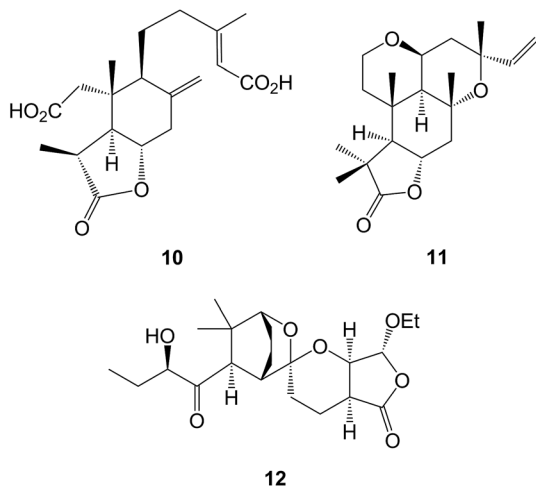


Isodon species (Lamiaceae) are renowned for the tetracyclic diterpenoid constituents of their leaves. However examination of the roots of *I. adenantha* afforded³⁷ the labdanes, adenanthic acids A and B (e.g. A, **7**) and the adenanthosides A–C whilst two other labdanes were obtained³⁸ from *I. yuennanensis*.

The cleavage of ring A has been encountered in a number of diterpenoids including labdanes. A 3-nor-2,3-secolabdane structure **10** has been assigned⁴⁵ to penioxalicin which was obtained from the fungus, *Penicillium oxalicum* and to paecilomycine A from an insect pathogenic fungus, *Paecilomyces* sp.⁴⁶ Further examination⁴⁷ of the stems of the highly poisonous mangrove plant, *Excoecaria agallocha* (Euphorbiaceae) gave



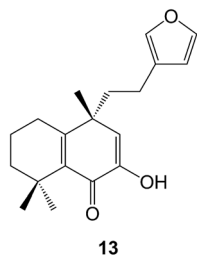
excolide **11** in a study which also led to a revision of the structure of rhizophorin A. The structure of the spiro-ketal, leonuketal **12** obtained⁴⁸ from *Leonurus japonicus*, may be derived by a retro-Prins cleavage of the 8:9-bond in a 7,9-dihydroxylabdane followed by a cyclization involving the 3-hydroxyl group, the 9-ketone and C-15.



Derivatives of the readily available labdanes such as polyalthic acid⁴⁹ and copalic acid⁵⁰ have been evaluated for the treatment of various diseases. The merosesquiterpenes, neopterosiquinones A and B have been synthesized⁵¹ from *trans*-communic acid. The anti-fungal activity of sclareol⁵² and some derivatives⁵³ has been examined. Sclareol has been used⁵⁴ as the starting material for the synthesis of the sesterterpenes, luffarin L and 16-epiluffarin and for a biomimetic synthesis of two salmahyrtisanes.⁵⁵ Work has continued^{56–58} to prepare derivatives of andrographolide in order to study structure–biological activity relationships. The enzyme systems responsible for the biosynthesis of 13(*R*)-manoyl oxide have been transferred⁵⁹ from Sitka spruce to a cyanobacterium, *Synechocystis* sp.

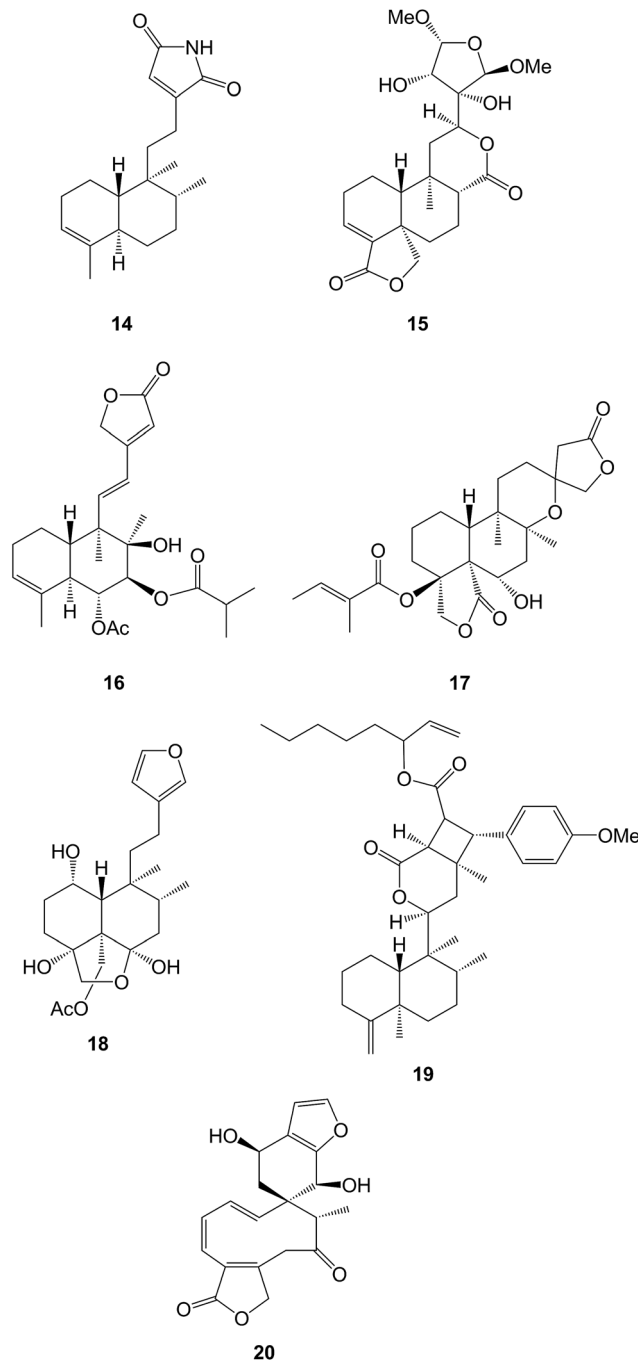
3.2 Halimanes and clerodanes

18-Hydroxy-*ent*-halima-1(10),13(*E*)-dien-15-oic acid has been isolated⁶⁰ from *Hymenaea stigonocarpa* (Fabaceae) whilst investigations of the anti-microbial activity of *Vellozia kolbekii* (Velloziaceae) afforded⁶¹ 15,16-dihydroxy-*ent*-halima-1(10)-ene. The halimane structure **13** has been assigned⁶² to isoleojaponin from *Leonurus japonicus*.



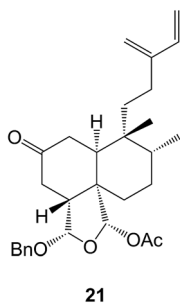
The clerodane pyrrole **14** was amongst⁶³ the anti-plasmodial constituents of *Polyalthia longifolia* varⁿ. *pendula* (Annonaceae), the bark of which is used in West African folk medicine for the

treatment of malaria. 2 β -Acetoxyhardwickiic acid and a number of other clerodanes were anti-bacterial constituents of *Salvia adenophora* (Lamiaceae)⁶⁴ and *S. buchananii*.⁶⁵ Further structural modifications of salvinorin have been made⁶⁶ including some 2-alkyl-2-methoxymethyl ethers in order to examine its structure–activity relationships as a selective κ -opioid receptor agonist. *ent*-2 β ,18,19-Trihydroxycleroda-3,13-dien-15,16-olide has been obtained⁶⁷ from *Crassocephalum bauchiense* (Asteraceae) which is a herb that is used in Cameroon folk medicine. The dichrocephnoids A–E (e.g. A, **15**) which possess anti-HIV integrase activity, were isolated⁶⁸ from *Dichrocephala benthamii* (Asteraceae). Further examination of the Chinese medicinal herb, *Scutellaria barbata* (Lamiaceae) has led to the isolation of



the anti-viral scutolides A–L (e.g. A, **16**)⁶⁹ and the scutebatins A–C⁷⁰ which inhibit NO production. The scutefolides (e.g. A, **17**) were obtained⁷¹ from *S. coleifolia* whilst the teufrintins A–G (e.g. A, **18**) were obtained⁷² from the aerial parts of the herb, *Teucrium fruticans* (Lamiaceae) which had been cultivated in China. Examination of *Isodon scoparius* (Lamiaceae) afforded⁷³ the scopariusicides A **19** and B which were unusual cyclobutane derivatives which were formed by the cycloaddition of an ester of 4-hydroxycinnamic acid to the clerodane side chain. The unusual spirocyclic ring system **20** which may be derived from a clerodane, has been assigned⁷⁴ to teotihuacanin, which was obtained from the Mexican plant, *Salvia amarissima*. It has shown activity against multi-drug resistance in cancer cells.

A number of new *cis*-clerodanes have been isolated including linarenone A from *Linaria japonica* (Plantaginaceae),⁷⁵ the croto-curins A–C from *Croton euophyllus* (Euphorbiaceae)⁷⁶ and the graveopenes A–J (e.g. A, **21**) from *Casearia graveolens* (Flacourtiaceae).⁷⁷ The latter were shown to stimulate NGF-mediated neurite out-growth which is of interest in the context of neuron degeneration in Alzheimer's disease. The related caseagrewifolins were obtained⁷⁸ from *C. grewifolia*. Further examination of *Tinospora sagittata* (Menispermaceae) gave⁷⁹ tinosporin A and B.

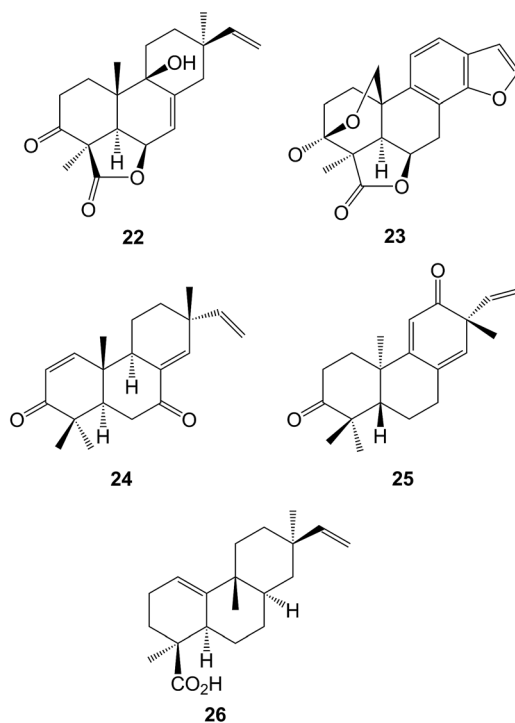


4 Tricyclic diterpenoids

4.1 Pimaranes

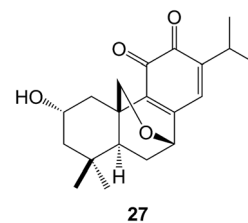
The arabinofuranoside of isopimara-7,15-dien-19-ol has been identified⁸⁰ amongst the anti-fungal constituents of *Sagittaria latifolia* (Alismataceae). A series of isopimaranes known as the kaempulchraols A–I have been obtained^{81–83} from the rhizomes of *Kaempferia pulchra* (Zingiberaceae). Some constituents of the roots of *Oryza sativa* (rice) including momilactone D **22** have been shown⁸⁴ to inhibit the production of NO. Further studies^{85–87} on the tubers of the Nigerian herbal medicine *Icacina trichantha* (Icacinaceae) have revealed the presence of more 9 β -H-pimaranes and some aromatic 17-norpimaranes, the icacinlactones A–H (e.g. A, **23**). The xylabisboeins A and B were anti-bacterial pimarane 14,16-ethers which were isolated⁸⁸ from an endophytic *Xylaria* sp. obtained from the leaves of *Bisboeckiera microcephala*. Isopimaranes (e.g. **24**) were amongst⁸⁹ the anti-inflammatory constituents of *Dysoxylum gotadhora*. A group of 16-norditerpenoids have been obtained⁹⁰ from the aerial parts of *Flickingeria fimbriata* (Orchidaceae) whilst some pentahydroxypimaranes were isolated⁹¹ from *Aerva lanata* (Amaranthaceae), a plant which is used in Ayurvedic medicine. The dienone **25** and the corresponding 11,14- α - and β -epidioxides and diols were isolated⁹² from the stems of *Croton*

insularis which was found in the Australian rain forest. A group of rosanes, e.g. stachyrosane I **26** have been reported^{93–95} as constituents of *Stachys parviflora* (Lamiaceae).



4.2 Abietanes

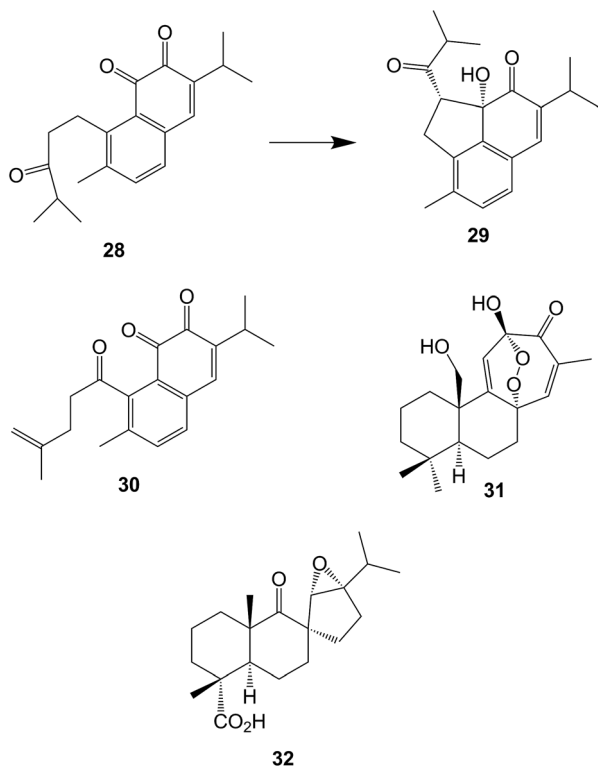
The intervention of quinone methides in the anti-oxidant activity of the phenolic diterpenoids ferruginol⁹⁶ and carnosic acid⁹⁷ has been described. The anti-fungal activity of some abietic acid esters in the context of their use as wood preservatives⁹⁸ and the anti-viral activity of podocarpic acid derivatives⁹⁹ have been examined. The action of a visible light LED on the *N*-chlorosulfonamide of dehydroabietylamine afforded¹⁰⁰ a 6 α -chloro compound. Dehydroabietic acid has been shown¹⁰¹ to regulate liver glucose levels which may be linked to the use of *Abies balsamea* in a folk medicine treatment for type 2 diabetes. The brevistylumsides A and B, obtained from *Illicium brevistylus* have been identified¹⁰² as glycosides of dehydroabietic acid. The structure **27** has been assigned¹⁰³ to the *o*-quinone teuvisone which was obtained from *Teucrium viscidum*. The dimeric biteuvisones A and B arose by addition of the corresponding *o*-catechol across the 8,9-bond.



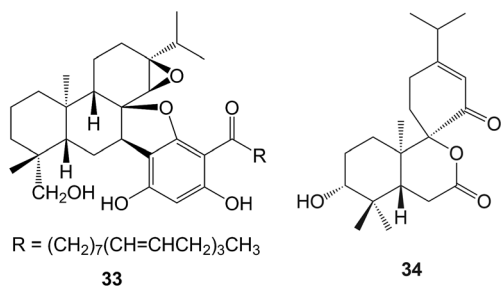
Further examples of diterpenoids in which ring A has been cleaved have been isolated from *Salvia* species. Thus salviaprione **29** was isolated¹⁰⁴ as a racemate from *S. prionitis*. It may be formed by the cyclization of salvisyrianone **28**. 1-Ketoethiopinone



30 was obtained¹⁰⁵ from the roots of *S. sahendica*. The diacetate of dihydroethiopinone inhibits the growth of breast cancer cells. The roots of *S. grandifolia* yielded¹⁰⁶ the grandifolias A–F (e.g. A, **31**). These include some modified abietanes arising from the cleavage of ring C. The quinone, caryopterone A possesses a methylcyclopropane ring in place of the isopropyl group of the abietanes. It was isolated¹⁰⁷ from the roots of *Caryopteris mongolica* (Lamiaceae). Some of the abietanes from this plant showed¹⁰⁸ cholinesterase inhibitory activity. The macrophyphenes A–E, obtained¹⁰⁹ from *Callicarpa macrophylla* (Verbenaceae) included some rearranged abietanes (e.g. A, **32**).

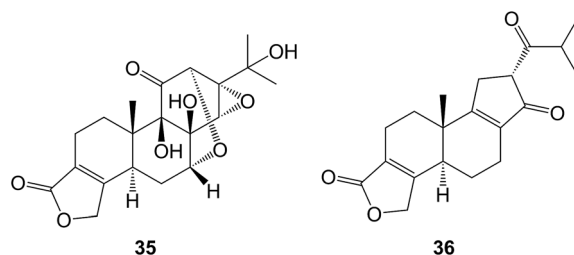


The constituents of the genus *Chloranthus* have been reviewed.¹¹⁰ *ent*-Abietanes have been obtained¹¹¹ from *C. henryi* whilst the chlorabietols A–C isolated¹¹² from *C. oldhamii* included an unusual phloroglucinol-abietane adduct (A, **33**). Rings B and C have been cleaved in the formation of various sessilifols A–N (e.g. C, **34**) obtained¹¹³ from *C. sessilifolius*.

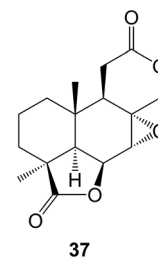


Further studies on the traditional Chinese medicine *Tripterygium wilfordii* (Celastraceae) have afforded more highly oxidized 18(4→3)-*abeo*-abietanoid derivatives including the tripterulides A and B (e.g. B, **35**),¹¹⁴ the wilfordosides A and B,¹¹⁵

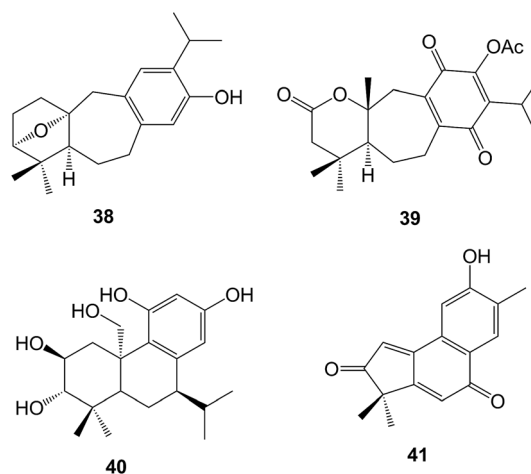
and the tripterulides A–F (e.g. A, **36**)¹¹⁶ in which ring C has also undergone rearrangement. A range of abietanes, pimaranes and kauranes have been isolated¹¹⁷ from *T. hypoglaucum*.



Examination of the anti-proliferative constituents of Ethiopian *Podocarpus falcatus* led¹¹⁸ to the isolation of 16-hydroxynagilactone F and a revision of the stereochemistry of 2 α -hydroxynagilactone F to the 2 β -epimer. The botryosphaerins G and H (e.g. G, **37**) which were obtained¹¹⁹ from a *Botryosphaeria* endophyte of *Huperzia serrata*, have a *seco* ring C structure or they may be tetranorlabdanes.

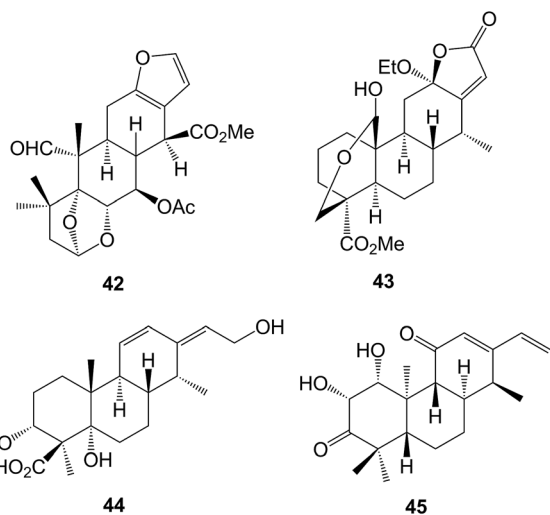


Some further icetexanes have been isolated¹²⁰ from *Perovskia atriplicifolia* (Lamiaceae). The hispidanols A and B (e.g. B, **38**) were sempervirane relatives which were obtained¹²¹ from the rhizomes of *Isodon hispida*. The roots of *Pygmaecopremna herbacea* (Verbenaceae), which have been used in Ayurvedic medicine as an anti-inflammatory agent, yielded a quinone which was assigned¹²² the somewhat unusual structure **39** in which ring B has been expanded but the C-20 methyl group has been retained. Another unusual structure **40** involving a curious biosynthesis, has been assigned¹²³ to plebeianiol A which was obtained from *Salvia plebeia*. Neoboutomannin A **41** isolated¹²⁴ from the West African *Neoboutonia macrocalyx* (Euphorbiaceae) may be a degraded abietane.

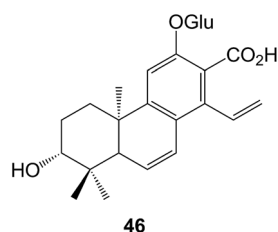


4.3 Cassanes

Cassane diterpenoids are characteristic constituents of the Caesalpiniaceae. Further examination of *Caesalpinia bonducella* has yielded¹²⁵ the bonducellpins H–P whilst *C. crista* afforded¹²⁶ the phangininoxys D and E. The echinalides H–U were obtained¹²⁷ from *C. echinata*. Many of these compounds have been shown to possess anti-inflammatory and anti-oxidative properties. The cassanes from several studies^{128–130} of *C. minax* have been examined in this context. These included the caesalmins I–M¹²⁸ and a *seco* ring A compound neocaesalminin A **42**.¹³⁰ The caesalsappanins A–L (e.g. A, **43**) which were isolated¹³¹ from *C. sappan*, have been studied for their anti-malarial and anti-proliferative activity. Other cassanes have been isolated from *Erythrophleum suaveolens*¹³² and *Swartzia simplex*.¹³³ The activation by epigenetic mining of a silent biosynthetic pathway in the fungus *Calcarisporium arbuscula* led to the isolation¹⁸ of arbusculic acid A **44**. A new phytoalexin phytocassane F **45** has been identified¹³⁴ in rice leaves that had been subjected to UV radiation.



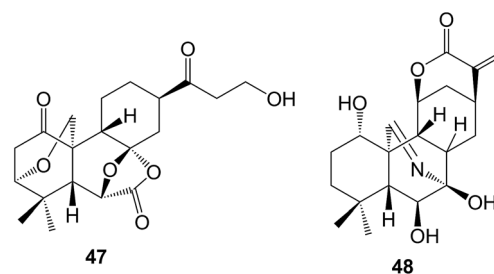
The cleistanthanes phyllanembloids A–F (e.g. A, **46**) have been obtained¹³⁵ from the roots of *Phyllanthus emblica* which are used in Chinese traditional medicine.



5 Tetracyclic diterpenoids

The *ent*-kauranes which have been obtained¹³⁶ from the fruits of *Annona glabra* (Annonaceae) as part of a study of their anti-inflammatory activity, include 7 β ,16 α ,17-trihydroxy-*ent*-kauran-19-oic acid. 4 β ,16 α ,17,19-Tetrahydroxy-18-nor-*ent*-kaurane has been isolated¹³⁷ from *Wedelia trilobata* (Asteraceae) whilst some *ent*-kauranoic acid glycosides have been found¹³⁸ in *Ageratina cylindrica*

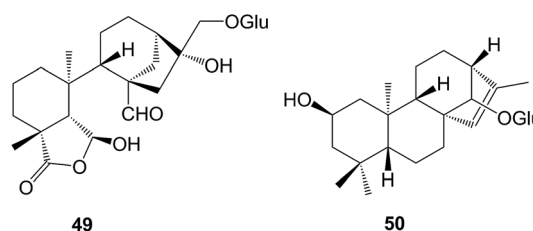
(Asteraceae). It has been estimated that over a thousand diterpenoids, many of which possess interesting biological activity, have been detected in *Isodon* (Lamiaceae) species. Further examples include the neolaxiflorins I–Y¹³⁹ and the unusual laxiflorol A **47**¹⁴⁰ from *I. eriocalyx* varⁿ. *laxiflora*. Extraction of *I. excisoides*,¹⁴¹ *I. parvifolius*¹⁴² and *I. scoparius*¹⁴³ provided other examples. The 7,20-azakaurenes, kaurines A and B (e.g. A, **48**) were isolated¹⁴⁴ from *I. rubescens* together with a compound containing an unusual 17-succinimide moiety. Xerophilusin B has been shown¹⁴⁵ to induce cell cycle arrest and apoptosis in esophageal squamous cell carcinoma. The total synthesis of maocystal V has been described.¹⁴⁶



The helikauroliides A–D which were obtained from *Helianthus annuus* varⁿ. *arianna*, have been assigned¹⁴⁷ structures based on a combination of a sesquiterpene lactone (heliypolide L) and an *ent*-kauranoic acid.

The steviol glycosides from *Stevia rebaudiana* have continued to attract attention particularly in the food industry. The relationship between the conformation of rebaudioside A in solution and its sweetness¹⁴⁸ and molecular modeling studies of the docking of rebaudioside A with the human sweet taste receptor¹⁴⁹ have been reported. Dereplication of the NMR profiles of mixed steviol glycosides¹⁵⁰ and the application of new separation techniques¹⁵¹ have been described. 15 α -Hydroxyrebaudioside M has been isolated¹⁵² from *S. rebaudiana*. The ready availability of isosteviol from the acid-hydrolysis of the mixed glycosides from *S. rebaudiana* has led to its use as the starting material for a number of studies.^{153–156} The X-ray crystal structure of a dimeric isosteviol sulfite has been described.¹⁵⁷

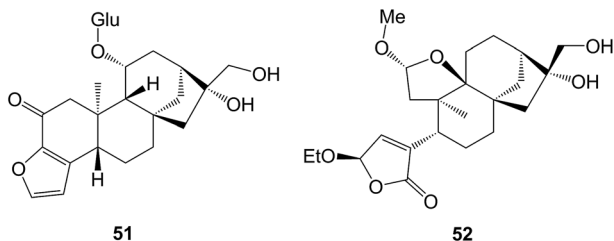
The priniosides A–C which were isolated¹⁵⁸ from *Prinsepia utilis* (Rosaceae) included the *seco*-ring B *ent*-kaurane (C, **49**). Two glycosides, ranunculosides A and B that were isolated¹⁵⁹ from *Ranunculus muricatus* (Ranunculaceae), were described as *ent*-kaurane glycosides but were drawn with an *ent*-phylloclādene structure **50**.



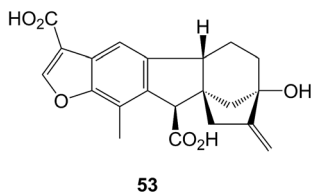
Cafestol has been shown¹⁶⁰ to stimulate insulin production and it has been suggested that cafestol may contribute to the effect of coffee on reducing type 2 diabetes. The known furanokaurane, mozambioside **51** has been identified¹⁶¹ as a bitter tasting glycoside that is specific to *Coffea arabica* as opposed to



C. robusta. The tricalysins A–H that were found¹⁶² in *Tricalysia fruticosa* (Rubiaceae), have been shown to be cafestol relatives and to have anti-inflammatory properties. The frutilactones A and B (e.g. A, 52) were 2,3-*seco*-cafestol relatives that were isolated¹⁶³ from the same plant.



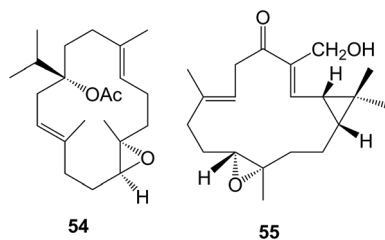
The gastroprotective activity of some derivatives of 18-hydroxybeyerenes has been described.¹⁶⁴ 2 β ,12 β -Dihydroxygibberellin A₁₂ has been isolated¹⁶⁵ from the leaves of *Schefflera sessiliflora* (Araliaceae) in a surprisingly high amount for a gibberellin. The synthesis of pharbinilic acid 53 starting from gibberellic acid has been described.¹⁶⁶ This is an allogibberic acid relative which had been obtained from Morning Glory (*Pharbitis nil*).



Further grayane diterpenoids have been obtained from the leaves of *Rhododendron micranthum* (Ericaceae)¹⁶⁷ and *R. molle*¹⁶⁸ both of which are used in Chinese traditional medicine. The total synthesis of atisane diterpenoids has been reported.¹⁶⁹ The biological activity of scopadulciol has been examined.¹⁷⁰

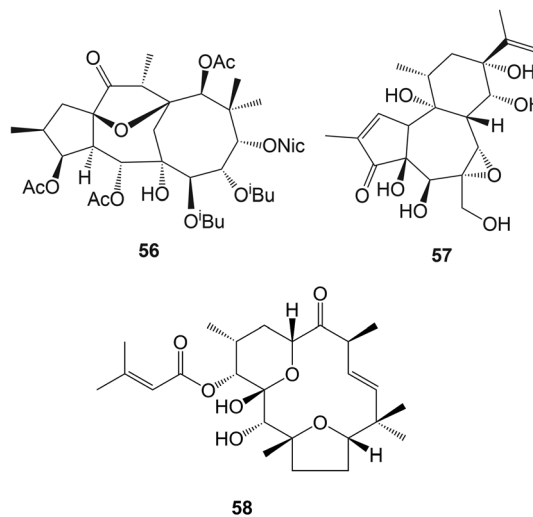
6 Macrocyclic diterpenoids and their cyclization products

Diterpenoids with the cembrane skeleton have been found in various resins. Thus the resin of the North American *Bursera microphylla* (Burseraceae) afforded¹⁷¹ microphyllanin 54 whilst the frankincense from *Boswellia carterii* (Burseraceae) yielded¹⁷² a further group of cembranoids including the boscartins. The regioselective oxidation of the tobacco component, β -cembranediol at C-9 and C-10 using cytochrome P₄₅₀ variants has been studied.¹⁷³ Some casbanes, e.g. pekinenin G 55 have been isolated¹⁷⁴ from *Euphorbia pekinensis*. A relative, sapidisin A was obtained¹⁷⁵ from *Sapium discolor* (Euphorbiaceae).



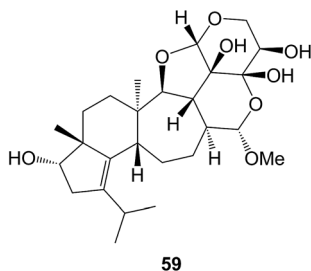
Preparative methods have been described¹⁷⁶ for the isolation of paclitaxel (taxol®) and of further taxanes from *Taxus chinensis* (*T. wallichiana* varⁿ. *mairii*).¹⁷⁷ The modification of the structure of ring D-*seco*-taxanes in the context of microtubule interactions has been examined.¹⁷⁸ Further synthetic studies directed at paclitaxel continue to be reported.¹⁷⁹

A large number of esters of jatrophanes, lathyranes, myrsinanes, daphnanes, tiglanes and ingenanes have been isolated, particularly from members of the Euphorbiaceae and Thymelaeaceae. Care must be taken in the separation of these compounds to avoid conditions that may lead to acyl migration and transesterification. The juxtaposition and consequent interactions between functional groups provide ample opportunities for these reactions in this closely related series of compounds and indeed may contribute to their biological activity. Molecular modeling and advanced NMR methods have been used in locating esters in the jatrophanes of *Euphorbia amygdaloides*.¹⁸⁰ Some cytotoxic lathyranes including lathyr-anlactone and jatrocursenone A have been isolated¹⁸¹ from *Jatropha curcas* cv. *nigroviens rugosus* whilst further jatropane and myrsinane esters have been obtained from *E. connata*,¹⁸² *E. dracunculoides*,^{183–185} *E. exigua*,¹⁸⁶ *E. osyridea*,¹⁸⁷ *E. prolifera*,¹⁸⁸ and *E. wallichii*.¹⁸⁹ A 12,17-cyclojatropane, euphowelwitschine A 56 was isolated¹⁹⁰ from *E. weiwitschii*. Venenatin 57 which had been obtained from *Excoecaria venenta* (Euphorbiaceae), showed¹⁹¹ inhibitory effects on human leukaemia cells. Further daphnane esters have been isolated from *Trigonostemon xypho-phylloides* (Euphorbiaceae),¹⁹² *Daphne genkwa* (Thymelaeaceae),¹⁹³ *Gnidia polycephala* (Thymelaeaceae),¹⁹⁴ and *Stellera chamaejasme* (Thymelaeaceae)¹⁹⁵ whilst some more tiglane (phorbol) esters with cytotoxic and anti-viral activity were obtained from *Croton tiglium* (Euphorbiaceae),^{196,197} *Daphne aurantica*,¹⁹⁸ and *Stillingia lineata* (Euphorbiaceae).¹⁹⁹ The anti-viral activity of these compounds (e.g. 58) against the chikungunya virus was examined. The evaluation of epoxy-lathyr derivatives in combating multi-drug resistance²⁰⁰ and the anti-viral activity of a number of phorbol and ingenol esters²⁰¹ has been reported. Some synthetic studies directed towards jatrophanes have been described.²⁰²

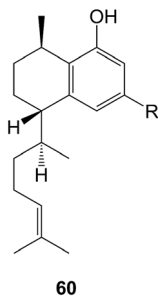


7 Miscellaneous diterpenoids

The synthesis of the 5,6,7-ring system of the mulinane diterpenoids has been achieved.²⁰³ A number of new cyathane diterpenoids have been isolated including the striatoids A–F (e.g. A, **59**) from the basidiomycetes, *Cyathus striatus*,²⁰⁴ and from *C. africanus*²⁰⁵ and *Hericium erinaceus*.²⁰⁶ The total synthesis of the guanacastepenes N and O,²⁰⁷ dolestatrienol,²⁰⁸ and the trichoaurantiolides C and D²⁰⁹ have been reported. Further derivatives of pleuromutilin have been prepared²¹⁰ in the context of their potential anti-tubercular activity.



Dehydrovibsanin G has been isolated²¹¹ from *Viburnum odoratissimum* and a total synthesis of vibsanin which unambiguously defines its stereochemistry has been reported.²¹² 8-Hydroxyserrulat-14-en-19-oic acid **60** (R = CO₂H) which was isolated from the Australian medicinal plant, *Eremophila neglecta* (Scrophulariaceae) has been shown²¹³ to break-up and disperse bacterial biofilms with the potential for use in wound management. A number of modified serrulatanes have been synthesized²¹⁴ from leubethanol **60** (R = Me) and examined for activity against *Mycobacterium tuberculosis*.



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