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Monoterpenoids

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Reviewing the literature published in 1991, 1992 and part of 1993
(Continuing the coverage of literature in *Natural Product Reports*, 1994, Vol. 11, p. 225)

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1 Introduction

This article provides a somewhat selective review of the developments in monoterpenoid chemistry which were reported during 1991, 1992 and part of 1993, and follows on from the previous article in the series.[1] A further article (in preparation) will review advances made during the latter part of 1993, 1994 and most of 1995. The recent resurgence of interest in this field, stimulated by continuing improvements in analytical methodology and by the ongoing quest for a 'perfect' chiral auxiliary, shows no sign of abating. Much useful data on known monoterpenoids has been catalogued,[2] and more recent aspects of the chemistries of acyclic,[3] monocyclic[3] and bicyclic[4] members of the series have been collated.

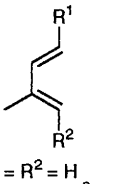
Croteau has summarised[5] the results obtained from a long series of investigations into monoterpenoid biosynthesis. The effects exerted by azide ion on the hydrolysis of some monoterpenoid diphosphates have been reported.[6] The metabolic fates of various monoterpenoids which occur in *Mentha* spp. have been reviewed,[7] and seasonal and environmentally-induced variations in the monoterpenoid content of *Origanum syriacum* have been described.[8] The occurrence and properties of monoterpenoid glycosides has been surveyed.[9]

Global concern about reactive gaseous species (or lack of them) in the upper atmosphere is reflected in the increasing number of studies of plant volatiles with respect to their atmospheric fates. The general subject has been reviewed,[10] as, more specifically, has the light-dependent emission of isoprene from plants.[11] The velvet bean (*Muncuna* sp.) emits isoprene (1) from its leaves at a rate which increases 125-fold as the leaves develop and then declines again as they age. Photosynthetic competence develops before isoprene emission begins to occur.[12] The leaves of *Populus tremuloides* contain a novel enzyme which catalyses the Mg^{2+}-dependent conversion of dimethylallyl diphosphate into isoprene in a reaction which may be generally responsible for its production in most isoprene-emitting species.[13]

Ecological aspects of fragrant terpenoids produced by angiosperms have been reviewed,[14] as has the ecological impact of monoterpenoids in general[15] and their allelopathic properties in particular.[16] The oil from *Tanacetum vulgare* contains monoterpenoids which repel females of the grapevine moth *Lobesia botrana*,[17] and the 2-*O*-β-D-glucoside of angelicoidenol which is found in *Pinus sylvestris* deters moose from feeding on the young plants.[18] Certain oils from *Mentha* species have been found to be strongly active as fungistatic agents against some dermatophytes.[19]

The use of essential oils as sources of natural aroma compounds,[20] and the employment of microbial cultures for the preparation of odorous monoterpenoids[21] have both been reviewed, as has the production of monoterpenoids from root cultures of *Mentha* species.[22] The use of plant cell cultures to facilitate biotransformations of monoterpenoids has also been reviewed.[23] A survey of the terpenoids which occur in coniferous species has been provided,[24] and geographical variations in the monoterpenoid content of *Pinus albicaulii* have been recorded.[25] Reviews on *Thymus* oils[26] and on the extraction and composition of *Citrus* oils[27] have been published. The use of rapid microwave techniques for the extraction of plant oils has been shown to afford products which are almost identical to those obtained *via* conventional steam distillation.[28]

Interesting new plant monoterpenoids which have been isolated during the period under review include the isoprenoid glycosides (2) and (3) which have been obtained from the roots of *Rhodiola crenulata*[29] and from *Ornithogalum montanum*[30] respectively. Also new are arnebinone (4), arnebifuranone (5) and the novel *ansa*-compound (6), all of which have been obtained from *Arnebia euchroma*.[31,32]



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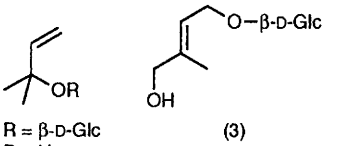
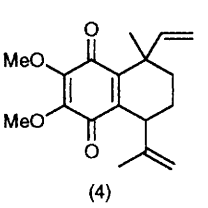
(7) $R^1 = OEt$; $R^2 = H$



(2) R = β-D-Glc
(8) R = H

(3)



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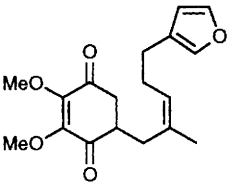

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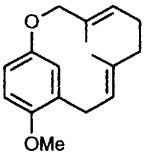

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Table 1 Sources of monoterpenoids

Species	Comment	Reference
Abies chensiensis Van Tiegh	Pinenes, limonene	66
Achillea biebersteinii Afan.	Cineol, camphor	67
Achillea grandiflora	Camphor, thujones	68
Achillea millefolium	Ascaridole	69, 70
Achillea millefolium ssp. *millefolium*	Cineol, sabinene	71
Agastache spp.		72
Alpinia galanga Willd.	Myrcene	73
Alpinia oxyphilia		74
Allosyncarpia ternata S. T. Blake	Pinenes, limonene	75
Artemisia lacinata chemotypes	(*a*) *cis*-Chrysanthemyl acetate, artemisia ketone; (*b*) Piperitone	76
Artemisia molinieri	Ascaridole	77
Artemisia moorcroftiana Wall.		78
Artemisia persica		79
Artemisia pallens		80
Buddleia asiatica Lour.	Citronellol	81
Calamintha arkansana (Nutt.) Shinners	Pulegone, menthone	82
Calamintha nepeta ssp. *glandulosa*	Limonene, piperitone oxides	83
Chaerophyllum bulbosum		84
Chamaecyparis lawsoniana		85
Chamaecyparis pisifera	Bornyl acetate, 3-carene	85
Chromolaena odorata	Bornyl acetate	86
Cinnamomum glaucescens	Cineol, α-terpineol	87
Cinnamomum longepaniculatum		88
Cinnamomum migao H. W. Li	Cineol, limonene, sabinene, α-terpineol	89
Cistus ladanifer	α-Pinene, isopinocamphone, camphene	90
Citrus aurantifolia		91
Cleonia lusitanica	α-Pinene, limonene	92
Conyza pinnata	(*E*)-β-Ocimene	93
Crithmum maritimum	γ-Terpinene, sabinene, methyl thymol	94
Cryptomeria japonica	Hydrocarbons (45%), alcohols (10%)	95
Cunninghamia lanceolata	Terpinyl acetate, terpinolene	96
Cymbopogon coloratus		97
Cymbopogon distans	α-Terpinene, piperitone	98
Cymbopogon travancorensis		99
Egletes viscosa	β-Pinene, *trans*-pinocarveyl acetate	100
Erigeron canadensis	Limonene, camphene	101
Eucalyptus bicostata	Cineol	102
Eucalyptus brassiana S. T. Blake	Cineol, α-pinene	103
Eucalyptus bridgesiana	Cineol	104
Eucalyptus camaldulensis	Cineol, *p*-cymene	105
Eucalyptus dealbata	Cineol, cryptone	106
Eucalyptus delgupta	α-Pinene, α-terpinene, *p*-cymene	102
Eucalyptus torelliana	α-Pinene, β-pinene	102
Eupatorium adenophorum Spring.	*p*-Cymene, bornyl acetate	107
Ferulago sylvatica (Besser) Reichenb.	α-Pinene	108
Foeniculum vulgare	Limonene	109
Forsythia spp.	Geraniol, geranial, linalool, α-terpineol	110
Gardenia jasminoides	Linalool, carveol	111
Geranium robertianum	Linalool, γ-terpineol	112
Grindelia robusta Nutt.	α-Pinene, bornyl acetate	113
Grindelia squarrosa Dun.	α-Pinene	113
Hedychium coronarium	Cineol, β-pinene	114
Hedychium coronarium Koenig	β-Ionone	115
Hedychium odoratissimum	α-Pinene	116
Helichrysum picardii	3-Carene	117
Heteropyxis natalensis	β-Ocimene, linalool, myrcene	118
Hyssopus officinalis	Pinocamphone, camphor, β-pinene	119
Juniperus sabina	Sabinene, sabinyl acetate	120
Kaunea longipetolia	Geranyl acetate	121
Lanata camara	Iridoids	122
Lepechinia urbanii (Briq.) Epling	3-Carene, β-phellandrene	123
Lepidophyllum quadrangulare (Meyen) Benth. and Hook.	α-Pinene, β-pinene	124
Libanotis laticalycina Shan *et* Sheh.	β-Pinene	125
Liquidambar orientalis Mill.		126
Litsea pungens Hemsl.	Cineol	127
Lonicera japonica Thunb.	Linalool, geraniol	128
Magnolia coco (Lour) DC.	β-Terpinene, 4-terpineol, α-pinene, linalool	129
Melaleuca spp.	Cineol	130
Melaleuca uncinata	Terpinen-4-ol	130
Melissa parviflora		131
Michelia alba DC.		132
Micromeria brownei var. *pilosiuscula*	Pulegone, menthone, neomenthol	133
Micromeria fruticosa Druce, ssp. *barbata*	Pulegone	134

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Table 1 (*cont.*)

Species	Comment	Reference
Micromeria fruticosa Druce, ssp. *brachycalyx* P. H. Davis	Pulegone	135
Micromeria fruticosa ssp.	Pulegone, piperitenone, piperitenone oxide	136
Monarda didyma cv. 'Cambridge Scarlet'	Linalool	137
Myrtus communis	Cineol, myrtenyl acetate	138
Nidorella resedifolia DC.	Hydrocarbons, lavandulyl esters	139
Nothopanax delavayi	β-Phellandrene, myrcene, α-pinene	140
Notopterygium incisum	α-Thujene	141
Osbornia octodonta F. Muell	α-Pinene, cineol, α-terpineol	142
Pelargonium spp.		143
Pelargonium quercifolium		144
Pelargonium vitifolium	Citronellic acid	145
Peristeria elata	Cineol	146
Pimenta racemosa (Miller) J. Moore		147
Pistacia integerrima	Pinenes, phellandrene, 3-carene	148
Polyalthia suaveolens	Myrcene	149
Rosmarinus officinalis	Myrcene, cineol, camphor, α-pinene	150
Sabina vulgaris	Sabinene	151
Salvia spp.		152
Santolina chamaecyparissus	Artemisia ketone, myrcene	153
Satureja grandiflora	Pulegone, isomenthone, menthol, neoisomenthol	154
Schinus latifolia Engl.	α-Pinene, β-pinene, sabinene	155
Seriphidium brevifolium	α-Thujone, β-thujone	156
Sideritis dichotoma	α-Pinene, β-pinene	157
Sideritis germanicopolitana subsp. Bornm.	Myrcene	158
Sideritis scardica		159
Strobilanthes callosus Nees.		160
Syzygium cuminii Skeel	Myrcene, α-pinene, β-pinene	161
Tagetes argentina	(*Z*)- and (*E*)-ocimenones	162
Thuja occidentalis		163
Thuja orientalis		163
Thymus riatarum	α-Terpinene, carvacrol, *p*-cymene	164
Tithonia diversifolia (Hemsl.) A. Gray	(*Z*)-β-Ocimene	165
Vitex trifolia	Cineol, terpinyl acetate, sabinene	166
Vitex trifolia var. *simplicifolia*		166
Zhumeria majdae Rech.	Linalool, camphor	167
Ziziphora clinopodioides Lam.	Cineol, pulegone	168

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The electron impact mass spectra of 19 monoterpenoids exhibit normal fragmentation patterns when obtained at 70 eV and 500 K, but give simpler spectra, especially at low *m/z* values, at 12 eV and 350 K.[33] A detailed study has been made of the mass spectra of a number of $C_{10}H_{16}$ monoterpenes, and evidence for significant contributions to their fragmentation pathways by a protonated cycloheptatriene structure has been obtained.[34] The ^{13}C NMR spectra of very many monoterpenoids have been collected together in a book,[35] and vicinal ^{13}C–^{13}C *J* values for a range of bicyclic monoterpenoids have been measured and their dependence on dihedral angle noted.[36]

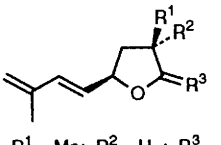
The use of coupled GC-MS methods for essential oil analysis has been reviewed,[37] as has the application of supercritical fluid chromatography for the same purpose.[38] There has been a flurry of publications (and a review[39]) on the use of chiral GC (and HPLC) methods for the enantioselective analysis of monoterpenoids. Enantioselective multidimensional GC techniques permit the simultaneous separation and stereoanalysis of essential oil components with a view to authenticating their natural origins.[40,41] All of the important unsaturated monoterpene hydrocarbons which occur in natural oils can be enantioselectively separated using dual GC capillary columns coated with heptakis(6-*O*-methyl-2,3-di-*O*-pentyl)-β-cyclodextrin and octakis(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin.[42] The preparations of these two modified cyclodextrin stationary phases have been described, together with that of the related octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin which may be utilised for the enantioselective separation of monoterpenoid alcohols.[43] Two reports on the enantioselective analysis of *Mentha piperita* oils using chiral phase GC have appeared.[44,45]

The chromatography of lemon peel oils on silica gel has been shown to lead to the formation of small quantities of oxygenated monoterpenoids, and this effect can be reduced (but not eliminated) by operating the column at 3 °C.[46]

The acid-catalysed aqueous reactions of many important monoterpenes have been reviewed, and the effects that the presence of sodium dodecyl sulfate micelles have on most of these processes have been noted.[47] The hydration reactions of various monoterpene hydrocarbons in the presence of synthetic zeolites has attracted some attention,[48,49] as has the addition of C_1–C_4 aliphatic alcohols to them under the same conditions.[50] The zeolite-catalysed reactions of monoterpenoids have been reviewed.[51]

The useful isoprenoid synthon (7) (see page 195) has been prepared,[52] and reaction of the alcohol (8) with oxalic acid has been shown to yield isoprene (1) (40%) together with a pleasantly fragrant mixture of 25 identified cyclic and acyclic monoterpenoids.[53]

The marmelo oxides *A* (9) and *B* (10) have been synthesised *via* palladium-catalysed cyclisation reactions,[54] and another synthesis of these oxides together with the corresponding



(9) R^1 = Me; R^2 = H ; R^3 = H_2
(10) R^1 = H; R^2 = Me; R^3 = H_2
(11) R^1 = Me; R^2 = H; R^3 = O
(12) R^1 = H; R^2 = Me; R^3 = O
(7) and (8) are with (1) and (2)

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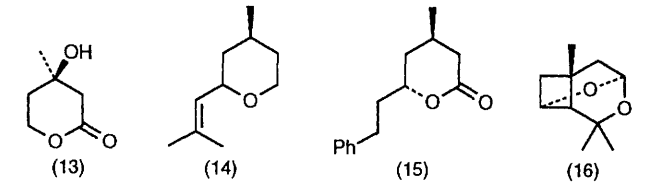
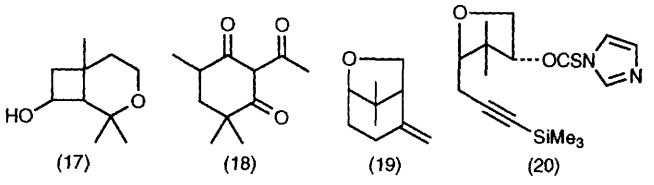
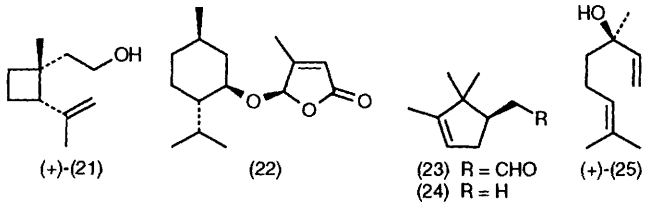
lactones (11) and (12) has been described.[55] An enantioselective synthesis of (*R*)-mevalonolactone (13) has been reported,[56] and (+)-*cis*-rose oxide (14) has been obtained *via* the lactone (15).[57] Lineatin (16), a pheromone of *Trypodendron lineatum*, has again been synthesised in racemic form,[58] and both enantiomers of (16) have been prepared from the intermediate (17) which was resolved *via* its diastereoisomeric esters with (−)-camphanic acid.[59] Progress towards a synthesis of paeoniflorin has been reported.[60] A route to angustione (18) has been published,[60] and both (+)- and (−)-karahana ethers (19) have been obtained *via* radical-induced 6-*exo*-*dig* cyclisation of the alkyne (20).[61] Both enantiomers of grandisol (21) have been synthesised *via* the sensitised photocycloaddition of ethene to the menthyloxy butenolide (22) followed by separation of the diastereoisomeric adducts.[62] In a transformation which is likely to prove useful elsewhere, the campholenic aldehyde (23) can be decarbonylated using Rh–Al_2O_3 to give (24) with only a slight amount of racemisation.[63] Methods for the stereoselective synthesis of acyclic monoterpenoids have been reviewed.[64]





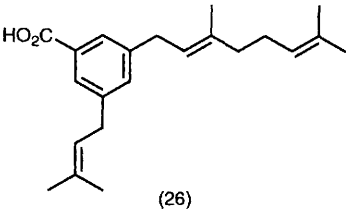


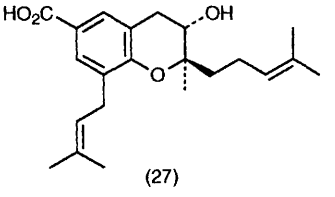
Some of the new monoterpenoids discovered during the period under review have been mentioned above, and other noteworthy findings are discussed under the appropriate headings later in this article. Table 1 on pages 196–197 collects together in a convenient format references to the results of a wide selection of investigations which have been carried out into plant species where known compounds have been detected, quantified and identified.

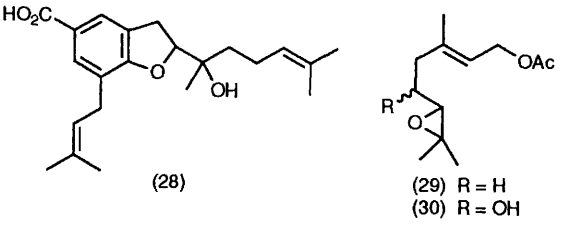
2 2,6-Dimethyloctanes

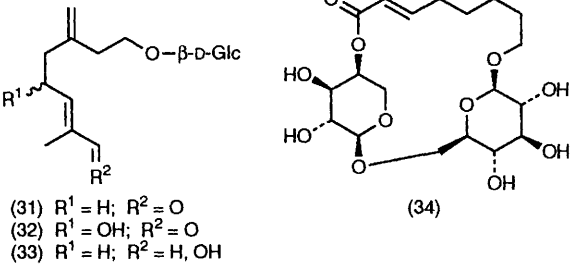
The α-L-arabinofuranosyl-(1–6)-β-D-glycopyranoside of (*S*)-(+)-linalool (25) has been isolated from a methanol extract of raspberry fruits,[169] and the three new geranyl derivatives (26)–(28) have been obtained[170] from the leaves of *Rapanea umbellata*. The novel epoxides (29) and (30) have been found[171] in *Jasonia montana*, and the glycosylated aldehydes (31) and (32), the related alcohol (33), and various derived acetylated sugar derivatives have been extracted[172] from *Hymenoxys nesiana*. The unusual bridged compound lonitoside (34) has been discovered[173] in *Lonicera nitida*, and the fruits of *Cydonia oblonga* provide the glycoside (35) which is a biosynthetic precursor for the isomeric marmelo oxides (9) and (10).[174] New compounds isolated[175] from *Artemisia salsoloides* include the spiro-bis(dihydrofuran) (36) and the dienone (37).

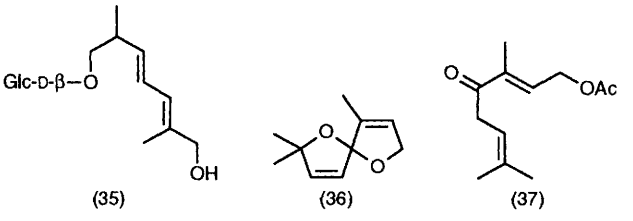
The role of divalent metal ions in the biosynthesis of cyclic monoterpenoids has been further probed by an examination of











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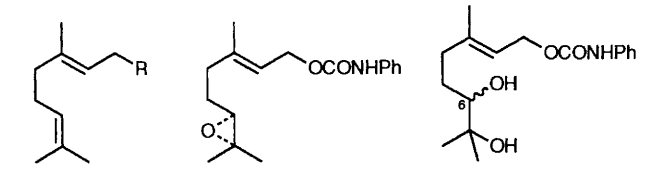
the ^{31}P and ^{13}C NMR spectra of geranyl diphosphate (38) in the presence and absence of Mg^{2+}. The results obtained indicate that magnesium ions bind in a 1:1 ratio with the diphosphate groups, with the metal ion being equidistant from each phosphorus atom.[176] The non-enzymic cyclisation reactions of geranyl, neryl and linalyl diphosphates in the presence of divalent metal ions have been studied.[177] A γ-terpinene synthase from the leaves of *Thymus vulgaris* which acts on geranyl diphosphate (38) has been purified and characterised.[178]

Geranyl *N*-phenylcarbamate (39) is biotransformed by *Aspergillus niger* to the 6,7-epoxide (40) which then undergoes a further enzyme-catalysed transformation at pH 6–7 to give the (6*R*)-diol (41). If the epoxide (40) is subjected instead to acid-catalysed hydrolysis at pH 2 then the product is the (6*S*)-diol (42).[179] The *N*-phenylcarbamates of (3*R*)-citronellol (43) and of its enantiomer (44) behave similarly, with the same stereochemical outcome at C-6 regardless of the configuration at C-3.[180] Racemic citronellol can be esterified by oleic acid in a lipase-catalysed reaction which takes place in supercritical CO_2. A partial kinetic resolution is possible since the (3*S*)-alcohol (44) reacts more rapidly than does its enantiomer.[181] Hydroxylation of myrcene cyclic sulfone (45) by cultures of *Sebekia benihana* NRRL-11111 provides modest yields of the allylic alcohol (46) which can be converted into ipsdienol (47). The hydroxylation of the related ocimene derivative (48) has also been investigated.[182] A synthesis of (3*R*)-(−)-[8,8,8-$^2H_3$]-linalool (49), potentially useful in probing biochemical and other mechanisms, has been reported.[183]

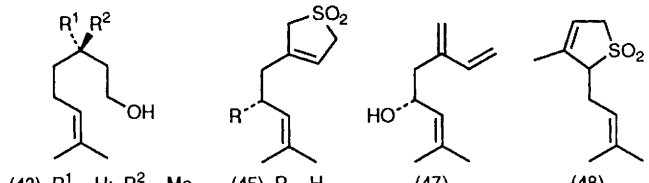
The toxicity of 6,7-dihydrogeraniol (50) has been reviewed, and the compound is not recommended for incorporation into fragrance compositions.[184]



(38) R = OPP
(39) R = OCONHPh
(51) R = OH
(68) R = *O*-palmitoyl
(72) R = OAc
(75) R = OMe
(78) R = Cl
(85) R = SH

(40)

(41) (6*R*)-OH
(42) (6*S*)-OH

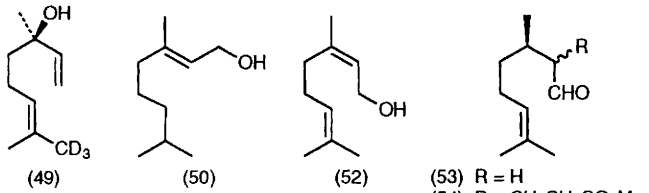


(43) R^1 = H; R^2 = Me
(44) R^1 = Me; R^2 = H

(45) R = H
(46) R = OH

(47)

(48)



(49)

(50)

(52)

(53) R = H
(54) R = $CH_2CH_2CO_2Me$

(51) is with (38)

β-Cyclodextrin which has been modified with methyl red, exhibits colour changes when it hosts geraniol (51) or nerol (52), with a 1.7-fold greater response towards the (*E*)-isomer (51).[185] Two reports describe methods for authentication of the natural origin of oils containing linalool (25). One of these involves the use of multidimensional enantioselective GC to determine optical purity,[186] whilst the other employs ^{13}C and ^2H NMR techniques which are also applicable to linalyl acetate.[187] GC analysis using the chiral stationary phase heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin has been used to resolve all four stereoisomers of linalyl oxide.[188]

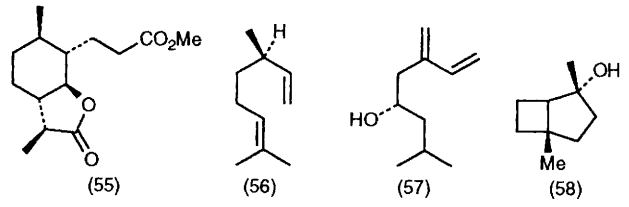
(*R*)-Citronellal (53) has been converted *via* its enamine into the Michael adduct (54) which undergoes a Lewis acid-catalysed intramolecular ene cyclisation to give (55), a degradation product of the anti-malarial quinghaosu, together with isomeric compounds.[189] In a reaction which is a valuable addition to the repertoire, the pyrrolidine enamine of (53) reacts sequentially with 9-BBN and then with methanol to yield β-citronelladiene (56). Enamines derived from ketones react analogously.[190]

Metallation of isoprene (1) by KDA, and then reaction with 3-methylbutanal or with 3-methylbut-2-enal leads to ipsenol (57) or to ipsdienol (47) in poor yields.[191] (*S*)-(−)-Ipsenol (57) has been synthesised from (*S*)-lactic acid,[192] and new routes to both enantiomers of ipsdienol (47) have been described.[193]

Both enantiomers of the bicyclic alcohol (58), a key intermediate for the synthesis of grandisol (21), have been synthesised from the enantiomeric linalools (43) and (44).[194] A synthesis of α-acaridial (59) has been described,[195] and citral (*E*/*Z*)-(60) has been efficiently converted into ψ-ionone (61) *via* condensation with acetone in the presence of KF–Al_2O_3.[196]

The selective hydrogenation of citral (60) to yield the allylic alcohols geraniol (51) and nerol (52) has been achieved by using Ru or Rh complexes of sulfonated phosphines in an aqueous–organic two-phase solvent system. The regioselectivity depends strongly upon the metal, with Ru being preferred.[197] Citral (60) has also been hydrogenated to geraniol and nerol with a tin-modified silica-supported Rh catalyst, this time with 96% selectivity for reduction of the carbonyl group at 100% substrate conversion.[198] Hydrogenation of geranial (*E*)-(60) to give (+)-citronellal (53) of 62% ee has been carried out using a catalyst generated *in situ* from [$Rh(CO)_2$acac] and (−)-DIOP. Neral (*Z*)-(60) similarly yields (−)-citronellal *ent*-(53) of 55% ee under the same conditions.[199]

Nerol (52) has been converted into the epoxide (62) of 66% ee *via* reaction with $Ph_2C(Me)OOH$–$Ti(OPr^i)_4$ in the presence of the salicylidene-(*S*)-valine (63).[200] The same epoxide (62), obtained by an alternative route, has been used as a synthon for (*R*)-mevalonolactone (13).[201] The kinetic resolution of the epoxides *rac*-(62) and *rac*-(64) using chiral Lewis acid catalysts such as the complex formed from the hydroxy-sulfonamide (65)

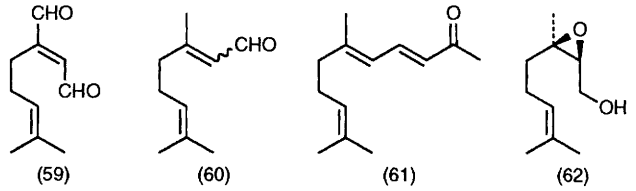


(55)

(56)

(57)

(58)

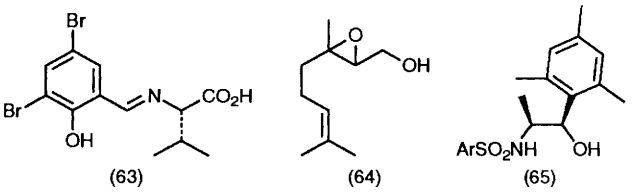


(59)

(60)

(61)

(62)



(63)

(64)

(65)

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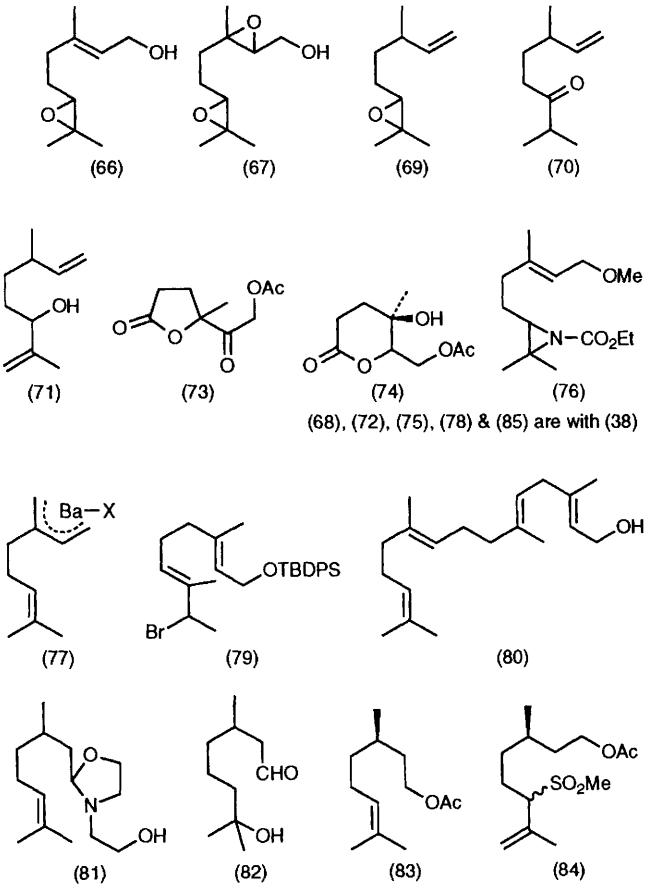
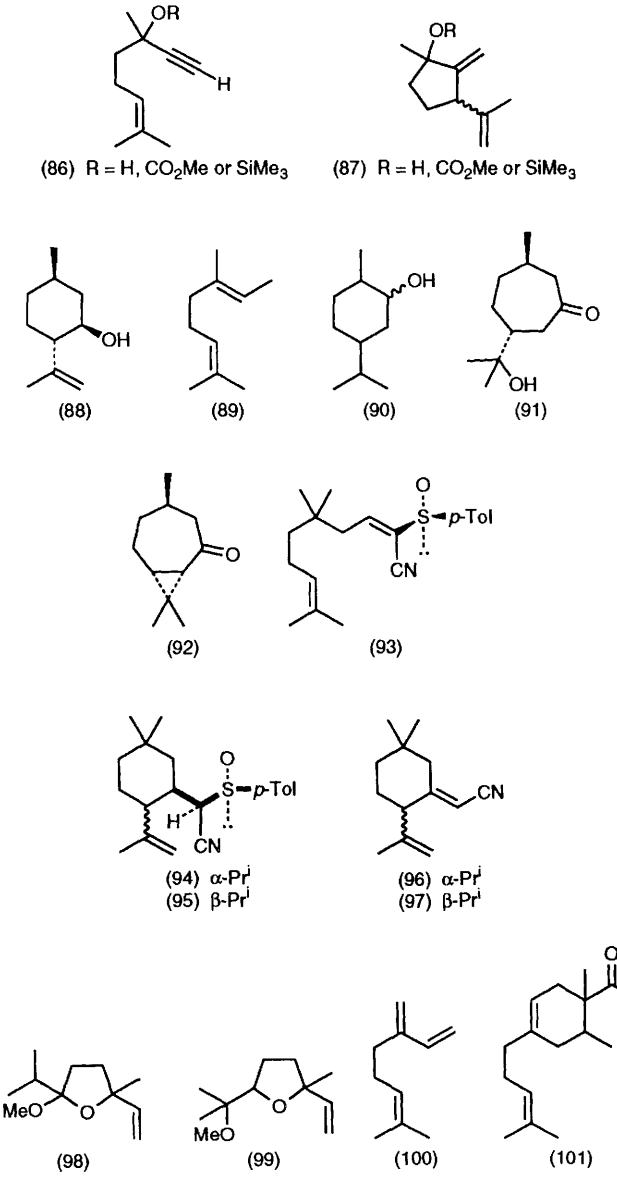
and $Ti(OPr^i)_4$ has been studied.[202] Epoxidation of geraniol (51) by monoperoxyphthalic acid in aqueous sodium hydrogen carbonate in the presence of a surfactant leads to the formation of a mixture of the three products (64) (28%), (66) (35%) and (67) (24%).[203] Epoxidation of geraniol (51) by the same peroxyacid in water alone is pH-dependent, giving good yields of (66) at pH 8.3 and excellent yields of (64) at pH 12.5.[204] Epoxidation of geranyl palmitate (68) using *m*-chloroperoxybenzoic acid in dichloromethane leads initially to the derived 2,3-epoxide which is then further oxidised at the 6,7-double bond.[205] Isomerisation of dihydromyrcene epoxide (69) to give (70) and/or (71) has been investigated.[206]

In a process which is general for 1,5-dienes, geranyl acetate (72) undergoes heterogeneous oxidation in the presence of potassium permanganate and catalytic copper(II) sulfate in aqueous CH_2Cl_2 to give the lactones (73) (59%) and (74) (10%).[207] Geranyl methyl ether (75) (and the neryl analogue) reacts[208] regioselectively with ethoxycarbonylnitrene to give the 6,7-adduct (76). Geranylbarium (77), which can be obtained[209] by reacting geranyl chloride (78) with equimolar Reike barium in tetrahydrofuran at −78 °C, can be coupled with the geraniol-derived bromide (79) to yield geranylgeraniol (80) without disturbance of alkene geometry.[210] After appropriate chemistry, the sequence can be repeated to synthesise higher homologues.



Citronellal (53) reacts rapidly with diethanolamine to give (81) which undergoes hydration and then hydrolysis in the presence of sulfuric acid to give the hydroxy-aldehyde (82) without significant competing cyclisation.[211] Reaction of (*R*)-citronellyl acetate (83) with thionyl chloride at −20 °C in the presence of catalytic Et_2AlCl and then with methanol yields the rearranged allylic sulfinate ester (84) *via* an ene-type process. Geranyl and linalyl acetates behave analogously.[212] Linalool (25) reacts with thiourea in the presence of hydrohalic acids to give geranyl thiol (85) after basic hydrolysis of the thiouronium salt which is formed.[213]

The cyclisation reactions of acyclic monoterpenoids continue to attract the attention of various groups. The dehydrolinalool derivatives (86) undergo thermal cyclisation to give the cyclopentanes (87) in 16–93% yield.[214] When (*R*)-citronellal (53) on silica gel is pressurised to 15 kbar (1 bar = 10^5 Pa), isopulegol (88) is formed in high yield *via* an ene-like reaction. The same cyclisation can, as expected, be effected using conventional Lewis acid catalysts such as $ZnBr_2$ or Me_2AlCl.[215] Dihydromyrcene (89) reacts in the presence of HSZ-620-HOA zeolite–$Al(OH)_3$–H_2O to give mainly the tetrahydrocarveol (90).[216] (*R*)-Citronellal (53) has been converted into the useful chiral synthons (91) and (92).[217] The sulfoxide (93) undergoes an asymmetric ene-cyclisation in the presence of, for example, catalytic Et_2AlCl to yield the diastereoisomeric products (94) (66–97% de) and (95). The former thermolyses to give the (−)-unsaturated nitrile (96) whilst the latter yields the enantiomeric product (97).[218,219]



Electrolysis of linalool (25) in methanolic sodium methoxide yields a mixture of diastereoisomers of the tetrahydrofurans (98) and (99).[220]

The Diels–Alder reaction between myrcene (100) and (*E*)-3-methylpent-3-en-2-one which is catalysed by $AlCl_3$ on layered graphite yields the odiferous compound Ambralux (101).[221] The effectiveness of various Lewis acids which catalyse the Diels–Alder reaction between myrcene (100) and methyl

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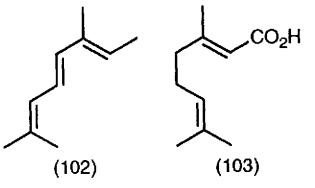
propenoate has been studied,[222] and $ZnCl_2$ has been found to provide optimum yields. The structures of the four isomeric Diels–Alder adducts which are obtained by reaction of the triene (102) with methacrolein have been determined,[223] and geranic acid (103) yields the expected cycloaddition product when it is reacted with cyclopentadiene.[224]

Reaction of citral *E*/*Z*-60 with aniline under mild conditions, followed by brief treatment with acid at 0 °C affords α-cyclocitral (104) in 60% yield.[225] The diene δ-pyronene (105), obtained from myrcene (100), can be regioselectively epoxidised using *m*-chloroperoxybenzoic acid to give the mono-epoxide (106) (75%) together with some of the di-epoxide (107) (25%).[226] Treatment of (106) with magnesium bromide converts it into a mixture which is largely γ-cyclocitral (108), whilst rearrangement using triflic acid gives mainly β-cyclocitral (109). The alternative mono-epoxide (110) can be obtained from δ-pyronene (105) *via* its reaction with *N*-bromosuccinimide to give a bromohydrin which is then cyclised using potassium carbonate.[226] β-Cyclocitral (109) has been converted into the (*Z*)-dienoic acid (111) under Perkin conditions,[227] and into the nor-ketol (112) by reaction with a peroxy acid followed by hydrolysis.[228] The epoxy ether (113) rearranges in the presence of $BF_3 \cdot Et_2O$ to yield the unexpected dihydropyran (114) together with only traces of the anticipated ketone (115).[229]



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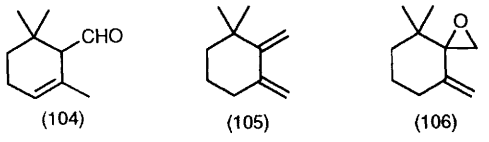

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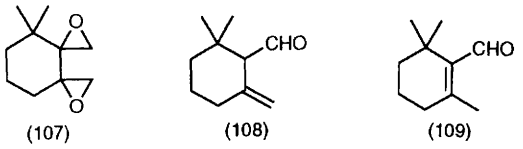

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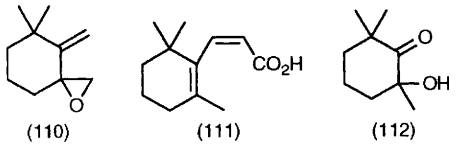

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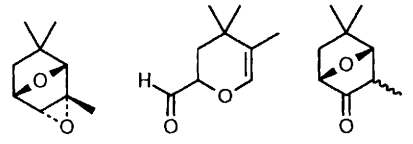
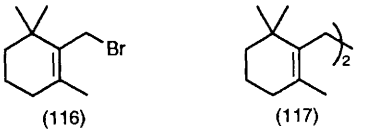
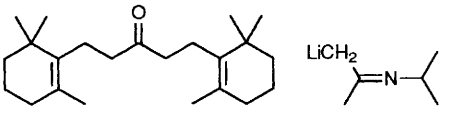


(113) (114) (115)

Reaction of β-cyclogeranyl bromide (116) with excess lithium di-isopropylamide affords the coupling product (117) together with the acetone derivative (118).[230] The authors presume the source of the three additional carbon atoms to be the rearranged lithio-derivative (119).



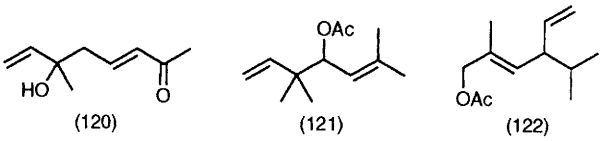
(116) (117)



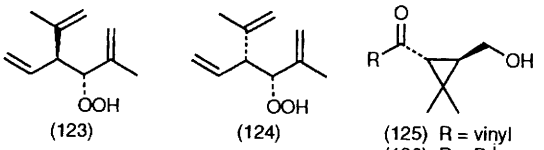
(118) (119)

3 Artemisyl, Santolinyl, and Chrysanthemyl Systems

The laevorotatory nor-monoterpenyl alcohol (120) has been isolated[231] from *Artemisia schimperi*, together with artemisyl acetate (121) and lyratryl acetate (122), and the novel diastereoisomeric hydroperoxides (123) and (124) have been obtained[232] from *Artemisia lancea*, which also contains the sesquiterpenoid antimalarial peroxide quinghaosu. The new chrysanthemyl compounds (125) and (126) have been isolated from *Artemisia tridentata cana*, and their structures confirmed by synthesis.[233]



(120) (121) (122)

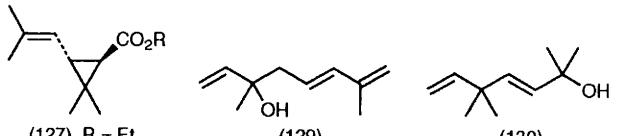


(123) (124) (125) R = vinyl (126) R = Pr^i

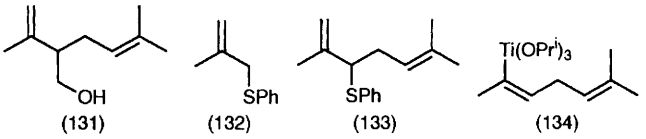
Three-bond ^{13}C–^1H *J* values have been measured for a series of *cis*- and *trans*-chrysanthemic acid derivatives, and these provide useful correlations for the assignment of stereochemistry.[234]

More than 228 strains of various microorganisms have been screened for their ability to enantioselectively hydrolyse ethyl chrysanthemate (127), and the most effective has been found to be *Arthrobacter globiformis* IFA-12958 which is capable of providing optically pure chrysanthemic acid (128).[235]

Racemic hotrienol (129) has been synthesised utilising hydroalumination chemistry,[236] and yomogi alcohol (130) has been efficiently prepared[237] *via* the *syn*-carboindation of 3-methylbutyn-3-ol by $(Me_2C{=}CHCH_2)_3In_2Br_3$. Lavandulol (131) has been synthesised in 70% yield in a two-pot sequence where the lithiated sulfide (132) reacts with prenyl bromide to give (133) which is then converted into the alkyltitanium (134) and thence to lavandulol.[238]



(127) R = Et (128) R = H (129) (130)



(131) (132) (133) (134)

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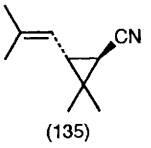
The chrysanthemum nitrile (135) has been synthesised *via* asymmetric epoxidation of the alcohol (136) to yield (137), the silyl ether of which undergoes Stork cyclisation to give (138) which is a precursor of (135).[239,240] The addition of bromine to the (*E*)- and (*Z*)-isomers of the vinylic chloride (139) affords the derived (1*R*,2*R*)- and (1*S*,2*S*)-dibromides, respectively, the structures of which were determined using NMR with the aid of lanthanide shift reagents.[241] The enantioselective synthesis of chrysanthemic acid and its derivatives has been reviewed.[242]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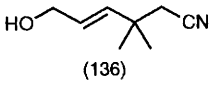
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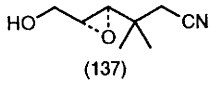
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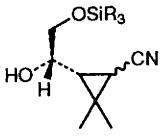
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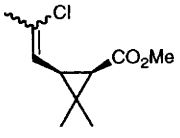
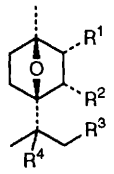

(139)

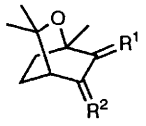
4 Cineol Derivatives

The biotransformations of 1,4-cineol (140) by *Aspergillus niger* have been extensively studied,[243–246] and the structures of the four hydroxylated derivatives (141)–(144) which are produced have been established.

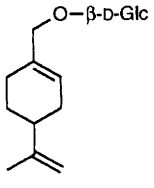
1,8-Cineol (145) undergoes[247] photo-oxidation to give the keto-cineols (146) and (147) when it is irradiated at 280 nm in the presence of oxygen and catalytic amounts of $(Bu_4N)_4W_{10}O_{32}$.



(140) $R^1 = R^2 = R^3 = R^4 = H$
(141) $R^1 = OH$; $R^2 = R^3 = R^4 = H$
(142) $R^1 = R^3 = R^4 = H$; $R^2 = OH$
(143) $R^1 = R^2 = R^4 = H$; $R^3 = OH$
(144) $R^1 = R^2 = R^3 = H$; $R^4 = OH$



(145) $R^1 = R^2 = H_2$
(146) $R^1 = O$; $R^2 = H_2$
(147) $R^1 = H_2$; $R^2 = O$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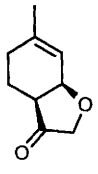
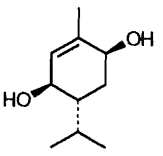

(149)

5 Menthanes

The new glycoside perilloside-A (148) has been isolated[248] from *Perilla frutescens*, and the nor-monoterpenoid tetrahydrofuranone lepalox (149) has been obtained[249] from *Ledum palustre*. The novel diol (150) and the related epoxide (151) have both been found[250] in the aerial parts of *Mikania saltensis*, (+)-1,2-epoxypulegone (lippione) has been isolated[251] from *Acrocephalus indicus*, and the interesting peroxyhemiacetal (152), for which no absolute configuration has been determined, is a constituent of *Adenosma caeruleum*.[252] New aromatic monoterpenoids which have been discovered include plucheoside-C (153) from[253] the roots of *Pluchea indica*, the thymol derivative (154) from[254] *Calea nelsonii*, and espintanol (155) which exhibits trypanicidal and leishmanicidal activities, and which has been isolated[255] from *Oxandra espintana* together with its methyl ether (156).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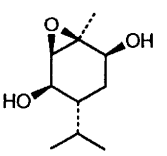
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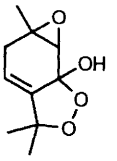
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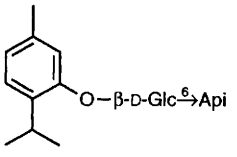
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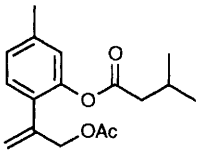
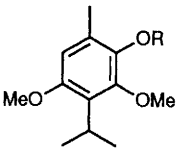
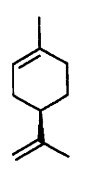
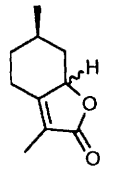
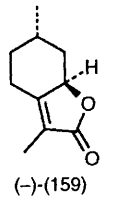

(154)

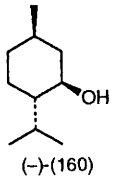

(155) R = H
(156) R = Me

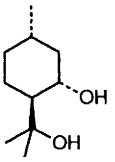
A limonene cyclase, for which the substrate is geranyl diphosphate (38), has been isolated[256] from the fruits of *Citrofortunella mitis*, and has been purified by ion exchange chromatography. An article which reviews the various biotransformations of limonene (157) which can be carried out using micro-organisms has been published.[257] The biosynthesis of (−)-mintlactone (158) and of (−)-isomintlactone (159) in *Mentha piperita* has been examined.[258] The biotransformation of (−)-menthol (160) by *Aspergillus niger* leads to a mixture of its 1-, 2-, 6-, 7-, 8- and 9-hydroxy derivatives, whilst the same fungus converts[259] (+)-menthol *ent*-(160) into its 7-hydroxy derivative (161). (+)-Menthone (162) is converted[260] into the lactone (163) by an *Acetobacter* sp. The major product obtained when racemic piperitone *rac*-(164) is metabolised by *Rhizoctonia solani* is the (−)-ketol (165) whose absolute configuration was determined *via* its Mosher ester.[261] Evidence has been obtained that pulegone (166) covalently binds to the prosthetic haem group of cytochrome P_{450}, and that this binding is responsible for loss of biological activity.[262] When (+)-pulegone (166) is metabolised by *Botrytis allii*, the major product is the ketol (167) which is formed[263] together with some piperitenone (168).[264] The latter may arise *via* dehydration of the alternative ketol (169), which is formed as the major product when

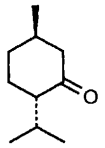

(+)-(157)

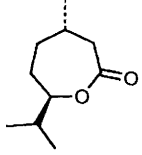

(−)-(158) α-H
(+)-(212) β-H

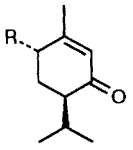

(−)-(159)

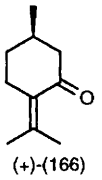

(−)-(160)

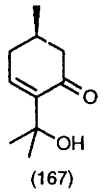

(161)

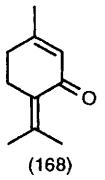

(162)

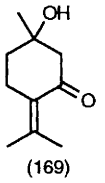

(163)


(164) R = H
(165) R = OH


(+)-(166)


(167)


(168)


(169)

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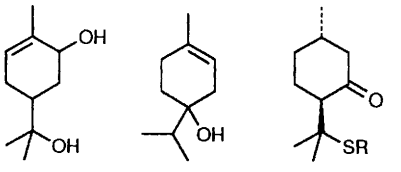
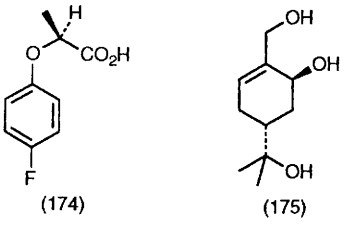
pulegone (166) is metabolised by *Aspergillus* sp., by *Mucor plumbeus* CBS-110-16, or by *Mortierella isabellina* MMP-108.[265] Racemic *trans*-sobrerol (170) has been effectively resolved by the action of Lipase-PS supported on Celite in *tert*-amyl alcohol as solvent and with vinyl acetate as donor. Using this system, the (−)-diol and the (+)-monoacetate are each formed in 100% ee at 50% conversion.[266]

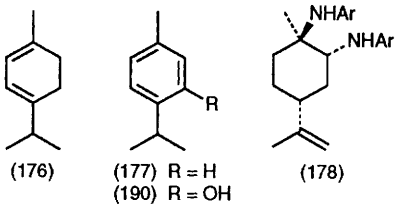
Coupled chiral and non-chiral CGC columns have been used to carry out an enantioselective analysis which can be employed to determine the authenticity of citrus (mandarin) oils *via* measurement of the optical purity of the limonene (157) which is present.[267] The enantioselective analysis of limonene can also be achieved by utilising a GC column coated with a solution of α-cyclodextrin in dimethylformamide as stationary phase,[268] whilst β-cyclodextrin stationary phases have been employed for determination of the contents of (*S*)-(+)-terpinen-4-ol (171) in lavender oils,[269] and of the flavoursome keto thiols (172) and *ent*-(172) [synthesised from (−)- and (+)-pulegone (166), respectively] which occur in buchu leaf oils.[270] The corresponding thiol acetates (173) have also been synthesised, and have been enantioselectively analysed by similar methods.[271]

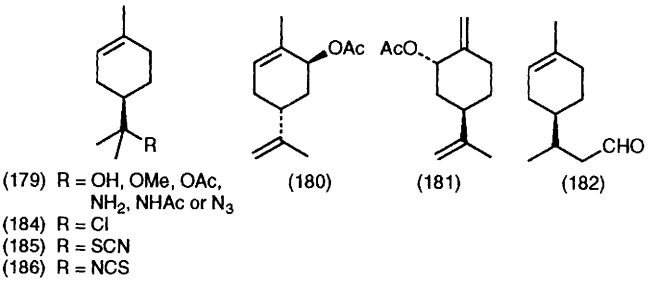
All eight diastereoisomers of the menthyl alcohol series (160) can be observed in the same ^{19}F NMR spectrum, obtained at 188.3 MHz, when their mixture is esterified with the acid (174) which is obtained from an appropriate ester of lactic acid *via* a Mitsunobu reaction with fluorophenol.[272] A study of the mass spectrometric fragmentation of the ^{18}O-labelled mucoactive triol (175) has indicated that loss of H_2O from its molecular ion involves only the tertiary hydroxy group.[273]

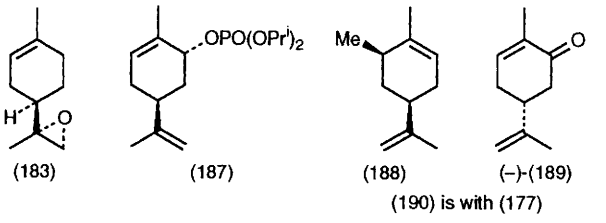


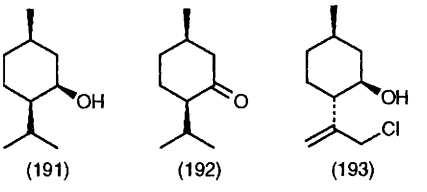


The mechanism of the process whereby the heteropolyanion $[PV_2Mo_{10}O_{40}]^{5-}$ catalyses the aerobic oxidative dehydrogenation of α-terpinene (176) to *p*-cymene (177) has been investigated.[274] When (+)-limonene (157) is reacted with a primary aromatic amine in the presence of $HgO–HBF_4$ it is converted into the useful chiral diamines (178),[275] whereas reaction of (157) with a nucleophile in the presence of $Hg(BF_4)_2$ followed by reduction of the organomercury intermediate using $NaBH_4$ leads[276] regioselectively to the products (179). Acetoxylation of limonene (157) with acetic acid in a reaction which is catalysed by $PdCl_2$ in the presence of either $CuCl_2$ or $Cu(OAc)_2$ leads mainly to the allylic acetate (180), whereas acetoxylation using $Pd(OAc)_2$ alone affords[277] an approximately equal mixture of (180) and the *exo*-methylene compound (181). Limonene (157) can be regioselectively hydrocarbonylated to give the aldehyde (182); isopulegol (88) and its acetate behave similarly.[278] The cyclopropanation of limonene (157) at either or both of its double bonds by various reagents and solvent combinations has been studied,[279] and the 8,9-epoxylimonene (183) and its diastereoisomer have been prepared in pure form.[280] The limonene hydrochloride (184) reacts with zinc thiocyanate to yield a mixture containing the thiocyanate (185) (53%) and the isothiocyanate (186) (22%),[281] and, in a reaction of general applicability, the allylic phosphate (187) is converted into the methylated derivative (188) when it is treated with methylmagnesium chloride in the presence of $CuCN \cdot 2LiCl$.[282] The addition and cycloaddition reactions which limonene (157) undergoes at the 8,9-double bond have been reviewed,[283] as have methods for the conversion of limonene into carvone (189).[284] The thermal and photochemical reactions of various *p*-menthadienes and *p*-menthatrienes have been studied.[285]









The conversion of thymol (190) into all-*cis* neoisomenthol *rac*-(191) by hydrogenation over a defined supported Pt catalyst has been shown[286] to proceed *via* the initial formation of isomenthone *rac*-(192). In a very convenient reaction, (−)-menthol (160) has been converted into the lactone *ent*-(163) in 95% yield by oxidation with *m*-chloroperoxybenzoic acid in the presence of a catalytic amount of the cyclic chromate ester derived from 2,4-dimethylpentan-2,4-diol.[287] Isopulegol (88) undergoes radical chlorination to yield (193) when it is reacted either with chlorine or with sulfuryl chloride.[288]

The optically pure selenonium ylid (194) has been obtained as a stable, crystalline solid *via* fractional recrystallisation of a diastereoisomeric mixture. The absolute configuration of (194) was determined by X-ray methods.[289,290]

The reductive amination of menthone (162) and of isomenthone (192) using ethanolic ammonia and a range of metal catalysts has been studied,[291] and it has been shown that Pd catalysts give the best results. Similar mixtures of neomenthylamine, isomenthylamine and menthylamine are formed from each of the ketones (162) and (192), suggesting that imine–enamine tautomerism intervenes during the reaction. No secondary amines are formed in either instance.

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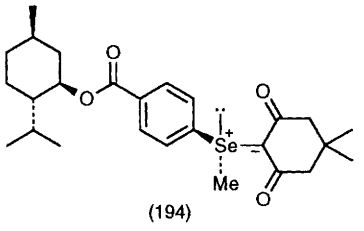
(+)-Pulegone (166) is a major constituent of Turkish-grown *Ziziphora tenuior*, composing *ca.* 87% of the derived oil.[292] Reduction of pulegone by the combination R_3SnH–Et_3B yields menthones,[293] and the pulegone hydrochloride (195) can be converted into the useful synthons (196) in a single-step process.[294] Reaction of (+)-pulegone (166) with $[(thf)_3Mo(CO)_3]$ or with $[(EtCN)_3W(CO)_3]$ affords the derived metal carbonyl complexes (197) as single stereoisomers.[295] The structure of the tungsten complex has been determined by X-ray methods. The allylic alcohol (198), derived from pulegone (166), has been cyclised to the cyclopentadiene (199) using $[Pd(Ph_3P)_4]$ in acetic acid.[296] A good heterogeneous catalyst for the selective hydrogenation of the conjugated double bond of carvone (189) to give the dihydro derivative (200) is Cu–Al_2O_3 which is active at 90 °C in toluene under one atmosphere of hydrogen.[297] The alternative selective heterogeneous hydrogenation of the 8,9-double bond of carvone (189) to give the menthenone (201) is best carried out using Rh supported on MgO.[298]



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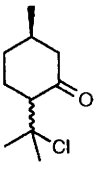

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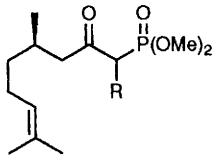
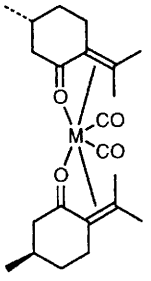
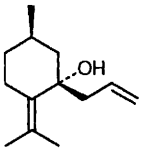


(196) R = H, alkyl or allyl



(197) M = Mo or W



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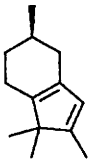

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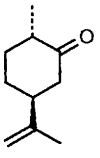

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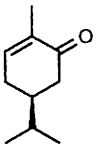

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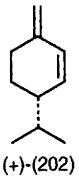
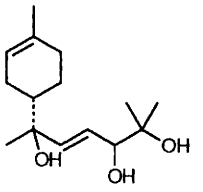


(+)-(202)

New synthetic routes to (sometimes old) monoterpenoids continue to be reported. The diene (+)-β-phellandrene (202), which occurs in the liverwort *Conocephalum conicum*, has been synthesised,[299] and (*S*)-(−)-limonene *ent*-(157) has been converted[300] into the diastereoisomers of quinghaosu *D* (203) *via* the hydroxy aldehyde (204). The terpinolene epoxide (205) reacts under mild conditions in the presence of montmorillonite K-10 to give karahanaenone (206) in 82% yield.[301] A new synthesis of (+)-menthofuran (207) proceeds *via* a [3+2π] intramolecular cyclisation of the nitrile oxide (208) which gives the intermediate adduct (210).[302,303] Menthofuran has also been synthesised from 4-methylcyclohexanone.[304] The related nitrile oxide (209) cyclises to yield the adduct (211) which has been converted[305] into (−)-mintlactone (158) and into (+)-isomintlactone (212). The two mintlactones (−)-(158) and (+)-(212) have also been synthesised *via* radical chemistry,[306,307] and the racemate of (158) has been cleverly obtained[308] by the dihydroxylation of ester (213) followed by one-pot lactonisation and dehydration of the resulting diol.



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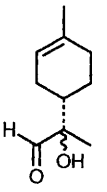

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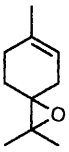

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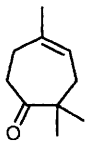

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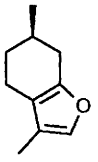
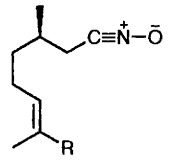
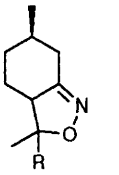


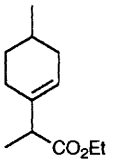
(+)-(207)



(208) R = CH_2OAc
(209) R = CO_2Et



(210) R = CH_2OAc
(211) R = CO_2Et

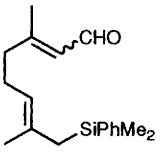


(213)

(212) is with (158)

Fluoride ion-induced cyclisation of the aldehydo-silane (214) leads to a mixture of *cis*- and *trans*-isopiperitols (215). The related secondary allylic silane (216) cyclises more rapidly and with better stereoselectivity under these conditions.[309] The more heavily functionalised silane (217) cyclises when it is treated with $TiCl_4$ to give mainly the *cis*-isomer of the hydroxy ester (218). Cyclisation using $BF_3 \cdot Et_2O$ yields a mixture of the *cis*- and *trans*-isomers of (218), and both of these hydroxy esters are readily lactonised.[310] The Wittig product (219), derived from citronellal (53), reacts with ozone at 0 °C to form an intermediate carbonyl oxide which undergoes intramolecular addition to the 6,7-double bond yielding the diastereoisomeric peroxides (220) and (221). These are converted by catalytic hydrogenation into the *p*-menthane diols (222) and (223).[310] The vinylic silyl ether (224), also obtained from ctironellal (53), reacts with ozone at −78 °C to give only the peroxide (225), but if (225) is reacted with ozone at 0 °C and the resulting mixture then hydrogenated the isomeric cyclopentyl diols (226) and (227) are obtained in 10:1 ratio.[311]

The chloride (193), obtained from isopulegol (88), can be coupled with prenylmagnesium chloride in the presence of CuI to yield the sesquiterpenol (228).[312]



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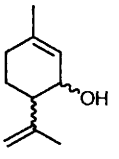

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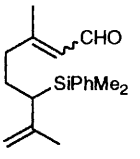

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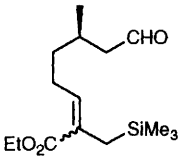

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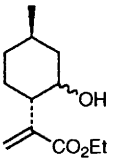

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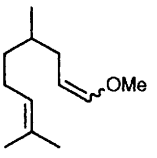

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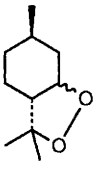
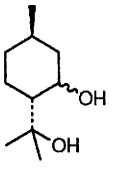
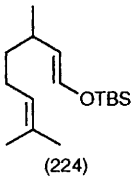


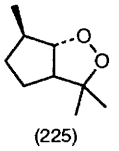
(220) α-configuration
(221) β-configuration



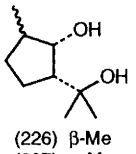
(222) α-OH
(223) β-OH



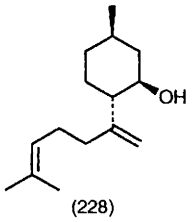
(224)



(225)



(226) β-Me
(227) α-Me



(228)

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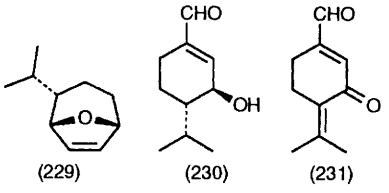
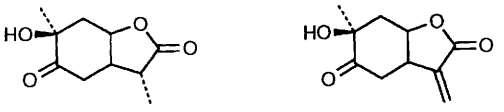
The unsaturated bicyclic ether (229) unexpectedly gives the rare *trans*-3-hydroxyphellandral (230) when it is reacted with chlorosulfonylisocyanate. A mechanism for this transformation has been proposed.[313] A synthesis of robinal (231), produced by the mite *Rhizoglyphus robini*, has been reported.[314]

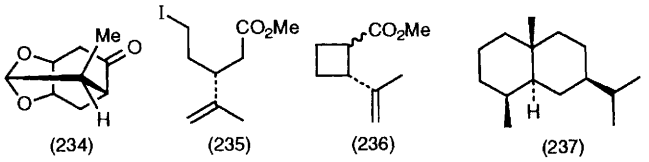
(−)-Carvone (189) has been converted into paeonilactones *A* (232) and *B* (233) and into (7*R*)-paeonimetabolin (234) and its (7*S*)-diastereoisomer, thus establishing the absolute configurations of these compounds.[315] (−)-Carvone (189) has also been utilised as a chiral starting material in syntheses of (+)-grandisol (21) which was prepared[316] *via* the intermediates (235) and (236), of (−)-patchouli alcohol,[317] and of 4α(*H*)-eudesmane (237).[318] The Diels–Alder reactions which are catalysed by $EtAlCl_2$ of (+)-carvone *ent*-(189) with various trimethylsiloxy-1,3-dienes have been studied in the context of sesquiterpenoid synthesis.[319]



(229) (230) (231)



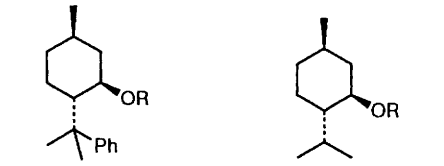
(232) (233)



(234) (235) (236) (237)

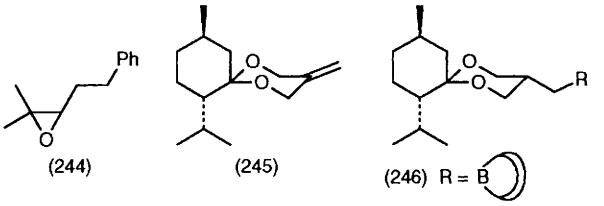
As alluded to in the Introduction, the utilisation of monoterpenoid derivatives as chiral auxiliaries and as reagents for asymmetric synthesis continues to expand. Whitesell has reviewed[320] the ways in which derivatives of (−)-8-phenylmenthol (238) can be exploited in this context. The (1*R*)-menthoxymethyl ether function is a chiral protecting group for hydroxy functions that allows measurement of ee values to be carried out by NMR at each step of a synthetic reaction sequence. These ethers are prepared *via* reaction of chloromethylmenthyl ether (239) with an alcohol in the presence of Pr^i_2NEt, and can be cleaved by zinc bromide in CH_2Cl_2.[321] An improved route to 8-phenylmenthyl isocyanoacetate (240) which proceeds *via* the chloroacetate (241) and the azide (242) has been described.[322] Menthyl cyanoformate (243) in combination with hydrogen peroxide epoxidises 2-methyl-5-phenylbut-2-ene to yield product (244) of undetermined absolute configuration and of 20% ee.[323]

Racemic 1,3-alkanediols can be kinetically enantiodifferentiated by acetalisation with, for example, (−)-menthone *ent*-(162).[324,325] The unsaturated acetal (245), formed from (+)-menthone, reacts with 9-BBN to afford the equatorial borane (246) which can then be coupled with alkenyl or aryl halides to give products (247). These can be further processed to yield optically active alcohols.[326] The menthyl derivative (248) can be converted into the fluoroester (249) of 98% ee by treatment with elemental fluorine in acetonitrile and then with methanolic potassium carbonate.[327] The related non-crystalline diastereoisomeric acetoacetate derivatives (250) and (251) have been prepared from (+)-menthone (162) by its reaction with *tert*-butyl 2-methyl-3-oxobutanoate in the presence of Ac_2O–H_2SO_4, and their structures have been determined by NMR.[328]



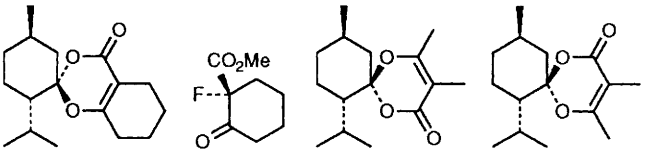
(238) R = H
(240) R = $COCH_2NC$
(241) R = $COCH_2Cl$
(242) R = $COCH_2N_3$
(256) R = $COCH{=}CH_2$

(239) R = CH_2Cl
(243) R = COCN
(252) R = $COCH{=}CH_2$
(258) R = COCl
(262) R = COCOPh or COCOMe



(244) (245) (246) R = B

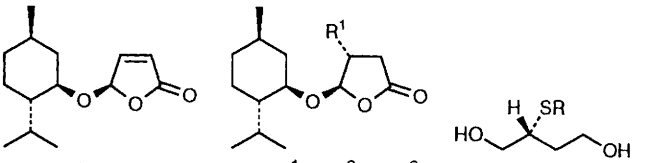
(247) R = alkenyl or aryl



(248) (249) (250) (251)

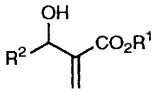
(−)-Menthyl acrylate (252) undergoes γ-alumina-catalysed Diels–Alder cycloaddition with cyclopentadiene to give the *endo*-adduct in good diastereoisomeric excess.[329,330] A study has been made of the effect of variations in solvent on the rate, *exo*/*endo* ratio, and diastereoselectivity of the same reaction.[331] The unsaturated menthyloxy lactone (253)[62] has been developed as a chiral dienophile, affording adducts of up to 99% de.[332] The compound (253) is also a Michael acceptor, reacting with thiols or with secondary amines to give the adducts (254). Reduction of (254) (X = S) using lithium aluminium hydride yields diols (255).[333]

Both (−)-menthyl acrylate (252) and the corresponding 8-phenylmenthyl derivative (256) undergo Baylis–Hillman addition with aldehydes to yield adducts (257) of 14–100% de. Best results were obtained when benzaldehyde was reacted with the menthyl derivative (252) in the presence of DABCO at a pressure of 7.5 kbar.[334]



(253) (254) $R^1 = SR^2$ or NR^2_2 (255)

(252), (256) & (258) are with (239)



(257) R^1 = (−)-menthyl or (−)-8-phenylmenthyl; R^2 = alkyl or aryl

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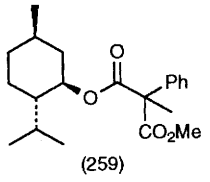
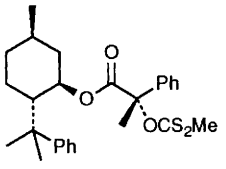
Menthyl chloroformate (258) reacts with the lithium enolate of methyl α-methylphenylacetate to give the malonate derivative (259) of good de,[335] and the xanthate (260), which is derived from 8-phenylmenthol, can be reduced using Bu_3SnH–AIBN to give a 63:37 mixture of the (*R*)- and (*S*)-diastereoisomers of the ester (261). Reductive cleavage of (261) using lithium aluminium hydride affords the corresponding phenylpropanol.[336]



(259)



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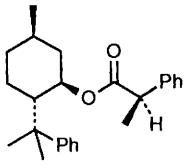
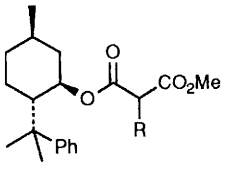


(261)

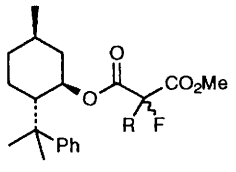
The menthyl glyoxylates (262) are diastereoselectively reduced by $LiAl(OR_3)H$ at −78 °C in THF to give the derived hydroxy esters.[337] The methylated (−)-8-phenylmenthyl acetoacetate (263) is fluorinated by 1-fluoro-2,4,6-trimethylpyridinium triflate in the presence of excess lithium hexamethyldisilazide to give a 3.8 : 1 mixture of the (*R*)- and (*S*)-fluoroesters (264), but the (*S*)-diastereoisomer of (265) is the major product when the desmethyl acetoacetate (266) is fluorinated.[338]

The tautomerism of the menthyl β-keto esters (267) has been investigated by NMR methods, and the cyclopentanone derivative, which undergoes a crystallisation-induced asymmetric transformation, has been found (X-ray) to possess the (*R*)-configuration at C-2 of its five-membered ring.[339]

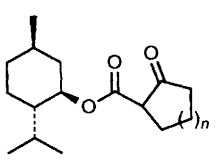
(+)-Dihydrocarvone *ent*-(200) undergoes electroreductive coupling with acetonitrile to give the imino alcohol (268) which has been further transformed into the β-amino alcohol ligand (269). The latter catalyses the enantioselective addition of diethyl zinc to aldehydes.[340] The Strecker-derived α-amino acid toluenesulfonamide (270) forms a complex with borane which, at a concentration of 0.2 mol%, catalyses the enantioselective condensation of terminal silyl enol ethers with aldehydes to give aldols (271) of 81–93% ee.[341]



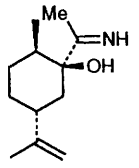
(263) R = Me
(266) R = H



(264) R = Me
(265) R = H



(267) *n* = 1, 3



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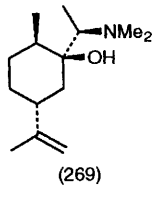

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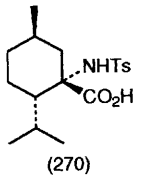

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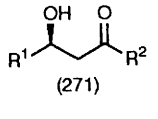


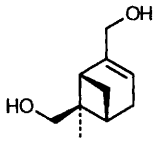
(271)

6 Pinanes

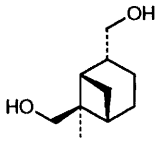
The three new diols (272)–(274) have been obtained from the roots of *Urtica dioica*.[342] (+)-*cis*-3-Pinen-2-ol (275) has been found to act as a pheromone for males of the beetle *Monocampus alternatus* Hope.[343]

The enantiomers of α-pinene (276) and of β-pinene (277) can be resolved by CGC using an α-cyclodextrin stationary phase.[268] The vibrational CD spectra of both α- and β-pinene have been measured and analysed,[344] and quantitative comparisons of the scattered and incident circular polarisation Raman optical activities of (−)-α-pinene *ent*-(276), (−)-β-pinene *ent*-(277), (−)-*cis*-pinane (278) and (−)-*trans*-pinane (279) have been made.[345] In a useful study, the ^1H and ^{13}C NMR spectra of 22 pinane derivatives have been measured and assigned.[346]

The isomeric pinanes (278) and (279) are oxidised by O_2 at 100 °C to give the hydroperoxide (280) and the peroxyhydroperoxide (281). The *cis*-alkane is oxidised most rapidly, and the products can be reduced to the corresponding alcohols.[347] Permethylated β-cyclodextrin which is linked to a Fe^{3+} or Mn^{3+} porphyrin species catalyses the enantioselective oxidation of racemic α-pinene *rac*-(276) by oxygen in the presence of visible light to give a mixture of epoxypinane, pinenols and pinenones.[348] Racemic α-pinene *rac*-(276) undergoes a kinetic resolution *via* double stereodifferentiation to give product of up to 65% ee when it is hydrogenated in the presence of chirally-modified Rh clusters.[349]



(272)



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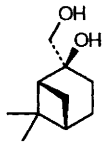

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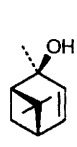
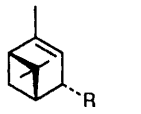
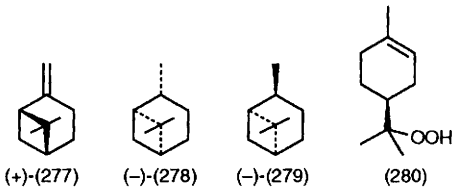


(+)-(275)

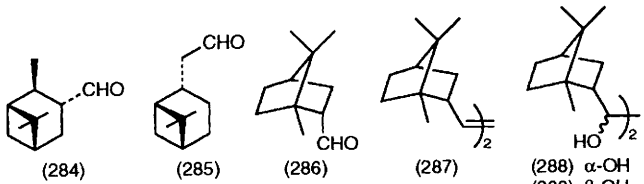


(+)-(276) R = H
(282) R = OAc
(283) R = OCOEt

The acyloxylation reactions of α-pinene (276) with $Pb(OAc)_4$, $Pb(OCOEt)_4$, $Hg(OAc)_2$ or $PhI(OAc)_2$ have been carefully investigated, and large scale routes to the allylic acetate (282) and to the propionate (283) have been devised.[350] Competing ring-opening reactions can be largely avoided by working in neutral media. α-Pinene (276) undergoes regiospecific hydrocarbonylation to yield the aldehyde (284), and β-pinene (277) behaves similarly to yield the 10-formyl derivative (285).[278] The aldehyde (286), derived from α-pinene (276), undergoes McMurry coupling to give the alkene (287) which can be dihydroxylated to yield the diastereoisomeric C_2-symmetrical diols (288) and (289).[351]



(+)-(277) (−)-(278) (−)-(279) (280) (281)



(284) (285) (286) (287) (288) α-OH (289) β-OH

(282) & (283) are with (276)

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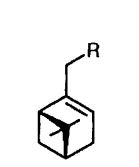
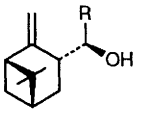
The use of biphenyl as sensitiser enhances the yields of the pinenol (290) which is obtained *via* singlet oxygen oxidation of *β*-pinene (277).[352] An improved route to crystalline *δ*-terpineol (291) from *β*-pinene has been described,[353] and the kinetics of the $AlCl_3$-catalysed ene-reaction which takes place between *β*-pinene and methyl propenoate have been measured as a function of solvent polarity.[354] The results suggest that the reaction may proceed *via* a transition state which possesses zwitterionic character.

Reaction of the allylic bromide (292) with aldehydes in aqueous THF in the presence of $Zn–NH_4Cl$ leads to alcohols (293) whose relative configurations at C-11 were determined by assuming that reduction of the derived ketones proceeded according to Cram's Rule.[355]



(290) R = OH
(292) R = Br
(307) R = OOH

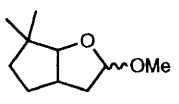
(291)



(293)

(294)

The epoxypinane (294) reacts with $HSO_3F–FSO_2Cl$ and then with methanol to give the acetal (295) (60%) together with other products,[356] and with $ZnBr_2$ or $ZnCl_2$ to give largely the campholenic aldehyde (23).[357] Reduction of the epoxide (294) with lithium in ethylenediamine is claimed[358] to yield the isomeric pinanols (296) and (297), but the stereochemistry attributed to the secondary alcohol seems doubtful. Pyrolysis of *ent*-(294) over synthetic zeolites which have been exchanged with Zn^{2+} or with Cu^{2+} affords *α*-campholenic aldehyde (23), whereas treatment of the epoxide (298) derived from *β*-pinene (277) yields *cis*-myrtanal (299).[359] Both diastereoisomers of the epoxide (298) react with $Me_3SiCN–ZnI_2$ to yield the array of products (300)–(304).[360]



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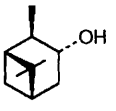

(297)

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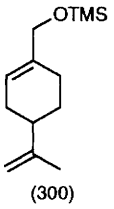
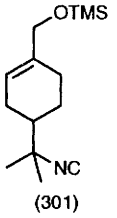
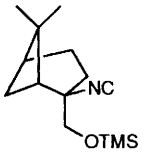


(300)



(301)

(302)



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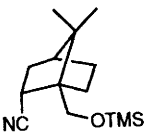
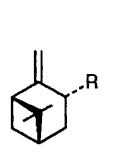


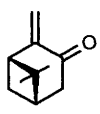
(304)

The hydroperoxide (305) reacts with $CuSO_4–NH_3$ to give (290) and (306)–(309), but gives only the cyclobutane (310) (94%) when it is exposed to $FeCl_3 \cdot Et_2O$ in the absence of a proton trap.[361]

The equilibrium mixture of isopinocamphone (311) and pinocamphone (312) undergoes Baeyer–Villiger oxidation to give the ketol (313) and the lactone (314), respectively, in poor overall yield.[362] *cis*-Verbanone (315) reacts with phenyllithium to give the derived tertiary benzylic alcohol. This then suffers a Ritter reaction when it is reacted with $RCN–H_2SO_4$ in a 1.0:0.1 molar ratio, yielding the amide (316). When $RCN–H_2SO_4$ in 1.0:0.1 molar ratio is used instead, the azabicyclononene (317) is formed.[363] Reaction of (*E*)-*cis*-verbanone oxime (318) with H_2SO_4 yields the Beckmann lactam (319), but the benzeneamine (320) is obtained when (318) is treated with HCl.[364]

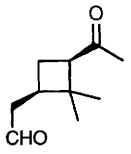


(305) R = OOH
(306) R = OH



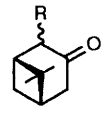
(308)

(309)

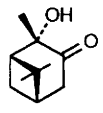


(310)

(307) is with (290)



(311) R = β-Me
(312) R = α-Me



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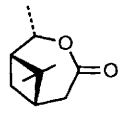
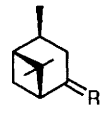
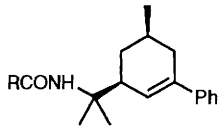


(314)



(315) R = O
(318) R = NOH



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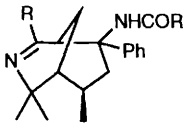

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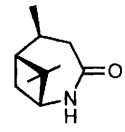
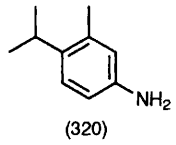
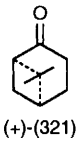


(319)

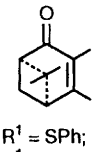
(+)-Nopinone (321) has been converted into several 4,4-disubstituted derivatives which are useful synthons for sesquiterpenoid synthesis,[365] and is the precursor of the vinylic sulfide (322) which is an intermediate in syntheses of (+)-vernolepin and of (−)-vernomenin.[366] The anion of the related sulfone (323) undergoes *γ*-alkylation with, *e.g.*, allyl bromide to yield mainly the diastereoisomer (324),[367] and this has been converted into the sesquiterpene (−)-kanshone *A* (325).[368] Synthetic applications of the sulfide (326) and of the sulfone (323) have been reviewed.[369] The closely-related ester (327) undergoes Diels–Alder cycloaddition with buta-1,3-diene or with isoprene (1) to give exclusively the adducts (328).[370] (+)-Nopinone (321)



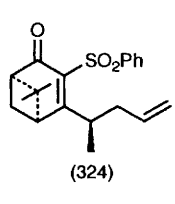
(320)



(+)-(321)



(322) R^1 = SPh; R^2 = Me
(323) R^1 = SO_2Ph; R^2 = Et
(326) R^1 = SPh; R^2 = H
(327) R^1 = CO_2Me; R^2 = H



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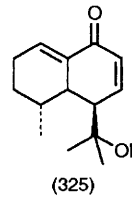

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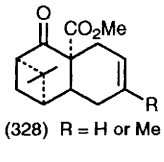

(328) R = H or Me

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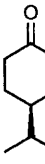
has been converted into (*R*)-(−)-cryptone (329) and into the (*S*)-(+)-dienone (330).[371]

Borane derivatives based upon the pinane skeleton continue to attract much attention as chiral reagents and auxiliaries. A one-pot procedure for the conversion of α-pinene (276) into diisopinocampheylchloroborane which obviates the necessity to isolate this air- and moisture-sensitive reagent has been described.[372] The Purdue group have found that chiral *B*-allylditerpenylboranes react rapidly with aldehydes at temperatures as low as −100 °C provided that magnesium salts formed during preparation of the reagents are removed.[373] The homodiisopinocampheylchloroborane (331) reduces 2,2-dimethylcyclopentanone to the corresponding (*R*)-alcohol of greater than 99% ee, and also reduces benzylideneacetone to the unsaturated (*R*)-alcohol.[374] The chiral conjugated enone (332) has been synthesised *via* (333) which was derived from the unsymmetrical borane (334).[375] The principal disadvantage associated with the utilisation of terpenyl boranes for asymmetric synthesis has always been the loss of the terpenoid auxiliary and the necessity for separation of at least molar equivalents of the derived monoterpenoid alcohol from the desired reaction product. The Brown group have now described three effective methods which permit recycling of these chiral auxiliaries. These methods include treatment with 2-methylpropanal and one equivalent of $BF_3 \cdot Et_2O$, treatment with ethanolamine, or treatment with 8-hydroxyquinoline.[376] The boronate (335) has been prepared, and reduces but-1-yn-3-one to give alcohol of 39% ee.[377]



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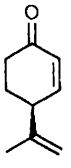

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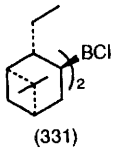

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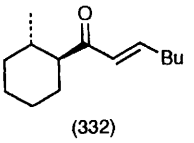

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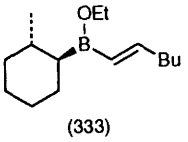

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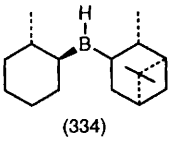

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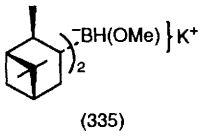
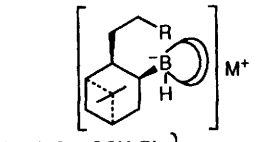


(335)

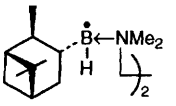
The origins of the stereoselectivity observed in aldol reactions of chiral boron enolates, especially of (*Z*)-enol diisopinocampheyl borinates, have been investigated with the aid of computational methods.[378]

A series of boronates (336)–(338) has been prepared, and the amino derivative (338) reduces acetophenone to (*S*)-α-methylbenzyl alcohol of 77% ee.[379] The optically-active amine–boryl radical (339) enantioselectively abstracts the benzylic hydrogen from racemic methyl α-methylphenylacetate (340), permitting a catalytic partial kinetic resolution of the ester. The (*S*)-enantiomer of (340) of 22% ee is obtained after 41% of the racemate has reacted.[380]

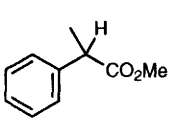
The phenyl derivative (341), and both diastereoisomers of the pinenol (342) have been prepared with a view to their possible use as chiral auxiliaries,[381] and the new auxiliary (343) has been synthesised.[382]



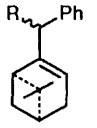
(336) R = OCH_2Ph
(337) R = SCH_2Ph
(338) R = NEtPh
} M = Li, K or Zn



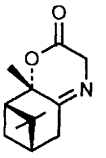
(339)



(340)



(341) R = H
(342) R = OH

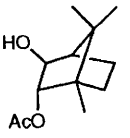


(343)

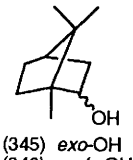
7 Camphanes and Isocamphanes

Vulgarole (344) of 100% ee has been isolated from *Artemisia vulgaris*.[383]

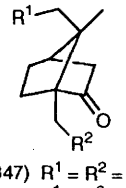
Simple europium-based lanthanide shift reagents have been found to aid the low-field NMR analysis of mixtures of borneol (345) and isoborneol (346). The Eu^{3+} ion preferentially complexes to the less hindered *exo*-hydroxy group of (346) and, by enhancing the rate of hydroxy proton exchange, also sharpens the α-carbinyl proton resonances in each case.[384] Solvent effects which are exerted on the n–π^* carbonyl transitions of camphor (347) and of 9,10-dibromocamphor (348) have been investigated, and the results indicate that camphor derivatives can induce chiral solvation structures about them even when the solvent molecules involved are achiral.[385] The mass spectral fragmentation patterns and the ^2H NMR spectra of the thioacetals (349)–(351) and of some of their bromo derivatives have been determined and analysed.[386]



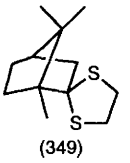
(344)



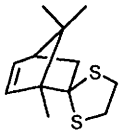
(345) *exo*-OH
(346) *endo*-OH



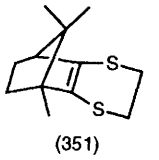
(+)-(347) $R^1 = R^2 = H$
(348) $R^1 = R^2 = Br$
(378) $R^1 = Br$; $R^2 = H$



(349)

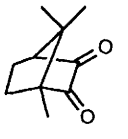


(350)



(351)

(352)



(+)-(353)

Enantioselective separations of racemic borneol (345) and racemic isoborneol (346) can be achieved by capillary GC when a permethylated β-cyclodextrin is used as stationary phase,[387] and the enantiomers of camphene (352) can be resolved over α-cyclodextrin by the same technique.[286,388]

The catabolism of (+)-camphor (347) by *Salvia officinalis* leads, *inter alia*, to its 6-hydroxy and 6-oxo derivatives,[389] and cells of the *Acinetobacter* sp. NCIB-9871 reduce racemic camphorquinone *rac*-(353) to a pair of diastereoisomeric *exo*-hydroxy ketones.[390]

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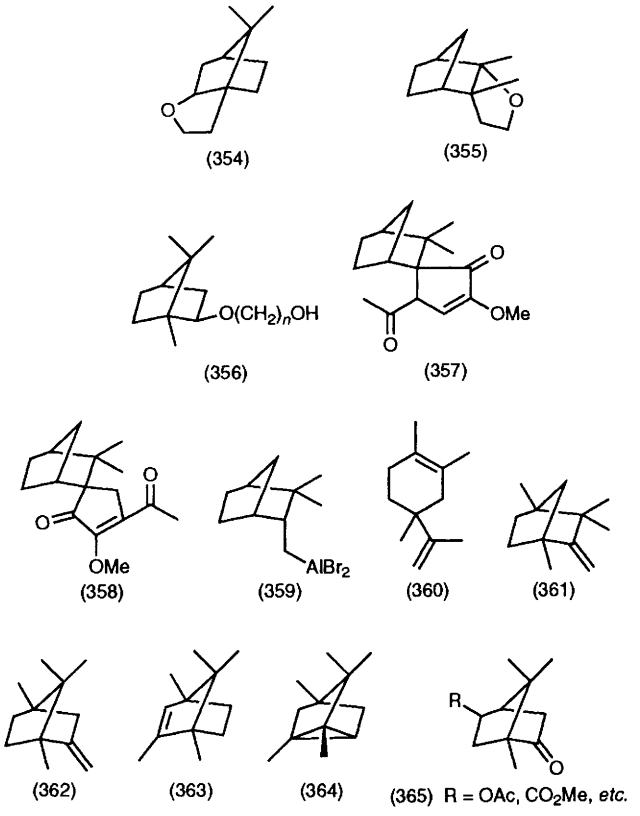
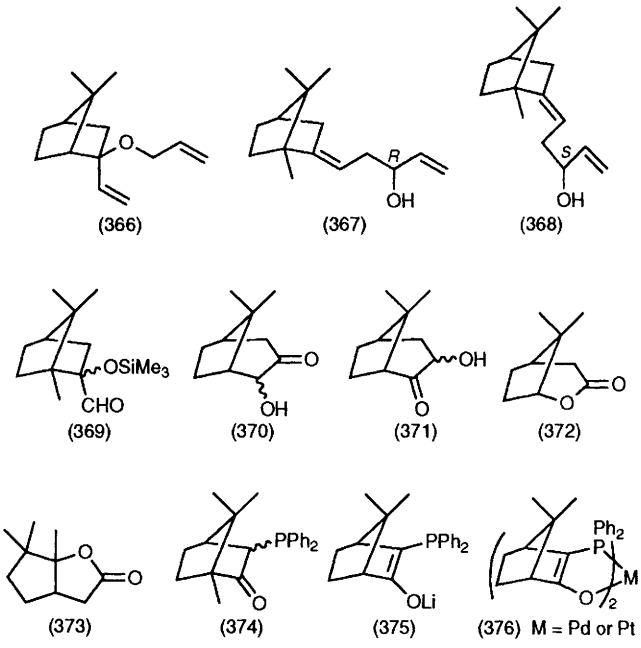
Camphene (352) reacts with formaldehyde in the presence of a calcined β-zeolite to afford the rearranged ethers (354) and (355),[391] and reacts with α,ω-alkanediols in the presence of H-Mordenite to give a series of hydroxy ethers (356).[392] Photoaddition of methyl 3-oxobutanoate to camphene (352) affords adducts which undergo mild acid-catalysed retro-benzylic acid rearrangement to yield (357) or (358).[393] The hydroalumination of camphene (352) by $LiAlH_4 \cdot 3AlBr_3$ in toluene leads to the novel Lewis acid (359).[394] An experimental and computational study of the equilibria involved in the formylation of camphene by formic acid has been carried out,[395] and reaction of the methylated *p*-menthadiene (360) with 97% formic acid has been shown to lead to the camphene derivative (361) together with the alkenes (362) and (363) and the tricyclene (364).[396]



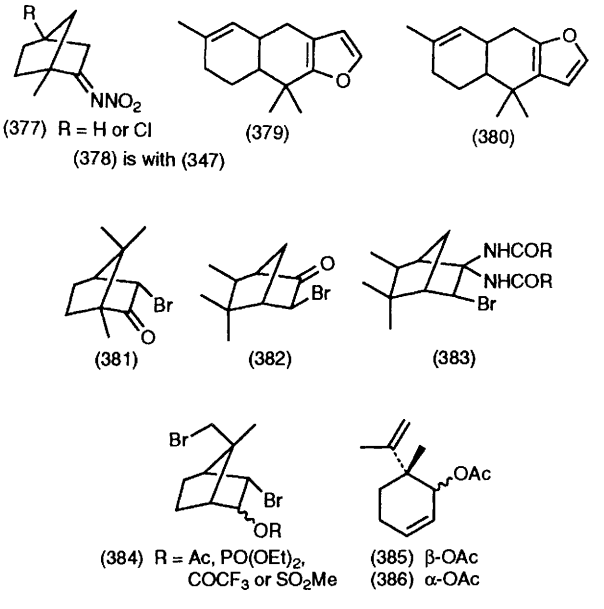
The enthalpies of complexation of BF_3 in CH_2Cl_2 with the carbonyl groups of various camphor derivatives (365) have been determined, and have been shown to correlate well with the corresponding polar substituent constants.[397] The Lewis acid complexes at both sites when the substituent is acetoxy but only at the ketonic carbonyl group when it is carbomethoxy.

(+)-Camphor (347) has been converted into the allyl vinyl ether (366) which undergoes a [2,3]-Wittig rearrangement to yield a 70:30 mixture of (*R*)-(367) and (*S*)-(368).[398] The silyloxy aldehyde (369), derived from (+)-camphor (347), undergoes acyloin rearrangement to give a mixture of the stable ketol (370) and the alternative ketol (371) which suffers facile aerial oxidation to yield homocamphoric anhydride.[399] Anodic oxidation of (+)-camphor in acetonitrile with 1 mol dm^{-3} H_2SO_4 as the supporting electrolyte delivers the lactone (372) in up to 96% yield. This undergoes further electrochemical transformation in more strongly acidic media, yielding the butanolide (373).[400] Treatment of the lithium enolate of (+)-camphor (347) with 1 equiv. of chlorodiphenylphosphine affords a mixture of the *exo*- and *endo*-keto phosphines (374), of which the *endo*-isomer is the more thermodynamically stable.[401] If the lithium enolate of camphor is treated instead with only 0.5 equiv. of Ph_2PCl then the salt (375) is formed, and this can be converted into the Pd and Pt complexes (376).



When the nitroimines (377) are exposed to ^{60}Co γ-radiation they form radical anions which can be studied by ESR.[402]

(+)-9-Bromocamphor (378) has been utilised as a chiral starting material in syntheses of the sponge metabolites (−)-furodysin (379) and (−)-furodysinin (380).[403] The mechanism of the reaction of *endo*-3-bromocamphor (381) with *N,N*-dimethylaniline at 200 °C which gives camphor (347) has been investigated.[404] The same result can be achieved at much lower temperatures by using Et_3N–di-*tert*-butyl peroxide in acetonitrile. The bromocamphor (381) does not undergo Ritter-style reaction with nitriles in the presence of acids, but *exo*-3-bromoisocamphor (382) reacts satisfactorily to yield the bisamides (383).[405] The 3,9-dibromo derivatives (384) fragment to yield monocyclic products of stereochemistries which depend upon that at the 2-position in the starting materials.[406] Thus, the *endo*-acetate (384) gives (385) when it is treated with the radical anion sodium dimethylamino(naphthalenide) whereas the isomeric *exo*-acetate affords (386). Both of these allylic acetates have been converted into the derived α,β-unsaturated ketone. If the 3-bromo substituent of (384) is replaced by hydrogen then the *exo*-methanesulfonate is the only derivative which undergoes the fragmentation reaction.



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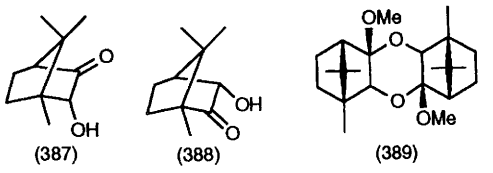
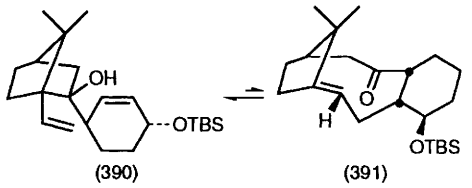
The reduction of (+)-camphorquinone (353) by zinc in acetic acid affords a mixture of the isomeric *endo*-hydroxy ketones (387) and (388). In a reaction which was first reported in 1902, the former reacts with HCl in dry methanol to give the symmetrical dimeric acetal (389) whose structure has now been unequivocally determined.[407]

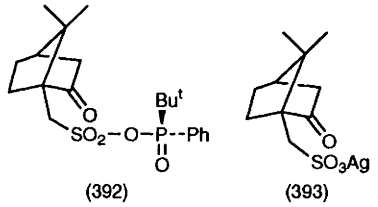
The reversibility of the thermal oxy-Cope rearrangement is clearly demonstrated when the borneol derivative (390) is heated in refluxing toluene to yield an equilibrium mixture with the ketone (391).[408]



(387) (388) (389)



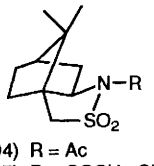
(390) (391)



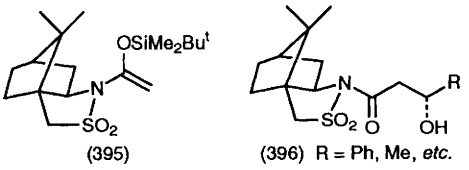
(392) (393)

The *P*-chiral mixed anhydride (392) and its diastereoisomer have been prepared from the silver salt of camphorsulfonic acid (393) *via* its reaction with Ph(*tert*-Bu)IP=O.[409]

The utilisation of camphor derivatives as reagents and auxiliaries for asymmetric synthesis continues to be developed, and the subject has been reviewed,[410,411] as have the myriad applications of camphorsultams.[412] The enantiomeric purities of the (*R*)- and (*S*)-camphors which are available from the chiral pool have been critically evaluated.[413]



(394) R = Ac
(397) R = COCH=CH$_2$

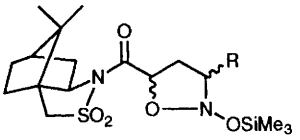


(395) (396) R = Ph, Me, *etc.*

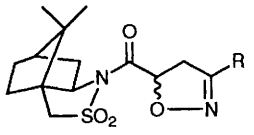
The acylated sultam (394) has been converted into the silyl enol ether (395) which, in a Mukaiyama-type reaction, affords diastereoisomerically pure aldols (396) when it is treated with an aldehyde in the presence of $TiCl_4$.[414] These can be cleaved to yield either *β*-hydroxy esters or *β*-hydroxy acids. The *N*-acryloyl sultam (397) undergoes 1,3-dipolar cycloaddition with nitronates RCH=N$^+$(O)OSiMe$_3$ to yield adducts (398) of good de which are converted into the 2-isoxazoline derivatives (399) when they are treated with toluene-*p*-sulfonic acid.[415]

A series of 3,3-dihalogenated camphorsulfonyloxaziridines (400) have been prepared, and the dichloro derivative is the best for the enantioselective oxidation of sulfides to sulfoxides (often greater than 95% ee).[416] Details of a large-scale preparation of both enantiomers of the oxaziridine (400) (R = Cl) have been published, together with those of an efficient route to the parent compound (401).[417]

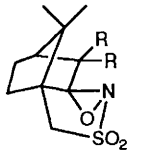
The diastereoisomeric sulfoxides (402), prepared from 10-sulfanylisoborneol (403), are good dienophiles, reacting with cyclopentadiene and with furan to give adducts of high de.[418]



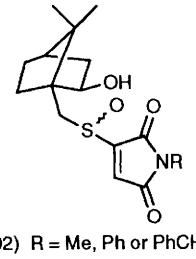
(398)



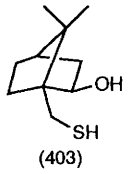
(399)



(400) R = Cl, Br or F
(401) R = H



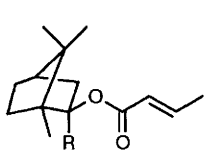
(402) R = Me, Ph or PhCH$_2$



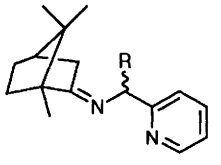
(403)

The conjugate addition of butylcopper species to the bornyl crotonates (404) has been studied, and the composition of the reagent has been found to exert a profound effect upon the stereochemistry of the newly introduced asymmetric centre. Thus, addition of $LiBu_3Cu_2$ leads to (*S*)-products of up to 57% de whilst addition of Li_2Bu_3Cu affords (*R*)-products of up to 90% de.[419]

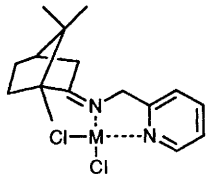
The pyridyl imine (405) which is derived from (+)-camphor (347) forms a lithium salt which can be alkylated to give compounds (406) of mainly (*R*)-stereochemistry and of 6–67% de.[420] This diastereoselectivity is enhanced if (405) is first converted into a metal complex (407), and an X-ray crystal structure of the Pd complex has been obtained.[421] The glycinate imine (408) can be alkylated to give, ultimately, (*S*)-alanine of good optical purity, and the effect of the double asymmetric induction resulting from the presence of the menthyl ester compares favourably with the results which are obtained using the alternative *tert*-butyl ester.[422]



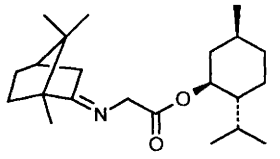
(404) R = Me, Ph or 1-naphthyl



(405) R = H
(406) R = alkyl



(407)



(408)

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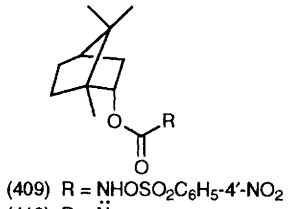
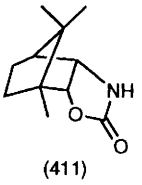
The isoborneol derivative (409) affords a nitrene (410) which exhibits no asymmetric induction in its (inefficient) aziridination reaction with styrene. In the absence of alkene, (410) is converted into the chiral auxiliary (411) which is useful in a variety of reactions including alkylation, acylation and aldol condensations. The oxazolidinone (411) is more conveniently obtained *via* thermolysis of the acyl azide (412).[423] A route to the isomeric oxazolidinone (413) commences with (+)-camphorquinone (353) which is sequentially oximated at C-3, reduced with $NaBH_4$ and then hydrogenated over Pt to yield the amino alcohol (414). The *N*-propionyl derivative of (413) affords the lithium enolate (415) which reacts with aldehydes to give mainly the aldol diastereoisomers (416).[424] The oxazolidinone (417) can be acylated and its propionyl derivative can then converted into the enolate (418) which is alkylated to give products (419) of good to excellent de.[425] Ethyl ketopinate (420) has been converted into the oxazinone (421) and thence to the propionyl derivative (422) which reacts with aldehydes in the presence of $TiCl_4$ to give aldols (423) of very good de.[426] The pinacolone enol acetal (424), derived from (+)-camphorquinone (353), reacts with aryl aldehydes under the same conditions to yield aldols with reasonable de.[427]



(409) R = $NHOSO_2C_6H_5$-4′-NO_2
(410) R = N:
(412) R = N_3



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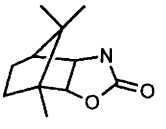
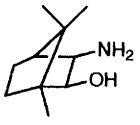


(413)



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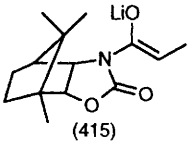

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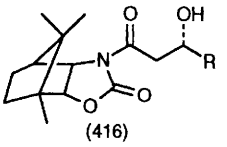
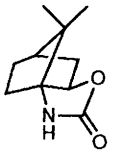


(416)



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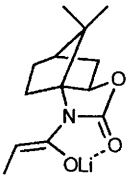
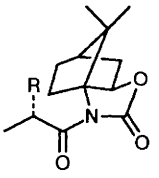


(418)



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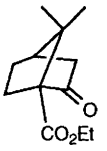

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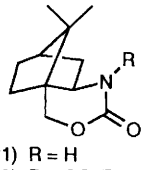
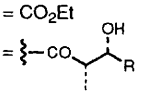
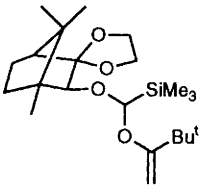


(421) R = H
(422) R = CO_2Et
(423) R = 

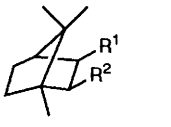


(424)

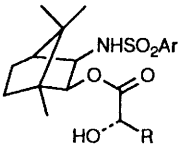
(+)-Camphorquinone (353) is also the precursor of the chiral auxiliaries (425) and (426). The derived glyoxylate (427), for example, can be diastereoselectively reduced to yield the hydroxy ester (428), and this can be hydrolysed using LiOH in aqueous THF to give the corresponding α-hydroxy acid.[428] The bornene (429) has been converted into the silanol (430) and thence to the chlorosilane (431). Replacement of chlorine with a suitable allylic function affords the Si-substituted compounds (432) which can be diastereoselectively epoxidised and the epoxides then fragmented using Bu_4NF to give allylic alcohols (433) of 49–70% de.[429] The two new chiral lactams (434) and (435) have been prepared, and some cycloaddition reactions of their crotonyl and methacryloyl derivatives have been investigated.[430]

A series of novel camphorsultam-based 2,2-bipyridyl and 9,10-phenanthrolyl ligands (436)–(440) have been synthesised, and the X-ray crystal structure of (436) has been determined.[431] The benzylidenecamphor derivative (441) affords a mixture of alcohols when it is reduced using Na–EtOH, and the useful pure diastereoisomer (442) can be obtained from this *via* fractional recrystallisation of its *p*-nitrobenzoate.[432]

The acetal (443), derived from (+)-camphorquinone (353), has been converted into the epichlorohydrin enantiomer (444).[433] An X-ray crystal structure and an NMR spectrum of the bis(iodomethyl)zinc complex (445) have been obtained.[434]

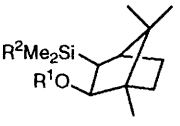


(425) R^1 = $NHSO_2Ar$; R^2 = OH
(426) R^1 = OH; R^2 = $NHSO_2Ar$
(427) R^1 = $NHSO_2Ar$; R^2 = OCOCOR

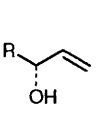


(428)

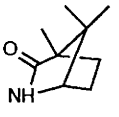
(429)



(430) R^1 = H; R^2 = Ph
(431) R^1 = CH_2Ph; R^2 = Cl
(432) R^1 = CH_2Ph; R^2 = 



(433)



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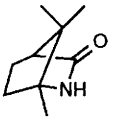

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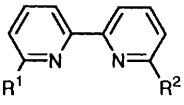
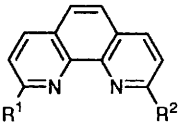
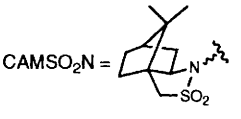
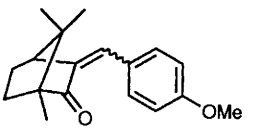


(436) R^1 = R^2 = $CAMSO_2N$
(437) R^1 = H; R^2 = $CAMSO_2N$
(438) R^1 = R^2 = CH_2CAMSO_2N

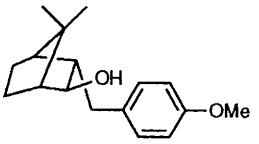


(439) R^1 = R^2 = $CAMSO_2N$
(440) R^1 = OH; R^2 = $CAMSO_2N$

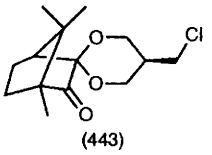




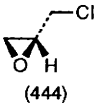
(441)



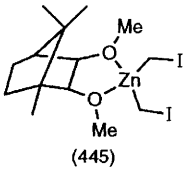
(442)



(443)



(444)



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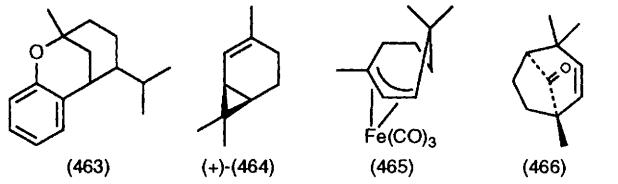
8 Caranes

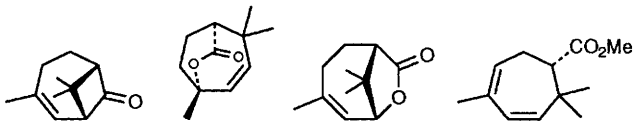
Long-range ^{13}C–^{1}H J values for (+)-car-3-ene (446) have been measured,[435] and a combined NMR and molecular mechanics investigation has led to the conclusion that the six-membered ring of (446) is practically planar.[436] Good agreement has been obtained between the calculated and experimental dipole moments of the keto sulfide (447), and the results suggest that the C–S bond is axially orientated and that it is parallel to the carbonyl group.[437] The conformation of the amino oxime (448) has been studied, and an X-ray crystal structure has been obtained.[438]

Fuel blends containing (+)-car-3-ene (446) combust efficiently under rocket conditions when red fuming nitric acid is utilised as oxidant.[439]

The organoborane derived from carene (446) has been carbonylated to yield the 4α-aldehyde (449),[440] and oxidation of (446) under Gif conditions has been shown[441,442] to afford the well-known enones (450) and (451) together with the *m*-menthadienol (452). When (+)-car-3-ene (446) is reacted with $Pb(OAc)_4$ in acetic acid it is converted into a mixture containing the ketone (453), the *p*-menthadienol (454), and the two *p*-menthenediols (455) and (456). An X-ray crystal structure of the diacetate of (456) has been obtained.[443] (+)-Car-3-ene (446) has been converted[444] into the allylic amines (457) and (458). Reaction of carene (446) with $PhSO_2NSO$ yields the car-2-ene derivative (459) which is converted into the dimeric cycloheptatrienyl disulfide (460) when it is treated with base. Reaction of (459) with 4 equiv. of RMgX in the presence of 5 mol% $CuBr \cdot Me_2S$ affords the cycloheptatrienyl sulfide (461), but the allylic displacement product (462) is obtained when 1 equiv. of PhMgBr is used under the same conditions.[445] When (+)-car-3-ene (446) is reacted with phenol in the presence of $(PhO)_3Al$ it is converted in 80% yield into the ether (463).[446] (+)-Car-2-ene (464) has been converted into the iron carbonyl complex (465), and this reacts with CO to yield the ketones (466) and (467).[447] The same complex (465) affords the lactones (468) and (469) when it is treated with CO in the presence of cerium(IV) ammonium nitrate, and these lactones are also formed, together with the cycloheptadienyl ester (470), when methanol is additionally present.



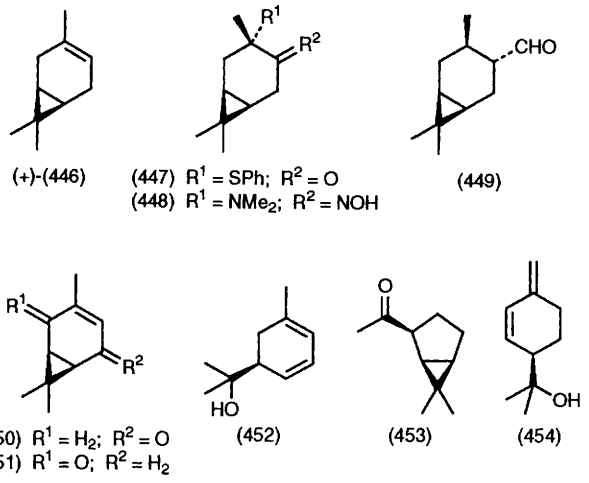
(463) (+)-(464) (465) (466)



(467) (468) (469) (470)

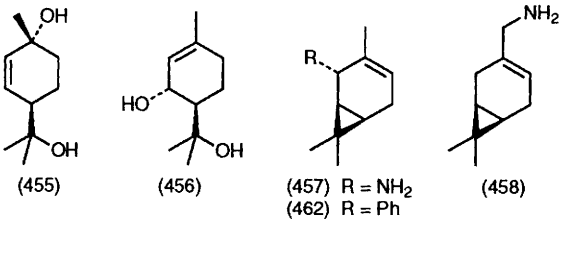
The 3α,4α-epoxycarane (471) has been converted into the azido alcohols (472) and (473), and the 3β,4β-epoxycarane (474) affords the corresponding azido alcohols (475) and (476).[448] Reaction of the α-epoxide (471) with thiourea in ethanol leads to the allylic 10-disulfide (477), but the hydroxy disulfide (478) is formed if EtONa is also present.[449] The alternative disulfide (479) is formed from the β-epoxycarane (474) under the same conditions. When the α-epoxide (471) is treated with HSO_3F–FSO_2Cl at −110 °C and then with methanol it is converted into a mixture of the acetal (480), the ethers (481)–(482) and the unsaturated ketone (483).[450]

The *gem*-dimethylcyclopropyl function of the carene skeleton makes it an attractive starting material for the synthesis of pyrethroids and a review on this subject has been published.[451] (+)-Car-3-ene (446) has been converted into the lactones (484)

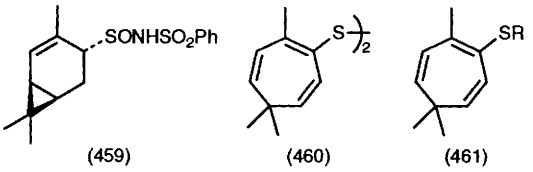


(+)-(446) (447) R^1 = SPh; R^2 = O; (448) R^1 = NMe_2; R^2 = NOH (449)

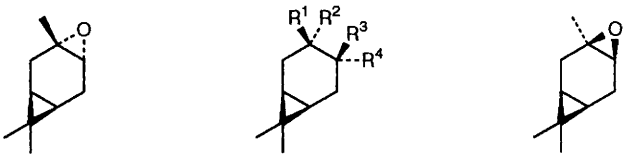
(450) R^1 = H_2; R^2 = O (451) R^1 = O; R^2 = H_2 (452) (453) (454)



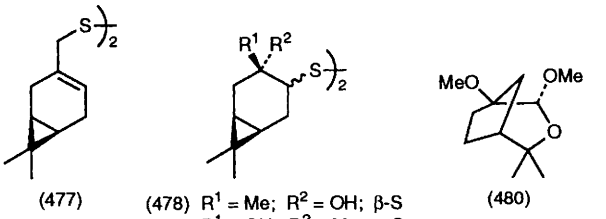
(455) (456) (457) R = NH_2; (462) R = Ph (458)



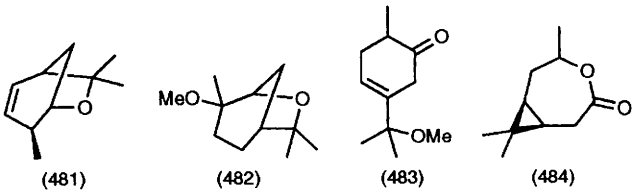
(459) (460) (461)



(+)-(471) (472) R^1 = N_3; R^2 = Me; R^3 = H; R^4 = OH; (473) R^1 = Me; R^2 = OH; R^3 = N_3; R^4 = H; (475) R^1 = Me; R^2 = N_3; R^3 = OH; R^4 = H; (476) R^1 = OH; R^2 = Me; R^3 = H; R^4 = N_3; (487) R^1 = R^4 = OH; R^2 = Me; R^3 = H (474)



(477) (478) R^1 = Me; R^2 = OH; β-S; (479) R^1 = OH; R^2 = Me; α-S (480)



(481) (482) (483) (484)

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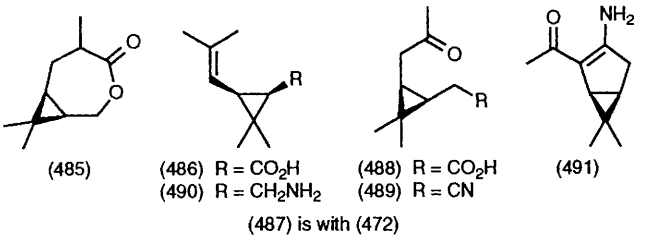
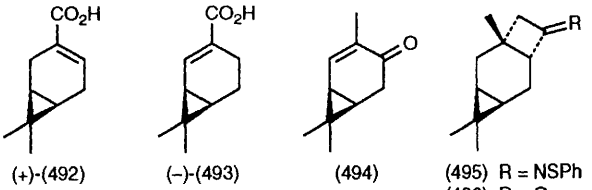
and (485), either of which can be further processed to yield *cis*-chrysanthemic acid (486),[452] and the diol (487), easily obtained from (+)-3α,4α-epoxycarane (471), is oxidised by O_2–$Co(AcO)_2$ to give a mixture which consists of the useful keto acid synthon (488) (50–80%).[453] The corresponding nitrile (489) has been converted into (1*R*)-*cis*-chrysanthemylamine (490),[454] and into the β-dicarbonyl derivative (491).[455]

The biotransformation of (+)-car-3-ene by *Mycobacterium smegmatis* DSM-43061 leads to (+)-chaminic acid (492), together with the enone (450) and the *m*-menthadienol (452).[456] Biotransformation of (+)-car-2-ene (464) by the same micro-organism leads to (−)-isochaminic acid (493) and car-2-en-4-one (494).

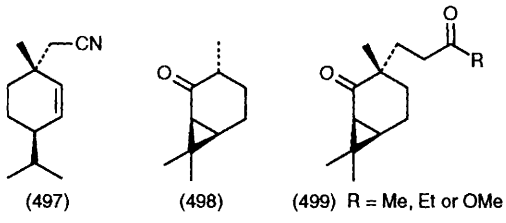


(485) (486) R = CO_2H (490) R = CH_2NH_2 (488) R = CO_2H (489) R = CN (491)

(487) is with (472)



(+)-(492) (−)-(493) (494) (495) R = NSPh (496) R = O



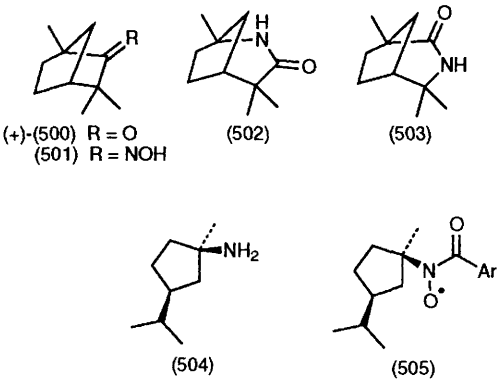
(497) (498) (499) R = Me, Et or OMe

The *S*-phenylsulfenylimine (495) has been prepared from the corresponding cyclobutanone (496), and undergoes a radical-initiated reaction in the presence of Bu_3SnH to give the nitrile (497) in high yield.[457] *trans*-Caran-2-one (498) undergoes Michael addition reactions with various acceptors to give products (499) which are useful intermediates in sesquiterpenoid synthesis.[458]

9 Fenchanes

Enantiomerically pure (+)-fenchone (500) has been detected in wild *Foeniculum vulgare*, and enantiomerically pure (−)-fenchone *ent*-(500) has been found in wormwood, tansy and cedarleaf oils.[459]

The ^1H, ^{13}C and ^{17}O NMR spectra of fenchone oxime (501) and of its various 5-, 6-, 7-, 8- and 9-chloro derivatives have been measured and analysed.[460] X-ray crystal structures of the *anti*-7-chloro oxime and of the 8-chloro oxime have been obtained.[461] Irradiation of fenchone oxime (501) in methanol solution affords, in poor yield, a 1:1 mixture of the two lactams (502) and (503).[462] Fenchone (500) has been converted into fenchelylamine (504) which is the precursor of the acyl aminoxyl radicals (505). These have been demonstrated to cause very slightly enantioselective oxidation of racemic 2-methyl-phenylpropanol, and the optical activity of unreacted alcohol was determined using a HPLC-based diode-laser polarimetric detector.[463]



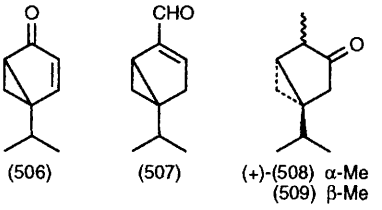
(+)-(500) R = O (501) R = NOH (502) (503) (504) (505)

10 Thujanes

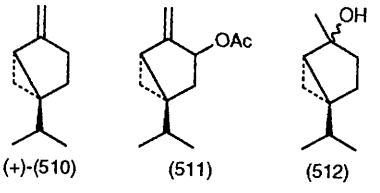
The new nor-monoterpenoid lebaicone (506) has been obtained from the oil of *Ledum palustre*, together with the aldehyde (507) and α-thujone (508).[464] Both α- and β-thujone, (508) and (509) respectively, are found in the oil from young plants of *Artemisia absinthum*, but *cis*-chrysanthemol predominates after flowering has occurred.[465] The oil from *Artemisia afra* Jacq. which contains the thujones (508) and (509) is utilised in African traditional medicine, and is active against a wide range of bacterial species.[466]

The enzyme-catalysed conversion of geranyl diphosphate into (+)-sabinene (510) has been reviewed.[467] The oil of *Salvia lavandufolia* contains sabinyl acetate (511), and a study of the potential teratogenicity of this compound suggests that there is significant risk associated with the uncontrolled use of this *Salvia* oil for aromatherapeutic purposes.[468]

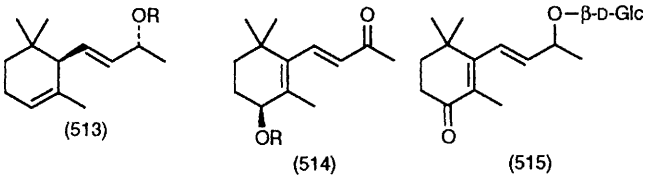
The quadrupole and ion-trap mass spectra of the *cis*- and *trans*-sabinene hydrates (512) have been measured.[469]



(506) (507) (+)-(508) α-Me (509) β-Me



(+)-(510) (511) (512)



(513) (514) (515)

11 Ionone Derivatives

The novel α-ionol disaccharide 9-*O*-α-L-arabinofuranosyl-(1–6)-β-D-glucopyranoside (513) has been isolated from fruits of the raspberry *Rubus idaeus*,[470] as have the 4-*O*-α-L-arabinofuranosyl-(1–6)-β-D-glucopyranoside of (4*S*)-4-hydroxy-β-ionone (514)[471] and the simpler β-D-glucopyranoside (515).[169] Other glycosides which have been discovered include

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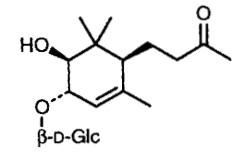
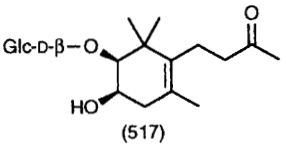
(516) from *Epimedium grandiflorum* var. *thunbergianum*,[472] icariside *B*9 (517) from *Epimedium sagittatum*,[473] the glucosides (518) and (519) from *Melia toosendan*,[474] compounds (520) and (521) from *Dendrathema shiwogiku*,[475] the related ketone ampelopsisonoside (522) from *Ampelopsis brevipendunculata* (Maxim.) Trautv.,[476] and (523) and the epoxide (524) from *Prunus spinosa*.[477] The acetals (525) and (526) have been obtained from *Cydonia oblongata* Mil., and their structures have been confirmed by synthesis.[478]



(516)



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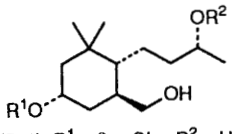
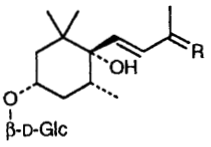
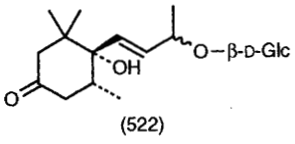


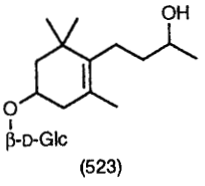
(518) R^1 = β-D-Glc; R^2 = H
(519) R^1 = H; R^2 = β-D-Glc



(520) R = H, OH
(521) R = O



(522)



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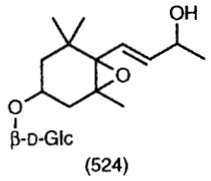

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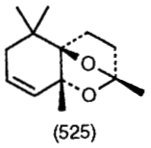

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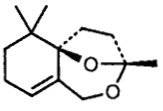

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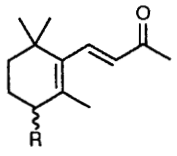
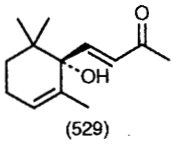


(527) R = OAc
(528) R = α-OH
(533) R = H
(539) R = OH or OR′

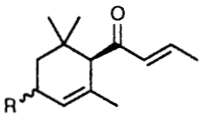


(529)

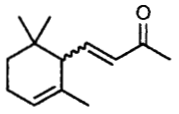
The acetate (527) can be resolved using a lipase, and the resulting 4-hydroxy-β-ionone (528) has been converted into 6-hydroxy-α-ionone (529) which is an intermediate in a synthesis of some abscisic acid analogues.[479] The biotransformations of α-damascone (530) by various strains of *Botrytis cinerea* have been investigated,[480] and the conformations of the isomeric *cis*- and *trans*-3-hydroxy-α-damascones (531) which are metabolites of the parent compound have been investigated by NMR methods.[481]

The individual enantiomers of α-damascone (530) have been converted into the (*R*)- and (*S*)-α-ionones (532) *via* a novel enone transposition sequence which proceeds without racemisation,[482] and the reverse transpositions wherein α-ionone (532) yields α-damascone (530) and β-ionone (533) affords β-damascone (534) have also been reported.[483] Thujone (508) has been converted into the damascones (530),[484] and stereocontrolled total syntheses of (+)-*cis*-α-irone (535) and of its enantiomer have been reported.[485]

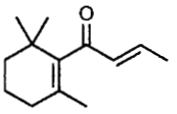
A useful heterogeneous catalyst for the selective hydrogenation of the conjugated double bonds of α- and β-ionone, (532) and (533) respectively, is Cu/Al_2O_3.[297] Photo-oxidation of α-ionone (532) affords the α- and β-isomers of the hydroperoxide (536) in 23:77 ratio. The former reacts in the presence of $Ti(Pr^iO)_4$ to give the corresponding alcohol (537), but the β-isomer yields mainly the epoxide (538) when it is treated with the same reagent.[486] Oxidation of either α- or β-ionone, (532) and (533) respectively, by I_2–cerium(IV) ammonium nitrate in aqueous or alcoholic media leads to a mixture containing the allylic alcohol or ether (539) together with the ketone (540).[487] The same ketone (540) is obtained in 98:2 ratio with the partially saturated analogue (541) when β-ionone (533) is treated with $VO(OEt)Cl_2$ in ethanolic solution under an oxygen atmosphere, but this ratio becomes 64:36 when the reaction is conducted under nitrogen.[488]



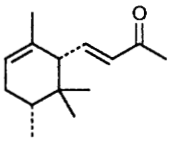
(530) R = H
(531) R = OH



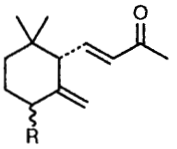
(*R*)-(532) β-configuration
(*S*)-(532) α-configuration



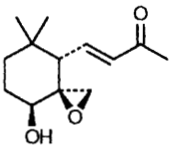
(534)



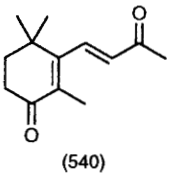
(+)-(535)



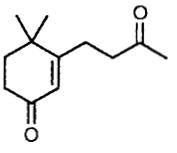
(536) R = OOH
(537) R = α-OH



(538)
(539) is with (527)



(540)

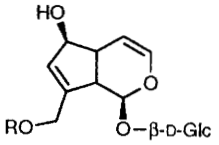


(541)

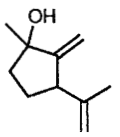
12 Iridanes

Recent developments in the chemistry, pharmacology and occurrence of iridoids have been reviewed,[489–492] and the distribution of iridoids in members of the *Hamamelidae* has been discussed.[493] Aucubin (542), which has been isolated[494] from *Buddleia americana*, has been found to act as an antidote against the toxins of the poisonous mushroom *Amanita virosa*, preventing hepatic damage by suppressing *m*RNA biosynthesis in the liver.[495]

Oxidative allylic rearrangement of the cyclopentanol (543) affords the aldehyde (544) which is a useful synthon for various iridanes.[496] Syntheses of racemic dihydronepetalactone (545),[497,498] and of racemic isodihydronepetalactone (546)[498] have been reported, and geniposide (547) has been converted



(542) R = H
(592) R = Ac



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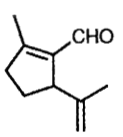

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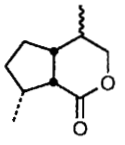
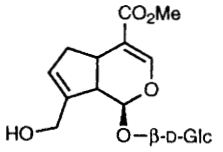


(545) β-Me
(546) α-Me



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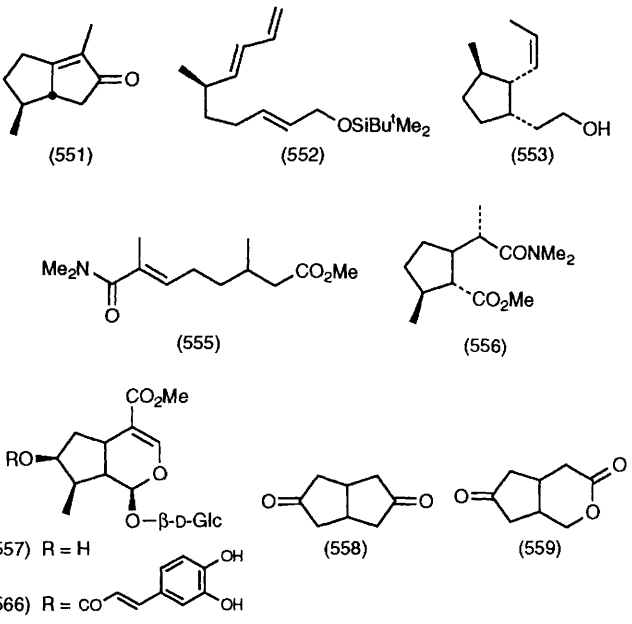
into nepetalactone (548), isodihydronepetalactone (546), and iridomyrmecin (549).[499] Zirconium-catalysed cyclisation of the (*S*)-enyne (550) leads, after further processing, to the ketone (551) which has been converted into (+)-iridomyrmecin (549),[500] and an iron-catalysed cyclisation of the silyloxytriene (552) affords the alcohol (553) which has been converted into (+)-isoiridomyrmecin (554) and into (−)-isodihydronepetalactone (546).[501] Intramolecular Michael reaction of the amido ester (555) leads to (556) which can then be converted into iridomyrmecin (549).[502] Racemic loganin *rac*-(557) has been synthesised *via* *m*-chloroperoxybenzoic acid oxidation of the symmetrical diketone (558), followed by further transformations of the product lactone (559).[503] In a sequence which



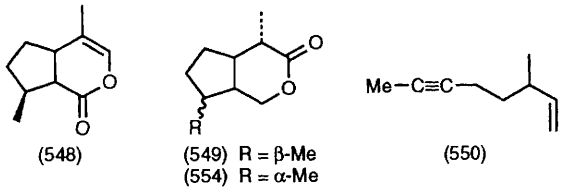


Table 2 Sources of iridoids

Species	Compound(s)	Reference
Ajuga repens	Ajureptoside (562)	505
Argylia radiata	Radiatoside *E* (563), Radiatoside *F* (564)	506
Buddleia davidii	Biridoside (565)	507
Buddleia japonica	Buddlejosides A_1–A_{16}	508
Cassinopsis madagascarensis	7-Caffeoylloganin (566)	509
Castilleja sessiliflora	6-*O*-Acetylmelittoside (567)	510
Coleospermum billardieri	10-Hydroxyloganin derivatives	511
Cornus officinalis Sieb. *et* Zucc.	(568)	512
Cydonia oblongata Mill.	β-D-Gentobioside	513
Duranta repens	Repenoside (569)	514
Fraxinus chinensis	Frachinoside (570)	515
Fraxinus formosana	Fraxiformoside (571)	516
Hedyotis diffusa	(572)–(574)	517
Jasminum amplexicaule	Jasamplexosides *I-III* (575)–(577)	518
Jasminum mesnyi	(578) and (579)	519
Lamiophlomis rotata	Lamiophlomiol *C* (580)	520
Lamium album	Alboside-*A* (581) and Alboside-*B* (582)	521
Linaria genistifolium	Genistifolin (583)	522
Linaria vulgaris	(584) and (585)	523
Nepeta leucophylla	Iridodials and (586)	524
Nepeta tuberosa	5,9-Dehydronepetalactone dimer (587)	525
Nyctanthes arbor-tristis	(588) and (589)	526
Oldenlandia corymbosa	Asperulosidic acid and scandoside esters	527
Orthocarpus attenattus	8-Deoxylaminol and 5,8-bisdeoxylaminol	528
Orthocarpus purpurascens	6β-Hydroxyboschnaloside	528
Pedicularis lasiophrys	Pedicularioside (590)	529
Pedicularis longiflora		530
Pedicularis nordmanniana	(591)	531
Plantago carinata Schrad.	10-Acetylaucubin (592)	532
Plantago major	Majoroside (593)	533
Premna japonica	Catalpol derivatives	534
Pseudocalymma elegans	Pseudocalymmoside (594)	535
Rehmannia glutinosa var. *purpurea*	(595)	536
Rogeria adenophylla	(596)	537
Scrophularia canina	(591)	538
Scrophularia koelzii	Koelzioside (597)	539
Siphonostegia chinensis	Siphonostegiol (598)	540
Stachys macrantha	Macranthoside (599)	541
Strychnos ligustrina	Ligustrinoside (600)	542
Swertia angustifolia	Angustiamarin (601)	543
Tabebuia avellanedae	Ajugol derivatives (602)–(604)	544
Triplostegia grandiflora	Triplostoside-*A* (605)	545
Veronica anagallis aquatica var. *anagalloides*	Anagalloside (606)	546
Villarsia exaltata	(607)	547

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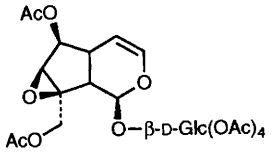
proceeds in the reverse direction, hexa-acetyl catalpol (560) has been converted into (+)-cyclosarcomycin (561).[504]

The number and complexity of novel iridoids and *seco*-iridoids which are isolated from plant sources continues to grow. In this Report, for the sake of brevity, these are listed by source in alphabetical order in Table 2 on page 215, and structural formulae are provided where appropriate.



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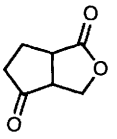
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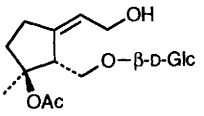

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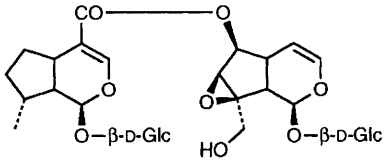

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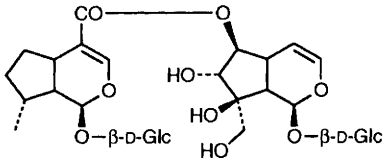

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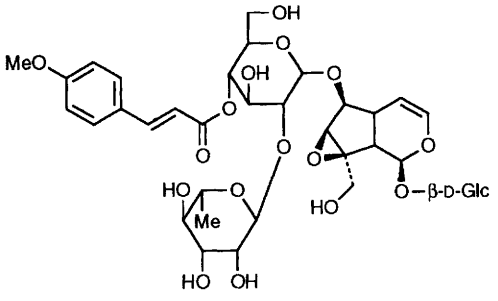
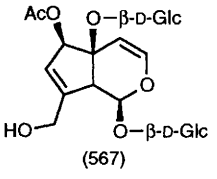


(565)

(566) is with (557)



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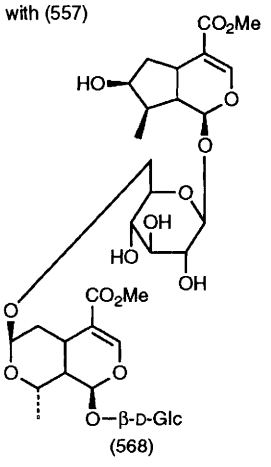

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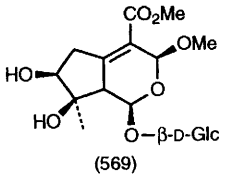

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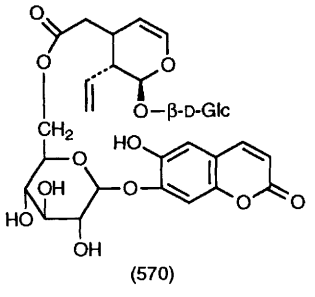

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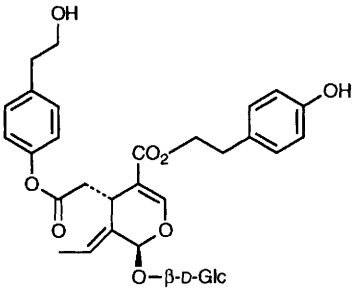

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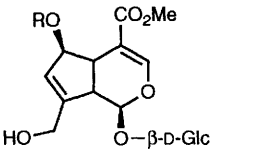
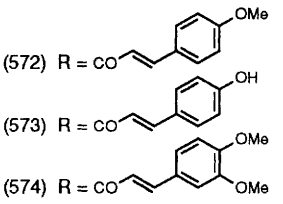
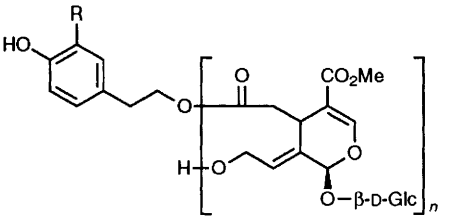
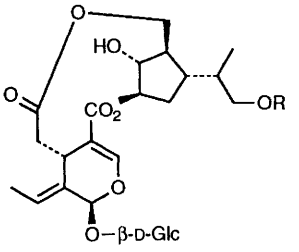


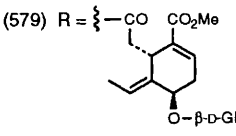


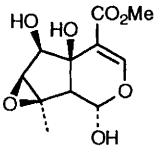


(575) R = H; $n = 2$
(576) R = H; $n = 3$
(577) R = OH; $n = 2$



(578) R = H





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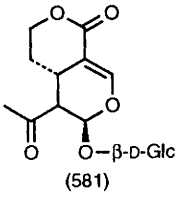

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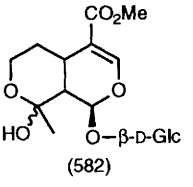

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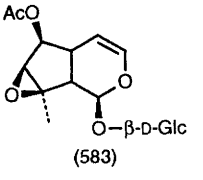

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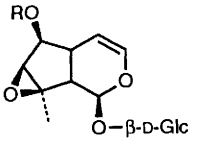
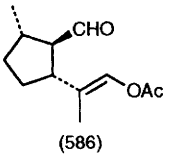


(584) R = (*E*)-*p*-coumaryl
(585) R = (*Z*)-*p*-coumaryl



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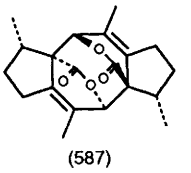
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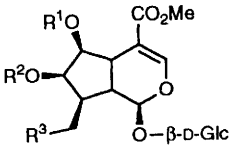
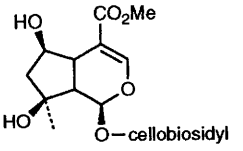


(588) $R^1 = R^2$ = PhCO; R^3 = OH
(589) R^1 = (*E*)-*p*-cinnamoyl; $R^2 = R^3 = H$



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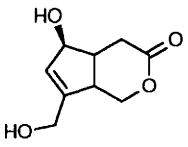

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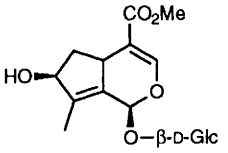
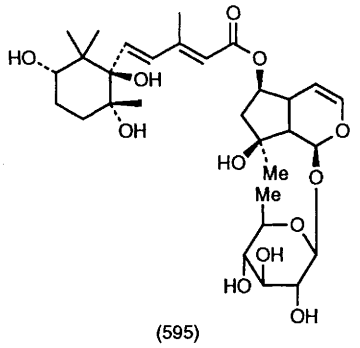


(593)

(592) is with (542)



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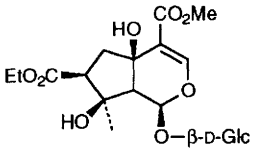

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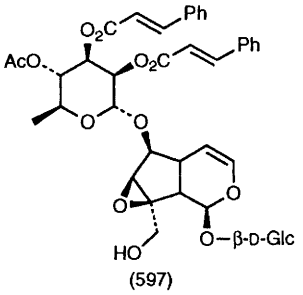

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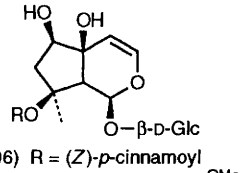
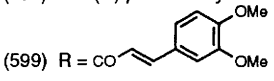
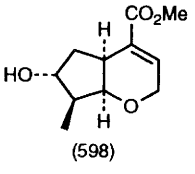


(596) R = (*Z*)-*p*-cinnamoyl



(599) R = CO



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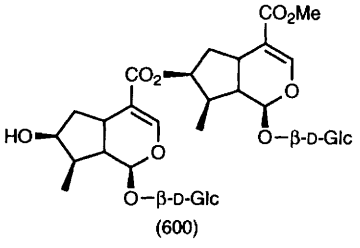

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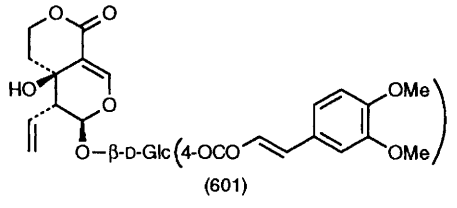

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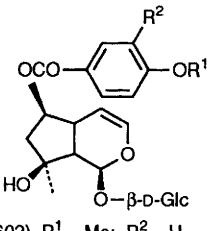
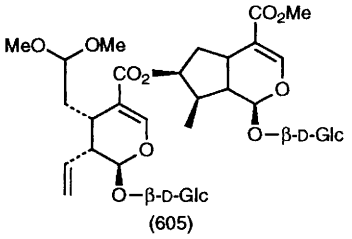


(602) R^1 = Me; R^2 = H
(603) R^1 = Me; R^2 = OMe
(604) R^1 = R^2 = H



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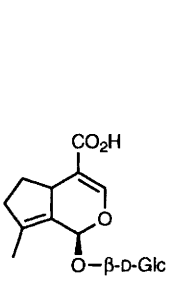

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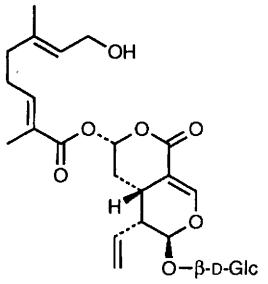
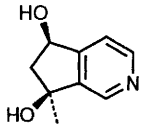


(607)

Two new tetrahydroisoquinoline–monoterpene glucosides have been isolated from *Alangium platanifolium*,[548] and a synthesis of oxerine (608), obtained from *Oxera morieri*, has been reported.[549] Isocantleyine (609) has been found in *Siphonostegia chinensis*.[550]

Geniposide (547) is metabolised to genipinine (610) by human intestinal bacteria, and gardenoside (611) is converted into gardenine (612) under the same conditions.[551] A synthesis of racemic tecomanine (613) has been reported.[552]



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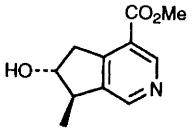

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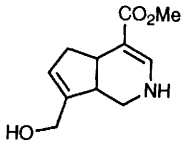

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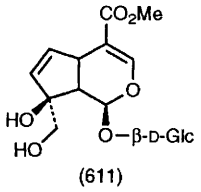

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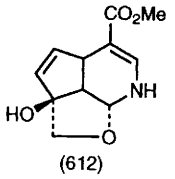

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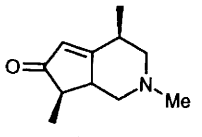
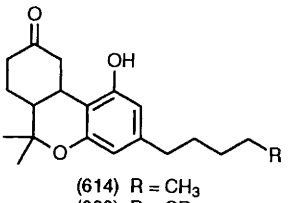


(613)

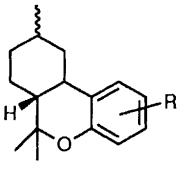
13 Cannabinoids

The ^{1}H NMR spectra of the racemic and optically active forms of the nor-ketone (614) are non-superimposable! Non-racemic mixtures of the enantiomers of (614) exhibit two sets of signals for their aromatic protons in ratios which reflect the composition of the mixtures. This self-induced non-equivalence appears to be caused by diastereoisomeric solute–solute interactions, and it is therefore possible to use NMR to determine the ee of a sample of (614) without employing a chiral shift reagent.[553]

Most of the (chemical) activity in this area has focused on synthesis. Citronellal (53) reacts with phenols in refluxing quinoline to yield hexahydrocannabinoids (615) *via* intermediate quinone methides (616).[554] Activated phenols can be



(614) R = CH_3
(623) R = CD_3



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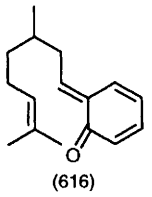

(616)

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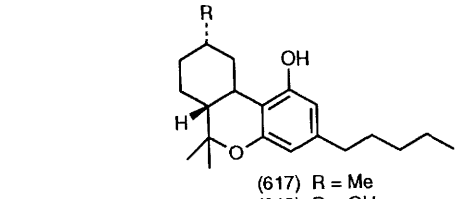
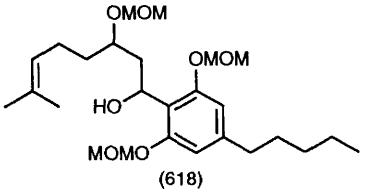
reacted under the milder conditions of boric acid in acetic acid.[555] A similar route has been employed in a synthesis of (−)-*trans*-hexahydrocannabinol (617).[556] The derivative (618) undergoes a related intramolecular reaction to yield 9-nor-9-hydroxyhexahydrocannabinol (619).[557]

Apoverbenone (620) has been converted into the racemic 11-nor-9-carboxy-Δ^9-tetrahydrocannabinol carboxylic acid (621) which is the principle human metabolite of Δ^9-tetrahydrocannabinol (622).[558] The labelled nor-ketone (623) and the labelled ester (624) have been synthesised from the related *apo*-bromoverbenone (625).[559] Reaction of 3,9-dibromocamphor with the aryllithium (626) in the presence of CuI affords (627) which has been converted into (−)-cannibadiol (628) and the corresponding dimethyl ether.[560] The intermediate (629) for a synthesis of Δ^9-tetrahydrocannabinol (622) is obtained in crystalline form when the *p*-menthendiol (630) is reacted with the phenol (631).[561] The thioacetal (632) has been converted into the THC-acid (621) by related means.[562] Protection of the phenolic hydroxy group of the aldehyde (633) by silylation permits oxidation at C-9 using $NaClO_2$–Na_2PO_4–Bu^{t}OH, thus providing another route to the acid (621).[563] New routes to *cis*-Δ^9-tetrahydrocannabinol and to *trans*-Δ^8-tetrahydrocannabinol (634), the main active ingredients of hashish, have been described.[564]



(617) R = Me
(619) R = OH



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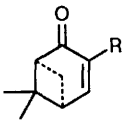
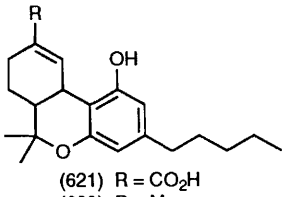
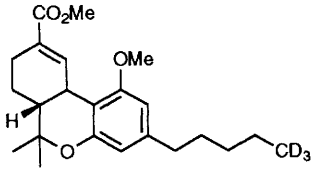


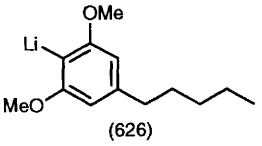
(620) R = H
(625) R = Br



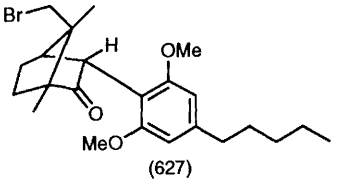
(621) R = CO_2H
(622) R = Me



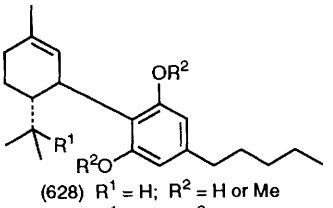
(624)



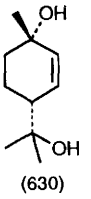
(626)



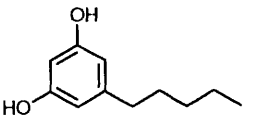
(627)



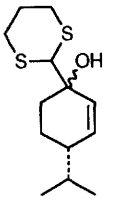
(628) R^1 = H; R^2 = H or Me
(629) R^1 = OH; R^2 = H



(630)



(631)



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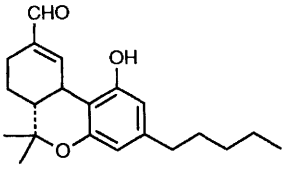

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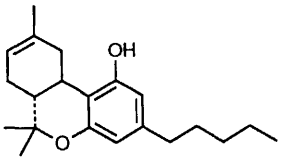
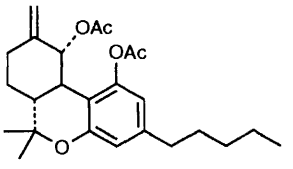


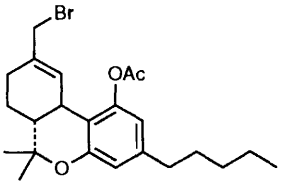
(634)

The diacetate (635) reacts with Me_3SiBr in the presence of catalytic $ZnBr_2$ to give the rearranged allylic bromide (636), and the isomeric acetate (637) provides the rearranged Δ^8-bromide (638) under the same conditions.[565] Cannabidiol (628) and the Δ^8-tetrahydrocannabinol (634) are both selectively halogenated in their aryl rings by LiCl or NaBr in the presence of [18]-crown-6 and *m*-chloroperoxybenzoic acid.[566]

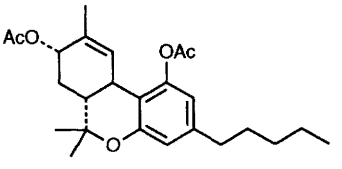
The two rotationally-restricted tetrahydrocannabinol ethers (639) and (640) have been synthesised with a view to testing theories of psychopharmacological activity.[567]



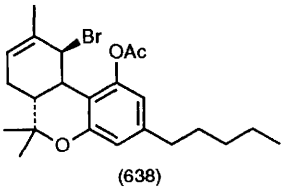
(635)



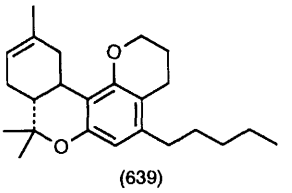
(636)



(637)



(638)



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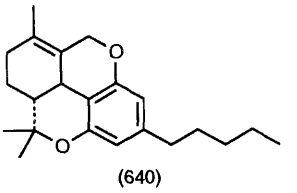

(640)

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