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清水, 邦義
九州大学大学院農学研究院

近藤, 隆一郎
九州大学大学院農学研究院

坂井, 克己
九州大学大学院農学研究院

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総　説

ヒノキ科樹木の抽出成分と生理活性*

清　水　邦　義**・近　藤　隆一郎**・坂　井　克　己**

抄　　録

日本において最も重要で優良な用材源の一つであるヒノキの付加価値の高い有効利用法開発の基礎資料とすべく，ヒノキ科樹木の抽出物に関する1991年以降に報告された知見を調査して報告する．新規化合物の構造決定や成分分析に関しては，新種のテルペノイドの報告並びに，ケモタキソノミー見地からの精油成分のGC-MSによる定性，定量分析の報告が多く，特に，テルペン類の構造の多様性に注目した研究が多い．利用に関しては，テルペン類の含量が高い針葉精油成分の用途開発に関する研究が多い．その中で，生理活性については，各種テルペン類の抗菌，殺虫，殺ダニ活性，心理作用への影響等が報告されている．また，トロポロン類，特にβ-thujaplicin（ヒノキチオール）の多岐に渡る生理活性（齧歯類の囓り抑制，抗菌，殺虫，殺ダニ，抗寄生虫，メタロプロテアーゼ阻害，チロシナーゼ阻害，抗酸化性，活性酸素種捕捉能，UV-Bによるアポトーシス誘導阻害等）が報告されている．

これらの知見を適切に利用すれば，用材としての利用後に残るヒノキ樹皮・枝葉あるいは除・間伐材の付加価値が向上すると期待される．

キーワード：ヒノキ科，抽出成分，新規化合物，成分分析，生理活性物質

1. はじめに

我が国は国土の約七割を森林が占め，世界の森林面積が陸地面積のわずか二割しかないのに比べて，かなり森林に恵まれているようには見えるが，その荒廃は年々進むばかりである．それは林業の不振，山村の過疎化，環境破壊などの現象として表れている．その原因は多岐に渡っているが，人工林の大部分を占めるスギ，ヒノキが，現状では十分な経済的利益の実現につながり難いことも一因であろう．そこで，従来の建築材等の利用だけでなく，スギ，ヒノキのもつ多面的な機能を高度に発揮させ，廃材，樹皮及び枝葉部等未利

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* Kuniyoshi SHIMIZU, Ryuichiro KONDO and Kokki SAKAI : The Extractives of Cupressaceae Trees and Their Bioactivities

** 九州大学大学院農学研究院森林資源科学部門森林機能開発学講座森林生物化学研究室
Laboratory of Forest Biology and Biochemistry, Division of Forest Bioscience, Department of Forestry and Forest Products Science, Faculty of Agriculture, Kyushu University, Fukuoka 812-8581

用部位の経済的付加価値を見出していくことも重要である．樹木成分は，化学的にはセルロース，ヘミセルロース，リグニン及び抽出成分に分類できるが，樹種による化学的性質の違いは抽出成分に拠るところが大きい．特に廃材等の抽出成分の利用を指向する場合には，その種に「特有な」抽出成分の「適切な」，「付加価値の高い」利用が鍵であり，そのためには，抽出成分に含まれる個々の成分の化学構造だけでなく，それらの物性，化学反応性，生理活性などを把握することが必須である．なかでも新規生理活性の開拓は，付加価値を格段に向上させる可能性を有する．

ヒノキに代表されるヒノキ科（Cupressaceae）は，21属約125種からなる常緑針葉樹で，11属が北半球，10属が南半球と，ほぼ半数ずつ南北に分かれて分布している．主要な森林構成要素として南北両半球で多様に分布している点は，針葉樹ではスギ科，マツ科が北半球に，ナンヨウスギ科，マキ科が南半球に主に分布していることに比べて特殊である．両半球ともにいくつかの属は高木になり，ヒノキだけでなくさまざまな種が木材として利用されている（大澤，1997）．日本には，ヒノキ属（***Chamaecyparis***），ビャクシン属（***Juniperus***），ネズコ属（***Thuja***），アスナロ属（***Thujopsis***）など4属およそ10種がある．

ここでは，国内の代表的な樹種を構成するヒノキ科樹木の抽出成分に着目し，高度利用に繋がる基礎的知見を得るために，それらの抽出成分に関する1991年以降の研究について概観する．それ以前に見出された主要抽出成分については，成書にまとめられている（今村・安江，1983）．

2. ヒノキ科抽出成分

ヒノキ科抽出成分に着目した研究を，大きく次の4つのカテゴリーに分類し，それぞれについて最近の知見を簡単に述べる．1．新規化合物の構造決定，2．成分分析，3．生理活性，4．その他．

2. 1. 新規化合物

*Chamaecyparis formosensis*の葉部のアセトン抽出物から新種のジノルセスキテルペン，3-hydroxymegastigm-5-en-9-one（**1**），(*S*)-9-hydroxymegastigm-5-en-4-one（**2**），megastigm-5-ene-3,9-diol（**3**），新種のジテルペン，3β-hydroxy-1-oxo-13-*O*-methyltotarol（**4**），12-*O*-methylpisiferanol（**5**），1β-hydroxypisiferanol（**6**），10-deoxy-4(18)-epoxy-12-methoxy-4,5-*seco*-pisiferan-19-ol（**7**），8α-hydroxylabda-13(16),14-dien-19-yl(*Z*)-4-hydroxycinnamate（**8**），8α-hydroxylabda-13(16),14-diene-19-yl(*E*)-4-hydroxy-3-methoxycinnamate（**9**），8α-acetoxylabda-12,14-dien-19-oic acid（**10**），及び新種のリグナン，(7*R*,8*R*)-9'-(β-rhamnopyranosyl)-3-methoxy-3':7,4':8-diepoxyneolignan-4,9-diol（**11**）が単離されている（Lin *et al.*, 1999）．*Chamaecyparis obtusa* の心材から新種のジテルペン，obtunone（**12**）（Kuo *et al.*, 1998a），11,14-dihydroxy-8,11,13-abietatrien-7-one（**13**），obtuanhydride（**14**），18,19-*O*-isopropylidene-18,19-dihydroxyisopimara-8(14),15-diene（**15**）が単離され（Kuo *et al.*, 1998b），葉油から新種のセスキテルペンアルコール，10-epi-cubebol（**16**）が単離されている（Hieda *et al.*, 1996）．*Cupressus bakeri*の枝葉より新種のセスキテルペン，*cis*-muurola-3,5-diene（**17**），*cis*-muurola-4(14),5-diene（**18**），*cis*-muurol-5-en-4α-ol（**19**），*cis*-muurol-5-en-4

β-ol (**20**), 2-ethylisomenthone (**21**), 2-(3-oxobutyl)-isomenthone (**22**) (Kim *et al.*, 1994), (+)-2-ethylmenthone (**23**), (+)-indipone (**24**) (Cool and Jiang, 1995a)が単離されている．また，新種のnor-acorane ヘミケタール型セスキテルペン，bakerol (**25**) も単離されたが、その約3%はケト型 (**26**) であった (Cool *et al.*, 1994). *Cupressus funebris*の葉部から新種のnorlabdan型ジテルペン，15-norlabda-8(20),12*E*-diene-14-carboxaldehyde-19-oic acid (**27**)が単離されている(Kobayashi *et al.*, 1991). *Cupressus macnabiana*の葉部から新種のセスキテルペン，macnabin (**28**)が単離されている (Cool and Jang, 1995b). *Juniperus chinensis*の樹皮から新種のジテルペン，12-hydroxycupressic acid (**29**) (Lee *et al.*, 1992), 12,15-dihydroxylabda-8(17),13-dien-19-oic acidの*E*, *Z*異性体(**30, 31**), 2α-hydroxycommunic acidの*E*, *Z*異性体 (**32, 33**), 15,16-bisnor-8,17-epoxy-13-oxolabd-11*E*-en-19-oic acid (**34**)が見出され (Fang *et al.*, 1993b), 根から新種のジテルペン，7β-hydroxysandaracopimaric acid (**35**) (Kuo and Chen, 1992a), 1,3-dioxototarol (**36**), Isototarolenone (**37**) , 1-oxo-3β-hydroxytotarol (**38**) (Kuo and Chen, 1994a)ならびに新種のセスキテルペン，8α,12-dihydroxycedrane (**39**) (Kuo and Chen, 1992b), chinensiol (**40**) (Kuo and Chen, 1994b)が単離されている．同材種の葉部から新種のリグナン，(8*S*)-3-methoxy-8,4'-oxyneoligna-3',4,9,9'-tetraol (**41**), (7*S*,8*S*)-3-methoxy-3',7-epoxy-8,4'-oxyneoligna-4,9,9'-triol (**42**), (7*R*,8*S*)-3-methoxy-3',7-epoxy-8,4'-oxyneoligna-4,9,9'-triol (**43**) (Fang *et al.*, 1992), 新種のジテルペン，abieta-8,11,13-trien-7β-ol (**44**), juniperolide (**45**), juniperal (**46**), norjuniperolide (**47**), secojuniperolide (**48**), chinanoxal (**49**) (Fang *et al.*, 1993a), 7α-hydroxyabieta-8,11,13-trien-19-yl acetate (**50**), 7α-hydroxyabieta-8,11,13-trien-19-al (**51**), 7α-hydroxyabieta-8,13-dien-19-al (**52**), 7-oxoabieta-8,13-dien-19-al (**53**), 12-oxoabieta-7,13-dien-19-al (**54**), 13β-hydroxy-7-oxoabieta-8(14)-en-19-al (**55**), 6α,13β-dihydroxy-7-oxoabieta-8(14)-en-19-al (**56**) (Lee *et al.*, 1994), 新種のノルジテルペン，19-norabieta-8,11-13-trien-4-yl formate (**57**), 18-norabieta-8,11,13-triene-4-hydroperoxide (**58**), 19-norabieta-8,11,13-triene-4-hydroperoxide (**59**), 4-hydroxy-18-norabieta-8,11,13-trien-7-one (**60**), 4-hydroxy-19-norabieta-8,11,13-trien-7-one (**61**), 4-hydroperoxy-19-norabieta-8,11,13-trien-7-one (**62**), 7α-hydroxy-19-norabieta-8,11,13-triene-4-hydroperoxide (**63**), 19-norabieta-7,13-dien-4-ol (**64**), 13β,14β-epoxy-4-hydroxy-19-norabiet-7-en-6-one (**65**) (Lee *et al.*, 1995)が報告されており，さらに，心材から新種のセスキテルペン，12-hydroxy-α-longipinene (**66**), 15-hydroxyacora-4(14),8-diene (**67**) (Kuo and Shiu, 1996), cedr-3-en-15-ol (**68**), junipercedrol (**69**)及びα-longipinen-12-ol (**70**), 新種の*cis*-himachalane 型セスキテルペン，2-himachalen-6-ol (**71**), 3-himachalen-6-ol (**72**), 2α,6α-epoxy-3-himachalene (**73**), 2α,6α-epoxyhimachalane-3β-ol (**74**), chinensiol (**75**) (Shiu *et al.*, 1999), 新種のジテルペン，15-hydroxylabda-8(17),11*E*,13*E*-trien-19-oic acid (**76**) (Fang *et al.*, 1996)が単離されている．*J. communis* subsp. *hemisphaerica* の葉部のヘキサン抽出物酸性画分より，天然から初めて15-*O*-palmitoyl isocupressic acid (**77**)が単離されている (San Feliciano *et al.*, 1991a). *J. excelsa*の葉部の95%EtOH抽出物から新種のジテルペン，3β,12-dihydroxyabieta-8,11,13-triene-1-one (**78**) (Mossa *et al.*, 1992), 漿果のヘキサン抽出物から新種のジテルペン，3α-acetoxylabda-8(17),13(16),14-trien-19-oic acid (juniperexcelsic acid) (**79**) (Topçu *et al.*, 1999)が単離されている．*J. foetidissima*の球果から，新種のジテルペン，(13*S*)-abiet-8(14)-en-13,19-

diol (**80**) (Sakar and San Feliciano, 1992), 13β-hydroxy-abiet-8(14)-en-19-al (**81**) (Sakar and San Feliciano, 1994)が単離されている. *J. formosana*の樹皮から, 新種のリグナン, formosalactione (**82**) (Kuo and Yu, 1993), 新種のジテルペン(13*S*)-15-hydroxylabd-8(17)-en-19-oic acid (**83**), (13*S*)-15-acetoxylabd-8(17)-en-19-oic acid (**84**), (13*S*)-15-octadecanoyloxylabd-8(17)-en-19-oic acid (**85**) (Kuo and Yu, 1996a), 新種のジテルペン, sugiol methyl ether (**86**), Δ5-dehydrosugiol methyl ether (**87**) (Kuo and Yu, 1996b), 心材から, 新種のジテルペン, 6β-hydroxyferruginol (**88**), formosaninol (**89**), formosanin (**90**) (Kuo and Yu, 1996c), 6-oxoferruginol (**91**)及び6α-acetoxyferruginol (**92**) (Kuo and Yu, 1997), 新種のセスキテルペン(−)-15-hydroxycalamenene (**93**), (−)-1-hydroxy-1,3,5-bisabolatrien-10-one (**94**) (Kuo and Yu, 1996d), junipenonoic acid (**95**) (Yu and Kuo, 1997), *cis*-4,5-dihydroxycorocalane (**96**), *trans*-4,5-dihydroxycorocalane (**97**), calamenen-10α-ol (**98**), 15-hydroxycadalene (**99**) (Kuo and Yu, 1999) が単離されている. *J. oxycedrus* ssp. *macrocarpa* の材部精油から新種のセスキテルペン, junicedranol (**100**)が単離されている (Barrero *et al.*, 1995). *J. occidentalis*の心材の精油から天然物としては未報告であったノルセスキテルペンである(+)-dihydromayurone (**101**)が単離されている (Zhou *et al.*, 1999). *J. phœnicea*から, 天然から初めてのビスフラノンプロパン誘導体であるphœniceroside (**102**) (Comte *et al.*, 1996a), 葉部から, 新種のフェニルプロパノイド, junipetriolosides A (**103**), B (**104**) (Comte *et al.*, 1997b), ジノルテルペン配糖体, 3-oxo-α-ionol 11-*O*-β-D-glucopyranoside (junipeionoloside) (**105**), 3-oxo-6-hydroxy-α-ionol 11-*O*-β-D-glucopyranoside (6-hydroxyjunipeionoloside) (**106**) (Champavier *et al.*, 1999), 地上部から, 新種のフラノン配糖体, phœnicein (**107**) (Comte *et al.*, 1996b), 新種のフェニルプロパン配糖体, juniperoside (**108**) (Comte *et al.*, 1996c), junipediol A (**109**), junipediol A 8-glucoside (**110**), junipediol B 8-glucoside (**111**) (Comte *et al.*, 1997a)が単離されている. *J. sabina*の葉部から, 新種のプロピオフェノン, 2-hydroxy-4-methoxy-6-methylpropiophenone (**112**), 2-hydroxy-3,4-dimethoxy-6-methylpropiophenone (**113**) (San Feliciano *et al.*, 1991b), 新種のリグナンであるナフタレン誘導体, junaphtoic acid (**114**), (-)-3-*O*-demethylyatein (**115**) (San Feliciano *et al.*, 1991c) が単離されている. *J. thurifera*の葉部から新種のリグナン, methyl deoxypodophyllotoxinate (**116**), 7β-hydroxydihydrosesamin (**117**), podophyllotoxinic acid (**118**) (San Feliciano *et al.*, 1991d), 新種の8-hydroxy-labdane型ジテルペン, 8-hydroxy-14-oxo-15-norlabd-13(14)-en-19-oic acid (**119**), sclareolic acid (**120**), episclareolic acid (**121**), 8,15-dihydroxy-14-oxo-labd-13(16)-en-19-oic acid (**122**), 8,15-dihydroxy-labd-13*E*-en-19-oic acid (**123**), 14(*S*)-8, 14, 15-trihydroxy-labd-13(16)-en-19-oic acid (**124**), 14(*R*)-8,14,15-trihydroxy-labd-13(16)-en-19-oic acid (**125**) (San Feliciano *et al.*, 1992a), 新種のlabdane acids,3α,15-dihydroxy-labd-8(17)-en-19-oic acid (**126**), (14*R*)14,15-dihydroxy-8,13-epoxy-labdab-19-oic acid (**127**), (14*S*)14,15-dihydroxy-8,13-epoxy-labdab-19-oic acid (**128**), 3α-hydroxy-13-oxo-14,15-dinorlabd-8(17)-en-19-oic acid (**129**), 3α,15-dihydroxy-14-oxo-labd-8(17),13(16)-dien-19-oic acid (**130**), (14*R*)3α,14,15-trihydroxy-labd-8(17),13(16)-dien-19-oic acid (**131**), (14*S*)3α,14,15-trihydroxy-labd-8(17),13(16)-dien-19-oic acid (**132**) (San Feliciano *et al.*, 1992b), 新種のジテルペン, 3α,15-diacetoxy-labd-8(17)-en-19-oic acid (**133**), 13ζ,14ζ-epoxy-15-oxo-labd-en-19-oic acid (**134-137**), 3α-acetoxy-13ζ,14ζ-epoxy-15-formyl-labd-

8(17)-en-19-oic acid (**138-141**), 3α-acetoxy-15-hydroxy-labd-8(17)-en-19-oic acid (**142**), 3α-acetoxy-15-hydroxy-labd-8(17),13*E*-dien-19-oic acid (**143**) (San Feliciano *et al.*, 1993a), 材部から新種の三環性セスキテルペン, sesquithuriferol (**144**), α-(**145**), β-duprezianene (**146**) (Barrero *et al.*, 1996)が単離されている. *Platycladus orientalis* の果皮から新種のモノリグノールであるdocosyl *trans*-3-hydroxyferulate (**147**)が単離されている (Kuo and Chen, 1999). *Thuja occidentalis*の枝から新種のリグナン, (-)-4-*O*-demethylyatein (**148**) (Kawai *et al.*, 1994)が, 材油から新種のguaiadiene誘導体, 9α,11-epoxy-1βH,5αH,7βH-guaia-3,10(14)-diene (**149**), 1βH,5αH,7βH-guaia-3,10(14)-dien-11-ol (**150**) (Weyerstahl *et al.*, 1996)が単離されている. *Thuja standishii* (Gord.) Carr. の樹皮から新種のabietane型ジテルペンであるstandishinal (**151**)が単離されている (Ohtsu *et al.*, 1999).

2. 2. 成分分析

成分分析については, テルペン類の詳細なGC-MS分析の報告が多い. 研究対象が多岐に渡っているため, 研究例を列挙するに留めた.

*Chamaecyparis pisifera*の根の抽出成分が調べられ、6種のセスキテルペンが単離されている (Yatagai and Takahashi, 1994). GC-MSにより*Cupressus bakeri*種子の脂肪酸が分析され (Rafii *et al.*, 1992a), また, 枝葉の54種のモノ-及びセスキテルペノイドが同定されている (Rafii *et al.*, 1992b). *Cupressus sempervirens*の球果の配糖体成分 (Milos *et al.*, 1998), また, 精油成分 (Loukis *et al.*, 1991), (Riaz *et al.*, 1996)の分析がなされている. *Juniperus*属については、*J. communis*の球果 (Chatzopoulou and Katsiotis, 1993a), (Koukos and Papadopoulou, 1997)及び葉部 (Looman and Baerheim Svendsen, 1992), (Chatzopoulou and Katsiotis, 1993b)の精油成分, 中国産*J. convallium* (Adams *et al.*, 1993a), 中国産*J. formosana* (Adams *et al.*, 1995b)及びネパール産*J. indica*の葉部(Adams and Chaudhary, 1996)のそれぞれの精油成分が分析されている. *J. oxycedrus* L. subsp. *macrocarpa* の球果と葉部の精油成分が分析され (Stassi *et al.*, 1995, Milos and Radonic, 2000), 又, 葉部からポリフェノール類が単離されている (Stassi *et al.*, 1998). *J. pachyphlaea*の葉部からビフラボンが単離されている (Qasim *et al.*, 1991). *J. phœnicea* subsp. *turbinata*の葉部からテルペン類が単離されている (San Fericiano *et al.* (1993b). *J. rigida* の葉部のフェノール成分がTLCにより分析されている (Singh *et al.*, 1993). 中国産*J. saltuaria*の揮発性葉油成分が分析されている (Adams *et al.*, 1993b). *Neocallitropsis pancheri*の心材の揮発成分が分析されている (Raharivelomanana *et al.*, 1993). *Thuja occidentalis*の枝葉 (Kamdem *et al.*, 1993), 材部 (Anderson *et al.*, 1995) の精油成分が分析されている. *Thuja orientalis*の葉部からジテルペンが単離されている (Sharma *et al.*, 1993). *Thujopsis dolabrata*の葉部から3種のテルペノイド配糖体, 7種のフェニルプロパノイド配糖体が単離されており (Obata *et al.*, 1997), また, 葉部精油のジテルペン (Nagahama *et al.*, 1996)がGC分析されている. *Platycladus orientalis* の果皮の化学成分が詳細に調べられている (Kuo and Chen, 1999). *Cypress sempervirens*及び*Thuja orientalis*の種子油の脂肪酸が調べられている (Riaz *et al.*, 1993). *J. phœnicea*及び*Cupressus semperivernsの*地上部のアルコール抽出物からフラボノイド類が単離されている (Maatooq *et al.*, 1998). インド産*J. semiglobosa*とギリシャ産*J. excelsa* の揮発性葉油の比較がなされている(Adams *et al.*, 1992). *J. monosperma* と*J. osteosperma*の揮発性テルペノイドの地理的

変化が調べられている（Adams, 1994）. *J. przewaskii*と*J. przewalskii* f. *pendula*の揮発性葉油成分が分析されている（Adams *et al.*, 1994a）. *J. chinensis*, *J. chinensis* var. *kaizuca*及び cv. *pyramidalis*の揮発性葉油成分の比較がされている（Adams *et al.*, 1994b）. 産地の違い（モンゴル, カザフスタン, ロシア, スコットランド）による*J. davurica*の揮発性葉油成分の組成が比較されている（Adams *et al.*, 1994c）. 北東中国, 韓国及び日本の*J. rigida*について産地の違いによる揮発性葉油成分の比較がなされている（Adams *et al.*, 1995a）. *J. communis*, *J. sibirica*及び*J. intermedia*のケモタキソノミーが精油成分組成を分析することにより検討されている（Caramiello *et al.*, 1995）. 中国産*J. squamata* var. *fargesii*とインド産*J. squamata* の葉の精油成分組成が比較されている（Adams *et al.*, 1996）. ハイティ島の*J. gracilior* var. *urbaniana*の葉油成分を他の西インド諸島のjuniperのものと比較している（Adams *et al.*, 1997）. ポーランド産のJuniper oilのモノテルペン炭化水素のキラル及びアキラル組成分析がなされ, 採取場所や季節により大きな変動が観察されている（Ochocka *et al.*, 1997）. ビャクシン属（*Juniperus*）の十種の葉部精油の組成が調べられ, ケモタキソノミーが検討されている（Adams, 1998）. インド産及びネパール産の*J. recurva*の葉部精油成分が分析され, 西部インドの*J. recurva*と比較されている（Adams *et al.*, 1998）.

2.3. 生理活性

針葉抽出成分の用途開発を目指し, 針葉の精油の揮発速度, 抗菌性試験, 植物生長制御作用, 粘着性能, 脱臭効果などが検討されている（Yatagai and Ohira, 1990）. *Chamaecyparis pisifera*及びその園芸品種に含まれるジテルペン, pisiferic acid（**152**）及びその類縁体が抗酸化作用, 殺ダニ作用を持つことが明らかされている（Yatagai *et al.*, 1991）. ヒノキ（*Chamaecyparis obtusa*）については, カラタチ及びイネの生長に及ぼす材中の生育阻害物質（Ishii and Kadoya, 1993）, 蒸煮処理した樹皮のポリフェノール成分とそのタンパク吸着能（Ohara and Ito, 1995）, 材の殺蟻活性に対する α-terpinyl acetate（**153**）の寄与（Y. Ohtani *et al.*, 1997）, 漏脂症ヒノキ樹脂のジテルペン, manool（**154**）, torulosol（**155**）, torulosal（**156**）の樹脂症病原菌に対する抗菌効果（Yamamoto *et al.*, 1997）, 樹皮のエタノール抽出物の, トマトの根腐れなどに関与する病原菌（*Fusarium oxysporum* f. sp. *radicis-lycopersici*, *Pseudomonas solanacearum*）に対しての抗菌性（Yu and Komada, 1999）が検討されている. *Cupressus arizonica*の花粉から植物生長調節物質brassinosteroids（BRs）の前駆体と思われる新種のステロイド, 6-deoxotyphasterol（**157**）及び3-dehydro-6-deoxoteasterone（**158**）が単離されている（Griffiths *et al.*, 1995）. *Cupressus macrocarpa*の堕胎活性成分としてisocupressic acid（159）が同定されている（Parton *et al.*, 1996）. 日本産針葉樹の葉部抽出物の抗菌活性が調べられ, *J. chinensis*より抗菌成分として8-acetoxyelemol（**160**）, 8-hydroxyelemol（**161**）, hinokiic acid（**162**）が単離され（Ohashi *et al.*, 1994）, 葉部から細胞毒性成分としてdeoxypodophyllotoxin（**163**）が単離されている（Kawazu *et al.*, 1997）. *J. excelsa*の葉部及び種子から抗菌活性を有するジテルペン, (+)-ferruginol（abieta-8,11,13-triene-12-ol）（**164**）及び(-)-sandaracopimeric acid（isopimara-8(14),15-diene-18-oic acid）（**165**）が単離されており（Muhammad *et al.*, 1992）, 漿果のヘキサン抽出物は, LNCaP, KB-V(+VLB)及びKB-V(-VLB)細胞に対して高い細胞毒性を示し, また漿果のヘキサン, メタノール抽出物及びヘキサン抽出物に含まれるjuniperexcelsic acid（**79**）に抗結核菌効果が報告されている（Topçu

et al., 1999). *J. oxycedrus*の葉部，樹皮及び漿果のクロロホルム，アセトン及びメタノール抽出物の抗菌活性が調べられている（Metin *et al.*, 1999). *J. phœnicea*から単離されたリポキシゲナーゼ阻害成分として単離されたsandaracopimaric acid（**165**)の結晶構造が報告されている（Comte *et al.*, 1995). *J. procera*の葉部及び樹皮から抗菌活性を有するジテルペン，(+)-*E*-communic acid（**166**)，(+)-*Z*-communic acid（**167**)，(+)-totarol（**168**)（Muhammad *et al.*, 1995)，又，樹皮から，新種のジテルペン，14,15-bisnor-13-oxolabda-8(17), 11(*E*)-dien-19-oic acid（**169**)を含む数種のジテルペンが単離され，強力な抗菌成分として，7β-hydroxyabieta-8,13-dien-11,12-dione（**170**)が見いだされた（Muhammad *et al.*, 1996). *J. sabina*の精油の着床阻害に関与する主成分は，sabinyl acetate（**171**）であることが示された（N. Pages *et al.*, 1996). *J. squamata*から単離されたcedranediol（**172**)のアセトキシ誘導体（**173**)の抗血小板並びに血管緊張低下作用が調べられている（Teng *et al.* 1994). ギリシャ産の*Juniperus*属の4種の精油の抗菌性が調べられ，抗菌成分としてα-terpineol（**174**）が見いだされた（Stassi *et al.*, 1996). *Thuja occidentalis*の葉部の70%エタノール抽出物の抗ウイルス成分として，deoxypodophyllotoxin（**163**)が単離されている（Gerhäuser *et al.*, 1992). ベイスギ（*Thuja plicata*)の腐朽抵抗性の指標としてトロポロン含量が調べられており（Debell *et al.*, 1997)，また，樹幹内のトロポロン含量の分布と腐朽抵抗性の関係について検討されている（Debell *et al.*, 1999). *Thujopsis dolabrata*については，青森ヒバ油の心理的ストレス緩和効果（Okabe *et al.*, 1992)，鋸屑中のマウスなどの齧歯類のかじり抑制（antignawing）成分であるthujopsene（**175**)，carvacrol（**176**)及びβ-thujaplicin（hinokitiol）（**177**)（Ahn *et al.*, 1995)，室内塵中ダニ（ヤケヒョウダニ）に及ぼすヒバ材油の影響（Miyazaki, 1996)，鋸屑中の*Thecodiplosis japonensis*への殺虫活性成分であるcarvacrol（**176**)（Lee *et al.* 1997)，鋸屑に含まれるcarvacrol（**176**)及びβ-thujaplicin（**177**)の殺虫活性及び殺ダニ活性（Ahn *et al.*, 1998)，材部から単離されたγ-thujaplicin（**178**)，β-dolabrin（**179**）及びβ-thujaplicin（**177**）の抗菌活性及びメタロプロテアーゼ阻害活性（Inamori *et al.*, 1999)について報告されている. *Chamaecyparis obtusa*及び*Thuja plicata*に含まれるα-（**180**)，β-（**177**)及びγ-（**178**）thujaplicinsの活性酸素種捕捉能が調べられている(Arima *et al.*, 1997). 森林香気に対する梨状皮質ニューロンの応答について調べられている（Kimoto, 1997). マンソン住血吸虫セルカリア(寄生虫）に対するβ-thujaplicin（**177**)の傷害作用が調べられている（Nargis *et al.*, 1997). UV-Bによるマウスケラチノサイトへのアポトーシス誘導に及ぼすβ-thujaplicin（**177**)の阻害効果について検討されている（Baba *et al.*, 1998). 精油を含むカーペットクリーナーの官能評価並びにダニへの効果が調べられている（Yamamoto *et al.*, 1998). *Biota orientalis*の葉部から，血小板活性化因子(PAF)アンタゴニストとしてpinusolide（**181**）が単離されている（Kim *et al.*, 1999). *Cupressocyparis leylandii*の葉部より，抗菌活性を有するビフラボンであるcupressuflavone（**182**)及び4'-*O*-methylcupressuflavone（**183**)が単離されている（Krauze-Baranowska *et al.*, 1999).

2.4. その他

酵母抽出物をエリシターとして用いて，*Cupressus lusitanica*の培養細胞によるβ-thujaplicin（**177**)の生産（Inada *et al.*, 1993)，(Sakai *et al.*, 1994)，生合成（Yamaguchi *et al.*, 1997, Sakai *et al.*, 1997）及び同培養系抽出物の生理活性（チロシナーゼ阻害，抗酸化性）

(Yamaguchi *et al.*, 1999)について検討されている．ヒノキアスナロ(*Thujopsis dolabrata*)の培養細胞によるβ-thujaplicin (**177**)の生産が検討されている(Fujii *et al.*, 1995)．*J. chinensis*の培養細胞によるpodophyllotoxin (**184**)の生産が検討されている(Muranaka *et al.*, 1998)．

*Cupressus bakeri*に含有される五つのmuurolane (**17-20**, **185**)及びnor-seco-muurolane (**186**)及びnor-muurolane (**187**)セスキテルペンが合成され，それらの化学反応性等が検討されている (Ngo and Brown, 2000)．*Chamaecyparis obtusa*幼苗から放散されるテルペン類の化学組成のエチレンによる変化を調べることにより樹木間相互作用について検討されている (Katoh *et al.*, 1993)．樹木からのテルペン放出の季節変動や，温度，光及び接触の及ぼす影響について検討されている(Yatagai *et al.*, 1995)．超臨界二酸化炭素を用いる抽出が、針葉樹材の揮発成分 (Terauchi *et al.*, 1993)，*Thuja plicata*からのトロポロン類 (Ohira *et al.*, 1994)，*Thujopsis dolabrata*材からのβ-thujaplicin (**177**) (Ohira *et al.*, 1996) 及び，*Chamaecyparis nootkatensis*, *J. communis* (Acda *et al.*, 1998)，等について検討されている．*J. oxycedrus*から以前単離されたアルコール (15-hydroxy-9-epi-β-caryophyllene)の構造が15-hydroxy-β-caryophyllene (**188**)であると訂正されている (Hinkley *et al.*, 1994)．*Thuja occidentalis* の枝部のリグナン類を単離，同定すると共に，[9-$^2H_2$, OC^2H_3] coniferyl alcohol のpinoresinol (**189**)及びlariciresinol (**190**)への取り込み実験を行い，生合成経路について検討されている(Kawai *et al.*, 1999)．ベイスギ(*Thuja plicata*)のpinoresinol-lariciresinol reductase について，それらのエナンチオ選択的変換が検討されている (Fujita *et al.*, 1999)．

3. ま と め

新規化合物の構造決定や成分分析に関しては，新種のテルペノイドの報告並びに，ケモタキソノミーからの精油成分のGC-MSによる定性，定量分析の報告が多く，特に，テルペン類の構造の多様性に注目した研究が多い．利用に関したものでは，テルペン類の含量が高い針葉精油成分の用途開発に関する研究が多い．その中で，生理活性については，各種テルペン類の抗菌，殺虫，殺ダニ活性，心理作用への影響等が報告されている．又，トロポロン類，特にβ-thujaplicin (**177**)の多岐に渡る生理活性（齧歯類の囓り抑制，抗菌，殺虫，殺ダニ，抗寄生虫，メタロプロテアーゼ阻害，チロシナーゼ阻害，抗酸化性，活性酸素種捕捉能，UV-Bによるアポトーシス誘導阻害等）は特記すべきである．また，テルペン類等揮発成分を多く含むヒノキ科樹木抽出成分の場合，不揮発性成分を多く含む他の植物抽出成分と比較して人体への影響が大きいことが予想される．それゆえ，今後，ヒノキ科樹木抽出成分の薬理作用や人体に対する影響を科学的に証明する研究は益々重要となるであろう．さらに，分析技術の発達により，抽出成分に含有される成分，特に微量成分に至るまで，化学構造が決定されつつある現在では，それらの生理活性と併せて，構造-活性相関データの蓄積とともに，抽出成分の用途に応じた付加価値の高い新規利用法の開発が期待される．特に，日本で最も優良な用材の一つとして，人工林の大部分を占めるヒノキについてその抽出物の付加価値を高める利用法の開発を期待したい．

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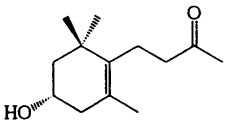
(2000年5月30日受付；2000年12月4日受理)

Summary

The present state of our knowledge on the chemical structures of new compounds, chemotaxisonomic GC-MS analysis and bioactivities of the constituents from Cupressaceae trees, are reviewed with particular reference since 1991. Cupressaceae trees are amongst those that are rich sources of terpenoid compounds. There are a large number of reports about GC-MS analysis of volatile terpenes in leaves. The essential oils and extractives from Cupressaceae trees have a variety of bioactivities, e. g. antimicrobial, insecticidal, miticidal activities, the relaxant effects against a psychological stress, etc. It is worthy of special mention that β-thujaplicin (hinokitiol) has been reported as having a variety of bioactivities, e.g. antignawing, antimicrobial, insecticidal, miticidal, parasiticidal, antimetalloprotease, antityrosinase, antioxidative activities, and scavenging activity against active oxygen, and inhibitory effect on UV-B-induced apotosis. With the development of many sophisticated spectral instruments and chromatographic techniques, isolation and structural elucidation of bioactive compounds in the extracts have become quite facilitation, subsequently to the accumulation of the knowledge of structure-bioactivity relationships. Thus, as research facilities are great improved, on the basis of bioactivity and the chemical structure of constituents in the extract, the exploitation of high valued utilization of the Cupressaceae trees, especially *Chamaecyparis obtusa* known as one of the most important timber in Japan, should be expected.

Key words: Cupressaceae, extractives, new compound, composition, analysis, bioactivity



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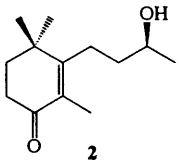

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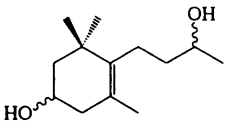

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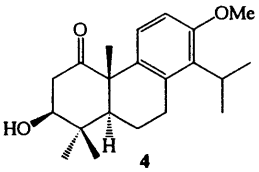

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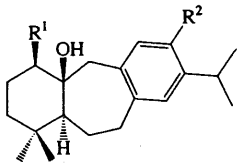
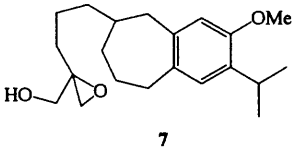


5 : R^1=H, R^2=OMe
6 : R^1=R^2=OH



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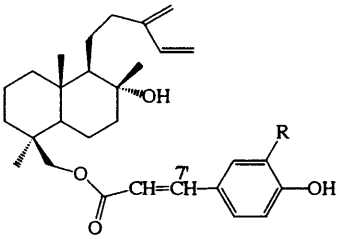
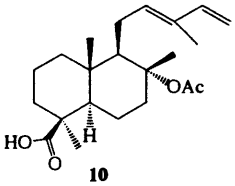


8 : (7'*Z*), R=H
9 : (7'*E*), R=H



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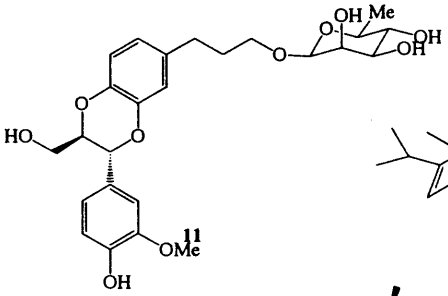

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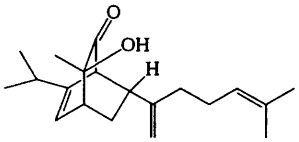

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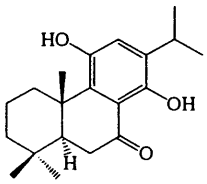

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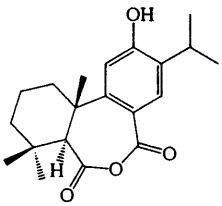

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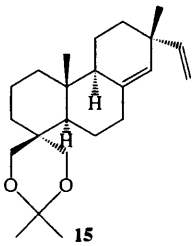

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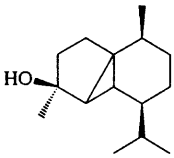

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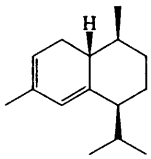

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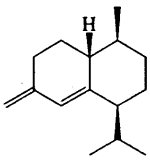

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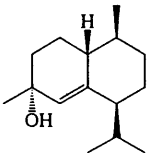

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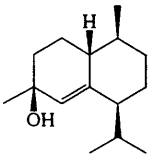

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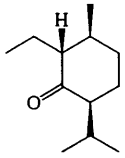
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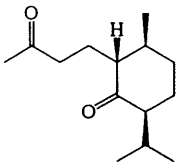
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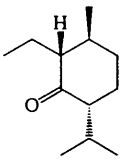
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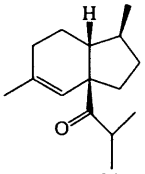
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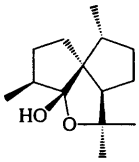
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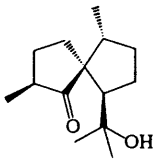
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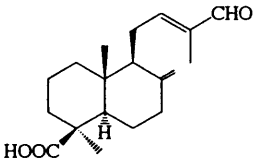
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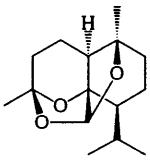
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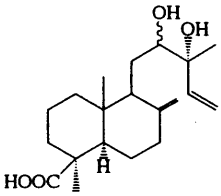
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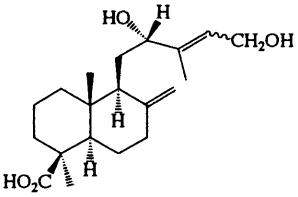
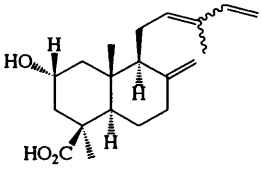

30(*E*)
31(*Z*)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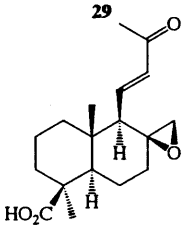
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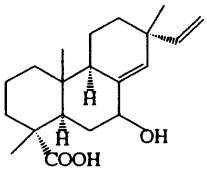
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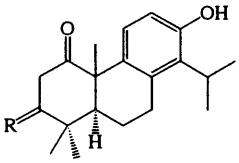
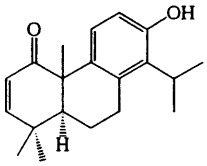

36: R=O
38: R=β-OH, α-H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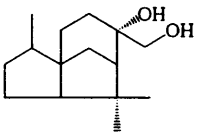
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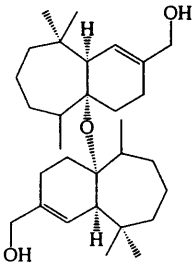
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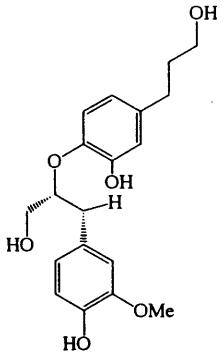

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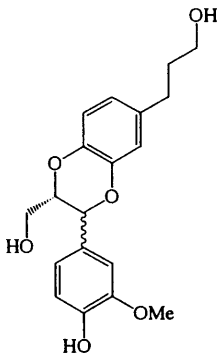
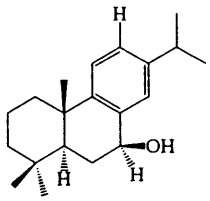


42 (trans)
43 (cis)



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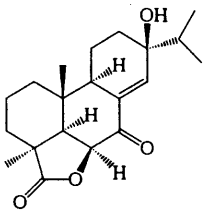

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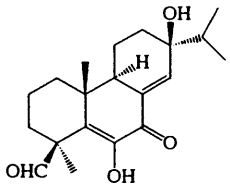

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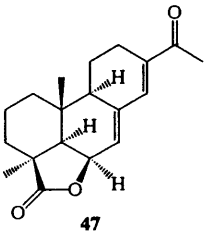

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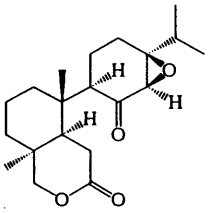

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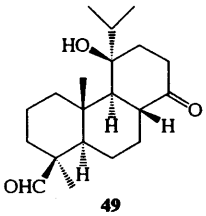

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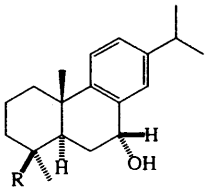
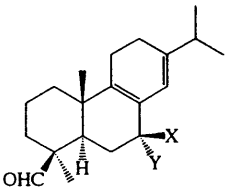
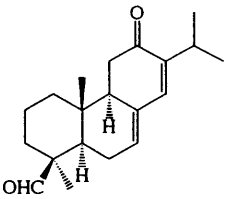


50: R=CH_2OAc
51: R=CHO



52: X=H, Y=OH
53: X, Y=O



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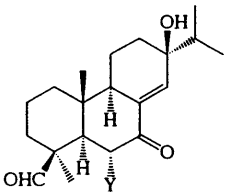
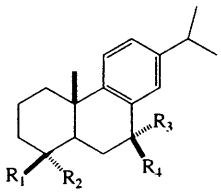
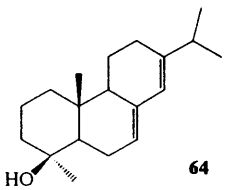


55: Y=H
56: Y=OH



	R_1	R_2	R_3	R_4
57:	OCHO	CH_3	H	H
58:	CH_3	OOH	H	H
59:	OOH	CH_3	H	H
60:	CH_3	OH	=O	
61:	OH	CH_3	=O	
62:	OOH	CH_3	=O	
63:	OOH	CH_3	OH	H



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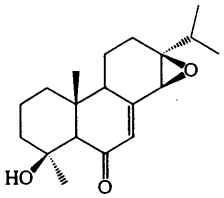

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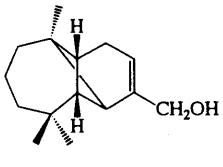

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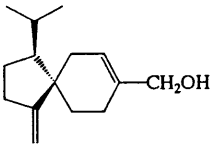

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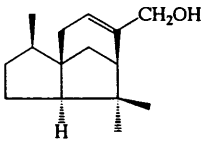

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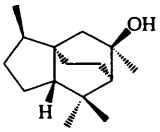

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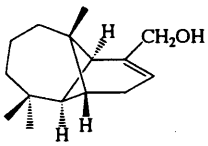

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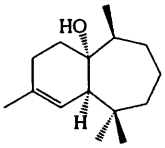

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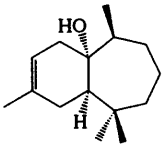

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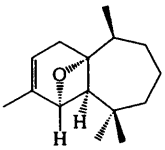

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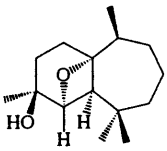

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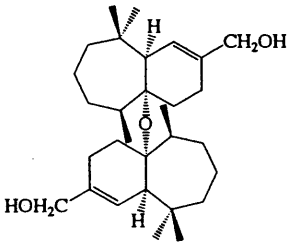

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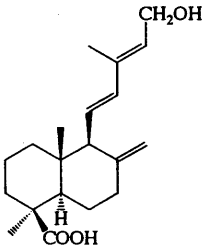

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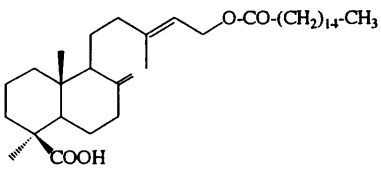

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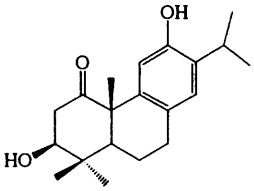

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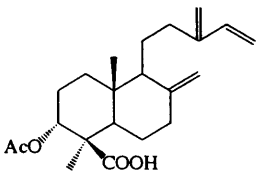

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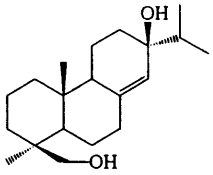

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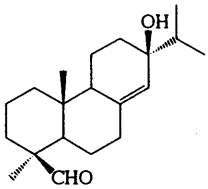

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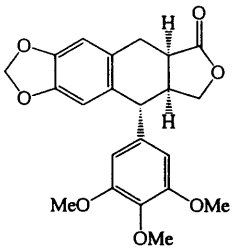

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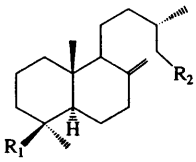
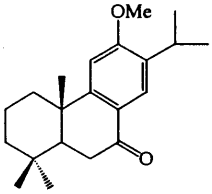


83: R_1=COOH, R_2=CH_2OH
84: R_1=COOH, R_2=CH_2OAc
85: R_1=COOH, R_2=$CH_2OC(O)(CH_2)_{16}CH_3$



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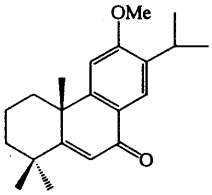

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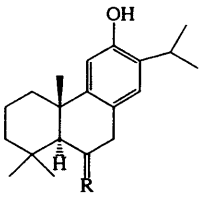
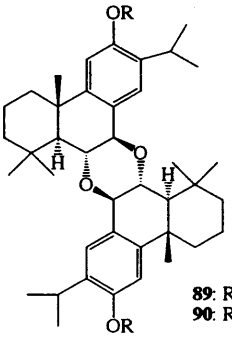
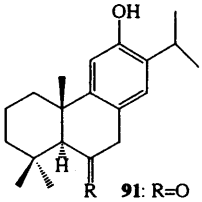


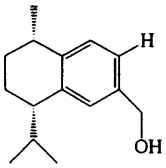
88: R=β-OH, α-H



89: R=H
90: R=Me



91: R=O
92: R=α-OAc, β-H



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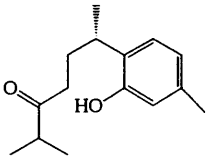

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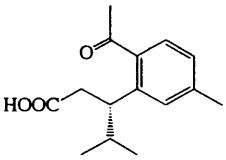

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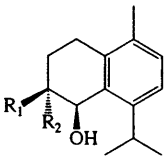
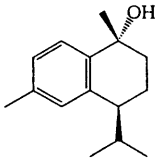


96 R_1=OH, R_2=CH_3
97 R_1=CH_3, R_2=OH



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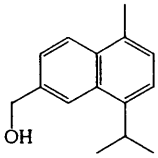

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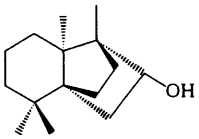

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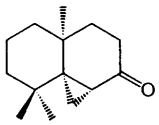

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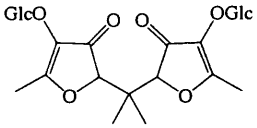

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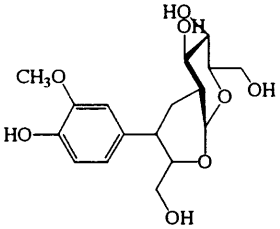

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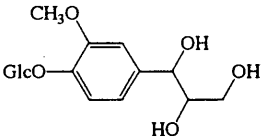

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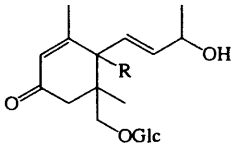
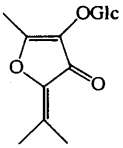


105: R:H
106: R: OH



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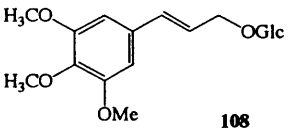

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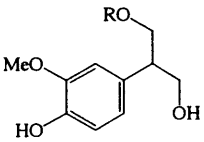
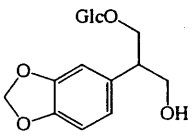


109: R=H
110: R=Glc



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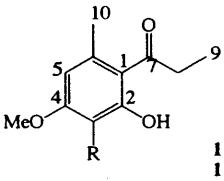
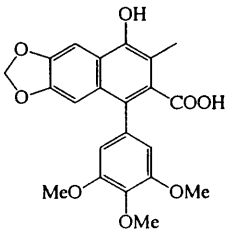


112: R=H
113: R=OMe



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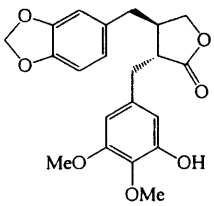

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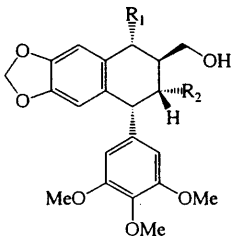
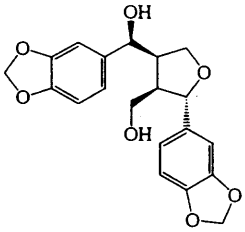


116: R_1=H, R_2=COOMe
118: R_1=OH, R_2=COOH



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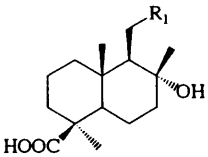
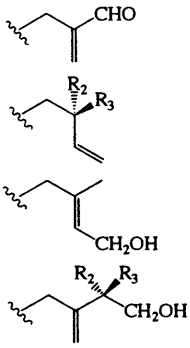


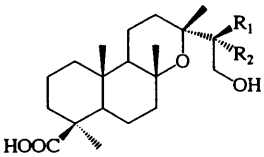


119

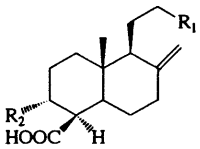
120: R_2=OH, R_3=CH_3
121: R_2=CH_3, R_3=OH

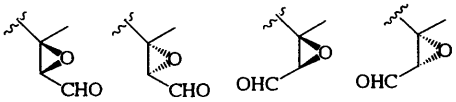
123

122: R_2, R_3=O
124: R_2=OH, R_3=H
125: R_2=H, R_3=OH

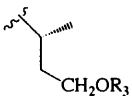


127: R_1=OH, R_2=H
128: R_1=H, R_2=OH

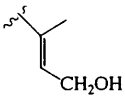




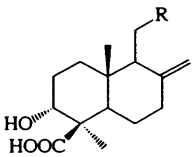
134, 135, 136, 137 : R_2=H
138, 139, 140, 141 : R_2=OAc

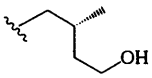


133: R_2=OAc, R_3=Ac
142: R_2=OAc, R_3=H

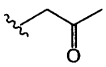


143: R_2=OAc

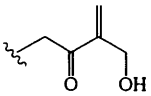




126



129



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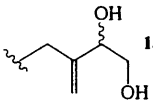
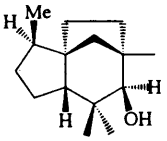


131 + 132



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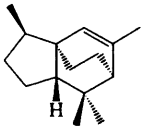

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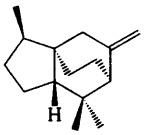

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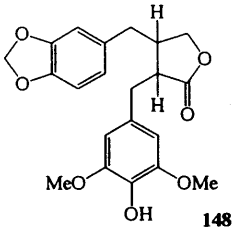

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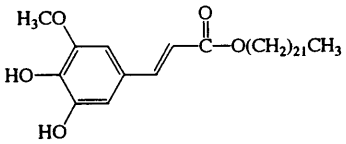

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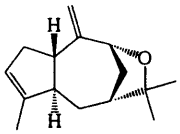

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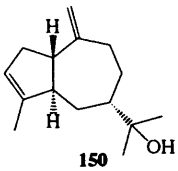

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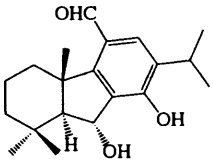

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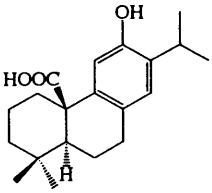

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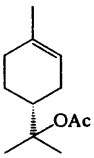

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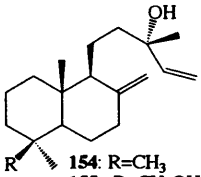
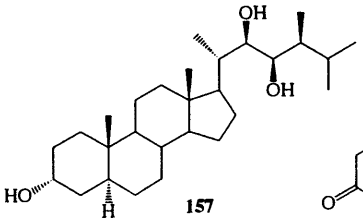


154: R=CH_3
155 : R=CH_2OH
156 : R=CHO



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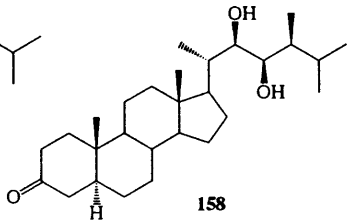

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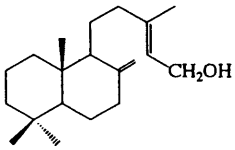
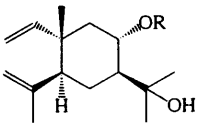
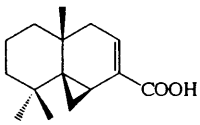


159



160: R=Ac
161: R=H



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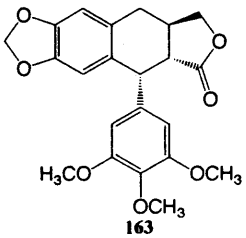

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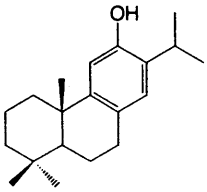

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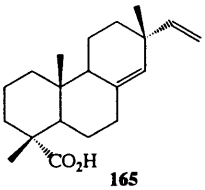

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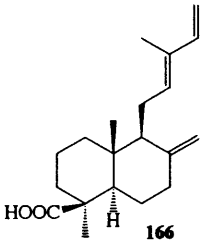

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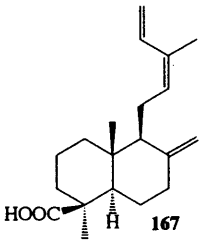

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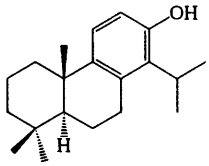

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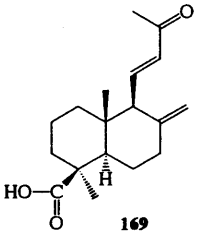

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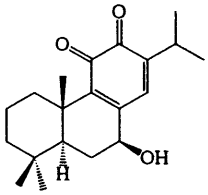

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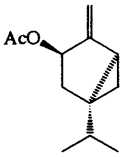

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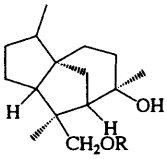
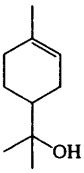


172 R=H
173 R=Ac



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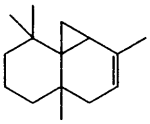

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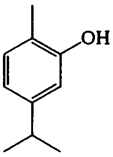

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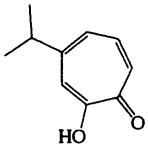

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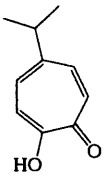

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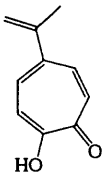

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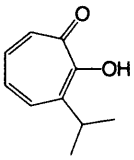

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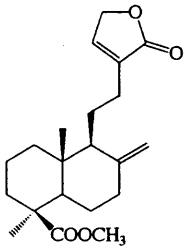

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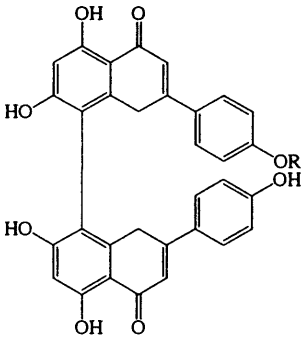
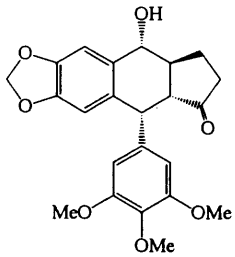


182: R=H
183: R=Me



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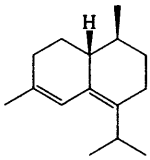

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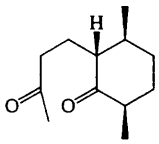

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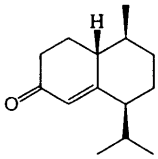

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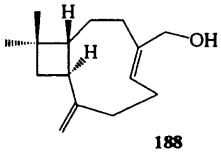

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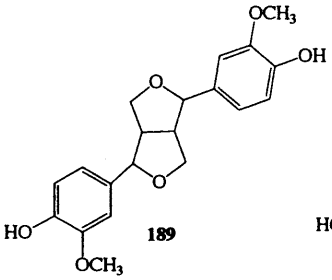

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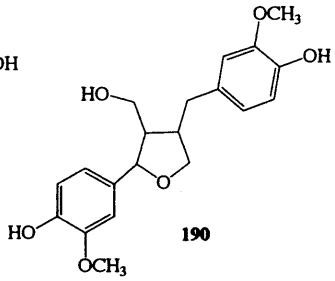

190