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Lignans, Flavonoids and Phenolic Derivatives from *Taxus mairei*

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From the twigs of *Taxus mairei*, 35 lignans, 2 sesquilignans, 4 flavonoids, 3 bisflavonoids, 13 phenolic derivatives, 2 sesquiterpenes, 3 bisnorsesquiterpenes, 3 long-chain carboxylic acids and 4 steroids were isolated. The new lignans and phenolic glucosides include 7′-hydroxynortrachelogenin, 7-hydroxymatairesinol, 3′-*O*-demethylepipinoresinol, taxiresinol 9-acetate, 3′-*O*-demethyltanegool, 8′-epitanegool, 3,3′-dimethoxy-4,4′,9-trihydroxy-7,9′-epoxylignan-7′-one, 3-*O*-demethyldihydrodehydrodiconiferyl alcohol, taxumaiglucoside A heptaacetate, taxumaiglucoside B heptaacetate, and taxumaiglucoside C heptaacetate. Their structures were determined by spectral methods.

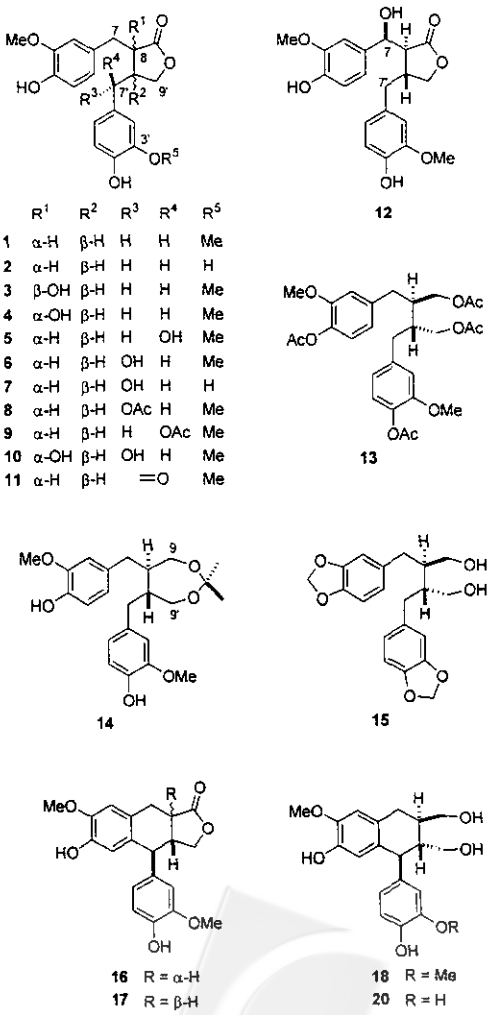
INTRODUCTION

Taxus mairei (台灣紅豆杉) is the only endemic species belonging to the genus *Taxus* found in Taiwan.[1] The chemical constituents of the plant[2-8] have been shown to contain a number of diterpenes, including abietanes, *abeo*-abietanes, taxanes and *abeo*-taxanes. The constituents of taxol,[9] taxamairin A[10] and taxamairin B[10] are known to exhibit antitumor activities. In continuation of our chemical investigation on *T. mairei*, we report herein the constituents of lignans, flavonoids, phenolic derivatives and other miscellaneous compounds.

RESULTS AND DISCUSSION

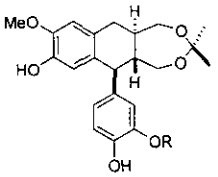
A concentrated acetone extract of the twigs of *T. mairei* was partitioned between water and ethyl acetate. The EtOAc-soluble part was concentrated and the components were separated by repeated chromatography. The fractions of high polarity were further subjected to acetylation and the corresponding peracetylation products were separated by chromatography. The contents of isolated compounds and their pertinent data are listed in the Experimental section. There are 35 lignans (**1-35**), 2 sesquilignans (**36** and **37**), 4 flavonoids (**38-41**), 3 bisflavonoids (**42-44**), 13 phenolic derivatives (**45-57**), 2 sesquiterpenes (**58** and **59**), 3 bisnorsesquiterpenes (**60-62**), 3 long-chain carboxylic acids (**63-65**) and 4 steroids (**66-69**).

The twigs of *T. mairei* are rich in lignans, flavonoids and phenolic derivatives. Among them, α-conidendrin (**16**), isotaxiresinol (**20**), epipinoresinol (**22**), 7′-hydroxylariciresinol (**31**) and procyanidin B-2 decaacetate (**42**) are the major components. Lignans of butyrolactone and bistetrahydrofuran types, such as matairesinol (**1**), nortrachelogenin (**4**) and pinoresinol (**24**), are known to possess antileukemia and cAMP-inhibitory activities.[11,12] Sesquilignans such as **36** and **37** are rare, and only found re-

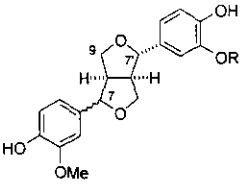


	R^1	R^2	R^3	R^4	R^5
1	α-H	β-H	H	H	Me
2	α-H	β-H	H	H	H
3	β-OH	β-H	H	H	Me
4	α-OH	β-H	H	H	Me
5	α-H	β-H	H	OH	Me
6	α-H	β-H	OH	H	Me
7	α-H	β-H	OH	H	H
8	α-H	β-H	OAc	H	Me
9	α-H	β-H	H	OAc	Me
10	α-OH	β-H	OH	H	Me
11	α-H	β-H	=O		Me

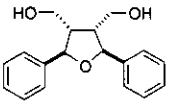
Dedicated to Professor Kung-Tsung Wang on the occasion of his 70th birthday.



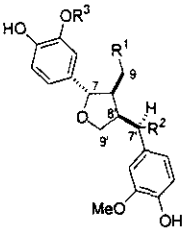
19 R = Me
21 R = H



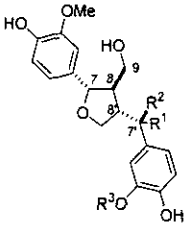
22 7β-aryl, R = Me
23 7β-aryl, R = H
24 7α-aryl, R = Me



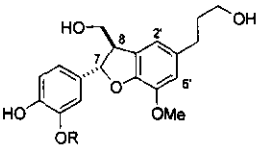
25 (*meso*)



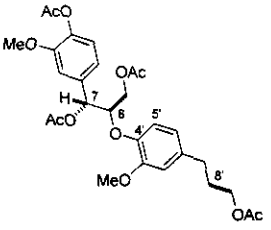
	R^1	R^2	R^3
26	OH	H	Me
27	OH	H	H
28	OAc	H	H
31	OH	OH	Me



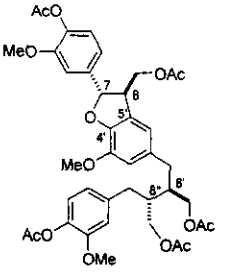
	R^1	R^2	R^3
29	H	OH	Me
30	H	OH	H
32	=O		Me



33 R = Me
34 R = H



35 (*threo*)



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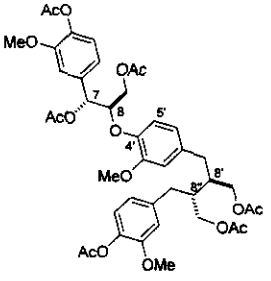

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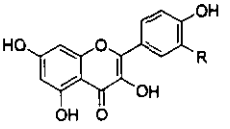
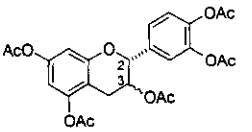
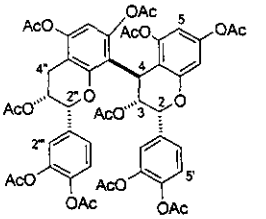


38 R = H
39 R = OH



40 3β-OAc
41 3α-OAc



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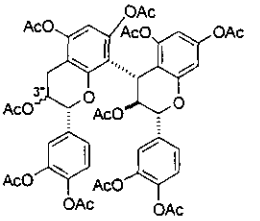
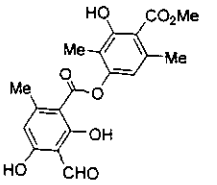


43 3"β-OAc
44 3"α-OAc



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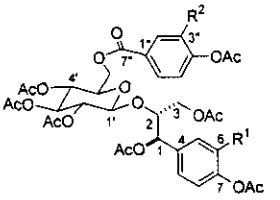
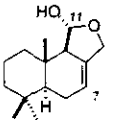


55 $R^1 = R^2 = H$
56 $R^1 = H$, $R^2 = OMe$
57 $R^1 = OMe$, $R^2 = H$



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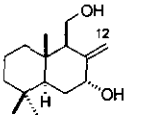

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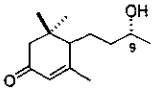

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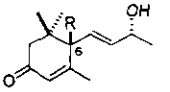
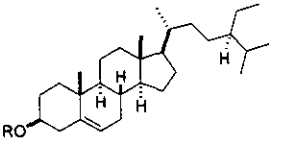
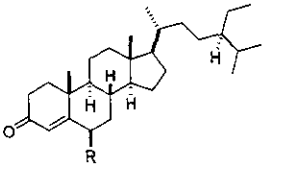


61 R = H
62 R = OH



66 R = H
67 R = Glu(OAc)$_4$



68 R = H
69 R = OH

cently in the wood of *Abies marocana*.[13,35] This study also revealed several new compounds including the phenolic glucosides **55-57**.

The known compounds were identified by comparison of their physical and spectroscopic properties (mp, [α], IR, MS, ^{1}H and ^{13}C NMR) with those reported in the literature, whereas the structures of new compounds were determined as follows.

The ^{1}H and ^{13}C NMR spectra of compound **10** exhib-

ited characteristics similar to those of nortrachelogenin (**4**), except for the signals of H-7′ and C-7′. Compound **10**, showing a molecular ion $[M]^+$ at *m/z* 390, was assigned as 7′-hydroxynortrachelogenin. The carbinyl proton (H-7′) occurred at δ_H 4.80 (d, J = 9.6 Hz) and the corresponding carbon (C-7′) appeared at δ_C 72.9. If one assumes that the two hydroxyl groups at C-7′ and C-8 are intramolecularly hydrogen bonded, the observed large coupling constant ($J_{7',8'}$ = 9.6 Hz) would account for a nearly eclipsed orientation of H-7′ and H-8′. Compound **10**, exhibiting a dextrorotation, was thus tentatively assigned to have the (7′*R*)-configuration.

Compound **12**, showing a molecular ion at *m/z* 374, was determined to be 7-hydroxymatairesinol by comparison of its ^{1}H and ^{13}C spectra with those of matairesinol[16] (**1**). The carbinyl proton (H-7) of compound **12** occurred at δ_H 5.45 as a doublet with a small coupling constant ($J_{7,8}$ = 2.4 Hz). A gauche orientation of H-7 and H-8 would fit such coupling constant when the C-7 hydroxyl group is hydrogen bonded with the C-9 carbonyl group. This deduction thus led to an assignment of (7*S*)-configuration for the dextrorotatory compound **12**.

Compounds **14**, **19** and **21** were readily recognized as the acetonides of secoisolariciresinol[23] (isolated as a tetraacetate **13** in this study), isolariciresinol[24] (**18**) and isotaxiresinol[28] (**20**). The characteristic signals for the isopropylidene groups in acetonides **14**, **19** and **21** occurred as singlets at δ_H~1.33. These acetonides are likely artifacts derived from the reactions of the parent lignan diols with acetone during the extraction procedure.

Compound **23**, showing a molecular ion at *m/z* 344, was determined to be 3′-*O*-demethylepipinoresinol by comparison of its ^{1}H and ^{13}C NMR spectra with those of epipinoresinol[29] (**22**). Pinoresinol[30] (**24**, $C_{20}H_{22}O_6$) with a C_2 symmetry displayed only 10 carbon signals in the ^{13}C NMR spectrum, whereas epipinoresinol (**22**), the C-7 epimer of **24**, showed all the 20 carbon signals. The C-7 and C-7′ protons in **24** appeared as a coalescent signal, whereas the corresponding protons in **22** (or **23**) were not equivalent, occurring as two sets of doublets. The resonances for C-2 and C-2′ in **22** showed at δ_C 108.3 and 108.5, whereas the corresponding resonances in **23** showed at δ_C 109.6 (C-2) and 113.0 (C-2′). Since the change of chemical shift at C-2′ is more prominent, the assignment of **23** as 3′-*O*-demethylepipinoresinol (instead of the 3-*O*-demethyl analog) is reasonable.

By analyses of the ^{1}H and ^{13}C NMR spectra, compound **28** was recognized as the 9-acetate derivative of taxiresinol[28] (**27**). The C-9 protons in **27** occurred at δ_H 3.67 and 3.83, whereas those protons in **28** appeared at lower fields of δ_H 4.15 and 4.32. Compound **30** showing a molecular ion at *m/z* 362, was assigned as 3′-*O*-demethyltanegool by comparison of its ^{1}H NMR spectrum with that of tanegool[32] (**29**). Both **29** and **31** showed molecular ions at *m/z* 376. Compound **31**, exhibiting the NMR spectral characteristics similar to compound **29**, was determined to be the 8′-epimer of **29**. Tanegool **29** is dextrorotatory whereas 8′-epitanegool (**31**) is levorotatory. Their NOESY spectra supported the stereochemical assignment. Both **29** and **31** displayed NOE correlations between H-7 and H-9. However, only the H-8 in **29** showed an NOE correlation with H-7′. No such correlation was found in **31**.

Compound **32** gave rise to a molecular ion at *m/z* 374.1305 in agreement with a molecular formula $C_{20}H_{22}O_7$. The IR absorptions at 3389 and 1683 cm^{-1} were attributable to the hydroxyl and conjugated carbonyl groups. The structure of **32** was determined to be 3,3′-dimethoxy-4,4′,9-trihydroxy-7,9′-epoxylignan-7′-one by the analyses of its ^{1}H and ^{13}C NMR spectra. Individual protons and carbons were assigned by the assistance of the COSY, HMQC and HMBC spectra. The resonances of H-7, H-8 and H-8′ occurred respectively at δ_H 4.57 (d, J = 9 Hz), 2.65 (m) and 4.09 (m), whereas the corresponding C-7, C-8 and C-8′ occurred respectively at δ_C 83.4, 52.3 and 48.8. These data are similar to those found in analogous compounds such as sesaminone[11] and sylvone.[14] The stereochemistry was supported by the NOESY spectrum, showing the correlation of H-8 (at δ_H 2.65) with the phenyl proton H-2 (at δ_H 6.88) as well as the correlation of H-8′ (at δ_H 4.09) with H-9 (at δ_H 3.62 and 3.72). The absolute configuration of the levorotatory compound **32** was tentatively assigned as (7*S*, 8*R*, 8′*S*) by analogy to those 7,9′-epoxy lignans **26-31** isolated from the same plant extract.

From the MS, ^{1}H and ^{13}C NMR spectra, compound **34** was readily determined to be the 3-*O*-demethyl derivative of dihydrodehydrodiconiferyl alcohol[33] (**33**). Compound **36** bears a skeleton of sesquilignan, which is constructed by a linkage of dihydrodehydrodiconiferyl alcohol with another nine-carbon moiety. After detailed analysis of the spectral properties of **36**, including COSY, NOESY, HMQC and HMBC spectra, the structure was determined to have the C8′-C8″ linkage.[13,35] Compound **37** is also a sesquilignan with a skeleton constructed by compound **35** and a nine-carbon segment.[13,35] The structure of **37** was confirmed by spectral methods including FAB-MS, IR, ^{1}H, ^{13}C (DEPT), NOESY, HMQC and HMBC NMR spectra. The C8-C8′ linkage in **37** is evident.

Compounds **55-57** are three phenolic glucoside peracetates. The molecular ion of **55** displayed at *m/z* 760.2186, consistent with a molecular formula $C_{36}H_{40}O_{18}$.

In the ^{1}H NMR spectrum, the signals at δ_H 7.01 (2H, d, J = 8 Hz), 7.18 (2H, d, J = 8 Hz), 7.27 (2H, d, J = 8 Hz) and 8.04 (2H, d, J = 8 Hz) were attributable to the eight aromatic protons on the two *para*-disubstituted phenyl rings. The moiety of 2,3,4,6-*O*-tetraacylglucoside was deduced from the six carbon signals at δ_C 62.5 (C-6′), 68.5 (C-4′), 71.2 (C-2′), 71.8 (C-5′), 72.8 (C-3′) and 100.9 (C-1′). The anomeric proton H-1′ (at δ_H 4.71) was axially oriented as it exhibited a relatively large coupling constant of 7.8 Hz. The glyceryl moiety was indicated by the three carbinyl carbons occurring at δ_C 63.1 (C-3), 74.7 (C-1) and 78.2 (C-2). The HMBC spectrum showed a correlation between H-1′ (at δ_H 4.71) and C-2 (at δ_C 78.2), indicating that the glycoside bond was connected with C-2. The structure of **55** (namely taxumaiglucoside A heptaacetate) was thus determined to be 1-(4-acetoxyphenyl)-1,3-diacetoxyprop-2-yl 6-*O*-(4-acetoxybenzoyl)-2,3,4-*O*-triacetyl-β-glucopyranoside. Individual protons and carbons were assigned by the assistance of the COSY, HMBC and HMQC spectra. As H-1 and H-2 exhibited a relatively large coupling constant of 7.2 Hz, compound **55** might have *threo* configuration by comparison with analogous glycerol derivatives.[15]

The molecular ion of **56** appearing at *m/z* 790.2119 was in agreement with a molecular formula $C_{37}H_{42}O_{19}$. Compound **56** exhibited a ^{13}C NMR spectrum similar to that of **55**, except for an additional carbon resonance at δ_C 56.1 attributable to a methoxy group. The structure of **56** (namely taxumaiglucoside B heptaacetate) was assigned as 1-(4-acetoxyphenyl)-1,3-diacetoxyprop-2-yl 6-*O*-(4-acetoxy-3-methoxybenzoyl)-2,3,4-*O*-triacetyl-β-glucopyranoside. The resonances at δ_H 7.18 (d, J = 2 Hz, H-2″), 7.63 (dd, J = 8, 2 Hz, H-6″) and 7.66 (d, J = 2 Hz, H-5″) were ascribed to the protons on a trisubstituted phenyl ring. On the other hand, the *para* disubstituted phenyl ring showed the four aromatic protons at δ_H 7.01 (2H, d, J = 8 Hz) and 7.27 (2H, d, J = 8 Hz). The HMBC spectrum showed a correlation of benzoyl carbon (at δ_C 165.3) with the aromatic proton at δ_H 7.63 (H-6″), thus confirming the position of the methoxy group at C-3″ instead of C-6. The large coupling constant of 7.2 Hz between H-1 and H-2 was in agreement with their *threo* relationship in the glyceryl moiety.[15]

Compound **57**, $[M]^+$ exhibiting at *m/z* 790.2294, is an isomer of **56**. The structure of **57** (namely taxumaiglucoside C heptaacetate) was assigned as 1-(4-acetoxy-3-methoxyphenyl)-1,3-diacetoxyprop-2-yl 6-*O*-(4-acetoxybenzoyl)-2,3,4-*O*-triacetyl-β-glucopyranoside according to the analyses of the ^{1}H and ^{13}C NMR spectra. The methoxy group of **57** is on the C-6 position differing from that of **56**. The three aromatic protons on the trisubstituted phenyl ring of **57** displayed at the relatively high fields of δ_H 6.85 (H-5), 6.87 (H-8) and 6.97 (H-9). The *threo* configuration of the glyceryl moiety was also supported by the relatively large coupling constant of 7.2 Hz between H-1 and H-2.[15]

EXPERIMENTAL

General

Yanagimoto micro melting point apparatus, Jasco Dip-180 digital polarimeter, Finnigan TSQ-46c mass spectrometer, Perkin-Elmer 983G infrared spectrophotometer, Bruker AM-300 WB nuclear magnetic resonance spectrometer (^{1}H NMR, 300 MHz; ^{13}C NMR, 75 MHz), Waters M-45 high-pressure liquid chromatograph (Waters R401 RI detector) with Hibar Lichrosorb Si 60 column (10 μm or 7 μm, 25 cm × 1 cm i.d.) were used. Merck 9385 silica gel (230-400 mesh) was used for flash CC. Merck 5554 Kieselgel 60 F254 sheets were used for TLC analyses.

Plant Material

The twigs (1.4 kg) of *T. mairei* were collected in the remote mountains in Tong-Shi, Taichung county, at an elevation of *ca.* 2100 m. A voucher specimen has been deposited in the Herbarium of National Taiwan University. The air-dried material was exhaustively extracted with acetone (7 L × 3). The acetone extract was concentrated to give 100 g of residue, which was diluted with water (200 mL) and extracted with EtOAc (100 mL × 3). The combined EtOAc extracts were concentrated to give an oil (75 g), which was absorbed with 110 g of SiO_2 and then chromatographed on a column packed with 650 g of SiO_2 by elution with gradients of hexane and EtOAc. Every 80-120 mL of eluent was collected in one fraction. Separation of chemical components was monitored by TLC analyses. Appropriate fractions were combined: (i) the elution with gradients of EtOAc/hexane (2:8, 4 L) giving compounds **66** and **68**; (ii) the elution with gradients of EtOAc/hexane (3:7, 2 L) giving compounds **45-50**, **58**, **60-65** and **69**; (iii) the elution with gradients of EtOAc/hexane (6:4, 2 L) giving compounds **1**, **14**, **19** and **51-54**; (iv) the elution with gradients of EtOAc/hexane (8:2, 2 L) giving compounds **4-6**, **8**, **9**, **11**, **12**, **16**, **17**, **22-29**, **32**, **33**, **38** and **59**; (v) the elution with EtOAc/hexane (9:1, 1 L) giving compounds **2**, **7**, **10**, **15**, **17**, **18**, **21**, **30**, **31**, **34** and **39**; (vi) the elution with EtOAc (1 L) giving compounds **13**, **20**, **35-37**, **40**, **41** and **67** after peracetylation (Ac_2O, pyridine, 25 °C, 24 h); (vii) the elution with gradients of EtOAc/Me_2CO (6:4, 1 L) giving compounds **42-44** after peracetylation; and (viii) the elution with EtOAc/Me_2CO (4:6, 1 L) giving compounds **55-57** after peracetylation. Purification of each compound was carried out by using flash CC

and HPLC.

The weight and percentage of each component (based on 28 g of EtOAc-soluble part) are listed as follows: (-)-matairesinol[16] **1** (17.1 mg, 0.061%), (-)-3′-*O*-demethylmatairesinol[17] **2** (13.4 mg, 0.048%), (-)-epinortrachelogenin[18] **3** (16.8 mg, 0.060%), (-)-nortrachelogenin[19] **4** (10.1 mg, 0.036%), (*S*)-(-)-7′-hydroxymatairesinol[20] **5** (9.0 mg, 0.032%), (*R*)-(+)-7′-hydroxymatairesinol[21] **6** (33.9 mg, 0.121%), (*R*)-(+)-7′-hydroxy-3′-*O*-demethylmatairesinol[21] **7** (11.5 mg, 0.041%), (*R*)-(+)-7′-acetoxymatairesinol[20] **8** (6.4 mg, 0.023%), (*S*)-(+)-7′-acetoxymatairesinol[20] **9** (6.7 mg, 0.024%), 7′-(+)-hydroxynortrachelogenin **10** (9.0 mg, 0.032%), 7′-(+)-oxomatairesinol[22] **11** (14.6 mg, 0.052%), 7-(+)-hydroxymatairesinol **12** (9.0 mg, 0.032%), (-)-secoisolariciresinol tetraacetate[23] **13** (344.4 mg, 0.123%), secoisolariciresinol-9,9′-acetonide[23] **14** (285.6 mg, 0.102%), (-)-dihydrocubebin[25] **15** (123.2 mg, 0.044%), (-)-α-conidendrin[26] **16** (179.8 mg, 0.642%), (+)-β-conidendrin[27] **17** (11.5 mg, 0.041%), (+)-isolariciresinol[24] **18** (10.1 mg, 0.036%), (+)-isolariciresinol-9,9′-acetonide[24] **19** (13.4 mg, 0.048%), (+)-isotaxiresinol[28] **20** (898.8 mg, 0.321%), (+)-isotaxiresinol-9,9′-acetonide[28] **21** (618.8 mg, 0.221%), (+)-epipinoresinol[29] **22** (10.1 mg, 0.362%), (+)-3′-*O*-demethylepipinoresinol **23** (7.8 mg, 0.028%), (+)-pinoresinol[30] **24** (11.5 mg, 0.041%), *meso*-neoolivil[31] **25** (6.4 mg, 0.023%), (+)-lariciresinol[24] **26** (24.4 mg, 0.087%), taxiresinol[28] **27** (397.6 mg, 0.142%), taxiresinol 9-acetate **28** (9.0 mg, 0.032%), (+)-tanegool[32] **29** (7.8 mg, 0.028%), (+)-3′-*O*-demethyltanegool **30** (7.3 mg, 0.026%), (-)-8′-epitanegool **31** (795.2 mg, 0.284%), (-)-3,3′-dimethoxy-4,4′,9-trihydroxy-7,9′-epoxylignan-7′-one **32** (8.1 mg, 0.029%), (-)-dihydrodehydrodiconiferyl alcohol[33] **33** (9.0 mg, 0.032%), (-)-3-*O*-demethyldihydrodehydrodiconiferyl alcohol **34** (4.5 mg, 0.016%), (-)-*threo*-3,3′-dimethoxy-4′,8-epoxyligna-4,7,9,9′-tetraol tetraacetate[34] **35** (12.6 mg, 0.045%), (-)-sesquipinsapol B pentaacetate[13,35] **36** (7.6 mg, 0.027%), (+)-sesquimarocanol B hexaacetate[13,35] **37** (4.5 mg, 0.016%), kaemferol[36] **38** (6.7 mg, 0.024%), quercetin[36] **39** (14.4 mg, 0.048%), (+)-catechin pentaacetate[37] **40** (34.4 mg, 0.123%), (-)-epicatechin pentaacetate[37] **41** (350 mg, 0.125%), procyanidin B-2 decaacetate[38] **42** (660.8 mg, 0.236%), procyanidin B-3 decaacetate[39] **43** (462.0 mg, 0.165%), procyanidin B-4 decaacetate[40] **44** (512.4 mg, 0.183%), 4-hydroxybenzaldehyde **45** (11.8 mg, 0.042%), methyl 4-hydroxybenzoate **46** (13.4 mg, 0.048%), 4-hydroxy-3-methoxybenzaldehyde **47** (10.1 mg, 0.036%), 4-hydroxy-3-methoxycinnamaldehyde **48** (3.1 mg, 0.011%), methyl-2,4-dihydroxy-3,6-dimethylbenzoate **49** (10.1 mg, 0.036%), 3-(4-hydroxyphenyl)propan-1-ol **50** (6.4 mg, 0.023%), 3-(3,4-dihydroxyphenyl)propan-1-ol **51** (3.9 mg, 0.014%), 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol **52** (7.0 mg, 0.025%), 2-(4-hydroxy-3-methoxyphenyl)propane-1,3-diol **53** (12.6 mg, 0.045%), 4-[(3-formyl-2,4-dihydroxy-6-methyl)benzoyloxy]-2-hydroxy-3,6-dimethyl benzoic acid methyl ester[41] **54** (9.0 mg, 0.032%), (+)-taxumaiglucoside A heptaacetate **55** (13.4 mg, 0.048%), (+)-taxumaiglucoside B heptaacetate **56** (9.0 mg, 0.032%), (+)-taxumaiglucoside C heptaacetate **57** (6.8 mg, 0.024%), isodrimeninol[42] **58** (10.1 mg, 0.036%), (-)-drim-8(12)-ene-7α,11-diol[43] **59** (4.5 mg, 0.016%), blumenol C[44] **60** (6.7 mg, 0.024%), (*R*)-(+)-9-hydroxy-4,7*E*-megastigmadien-3-one[45] **61** (3.4 mg, 0.012%), (+)-vomifoliol[46] **62** (17.6 mg, 0.063%), octadeca-9*Z*,12*Z*,15*Z*-trienoic acid **63** (7.8 mg, 0.028%), octadeca-9*Z*,12*Z*-dienoic acid **64** (10.1 mg, 0.036%), octadeca-9*Z*-enoic acid **65** (11.5 mg, 0.041%), (-)-β-sitosterol[47] **66** (65 mg, 0.234%), (-)-β-sitosteryl-β-D-glucopyranoside tetraacetate[48] **67** (24.1 mg, 0.086%), (+)-β-sitosterone[49] **68** (7.8 mg, 0.028%) and (+)-6β-hydroxy-β-sitosterone[49] **69** (6.7 mg, 0.024%).

7′-Hydroxynortrachelogenin (10)

Oil, $[\alpha]_D^{29}$ +12 ($CHCl_3$; *c* 0.9). IR (neat) 3438, 1746 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.66 (m, H-8′), 3.10 (d, *J* = 13.5 Hz, H-7b), 3.14 (d, *J* = 13.5 Hz, H-7a), 3.59-3.75 (2H, m, H-9′), 3.78 (OMe), 3.82 (OMe), 4.80 (d, *J* = 9.6 Hz, H-7′), 6.50-6.80 (6 ArH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.9 (C-7), 48.0 (C-8′), 55.8 (OMe), 55.9 (OMe), 67.5 (C-9′), 72.9 (C-7′), 76.5 (C-8), 109.1 (C-2′), 112.9 (C-5′), 114.3 (C-5), 114.5 (C-2), 119.8 (C-6′), 123.5 (C-6), 125.7 (C-1′), 132.7 (C-1), 145.0 (C-4), 145.9 (C-4′), 146.5 (C-3′), 146.8 (C-3), 177.9 (C-9). FAB-MS *m/z* 390 $[M]^+$.

7-Hydroxymatairesinol (12)

Oil, $[\alpha]_D^{29}$ +11 ($CHCl_3$; *c* 1.6). IR: 3425, 1750 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.59 (m, H-8), 2.73 (dd, *J* = 9.9, 14.7 Hz, H-7′a), 3.02 (m, H-8′), 3.16 (dd, *J* = 4.8, 14.7 Hz, H-7′b), 3.72-3.92 (2H, m, H-9′), 3.76 (s, OMe), 3.82 (s, OMe), 5.45 (d, *J* = 2.4 Hz, H-7), 6.50-6.80 (6 ArH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.4 (C-7′), 41.1 (C-8′), 47.3 (C-8), 55.7 (OMe), 55.8 (OMe), 60.3 (C-9′), 80.9 (C-7), 110.8 (C-5′), 107.3 (C-2′), 114.2 (C-2), 117.4 (C-5, 6′), 120.4 (C-6), 130.1 (C-1′), 130.5 (C-1), 144.0 (C-4′), 145.2 (C-4), 146.4 (C-3), 146.5 (C-3′), 178.0 (C-9). EI-MS (70 eV) *m/z* (rel. intensity) 374 (100) $[M]^+$.

Secoisolariciresinol-9,9′-acetonide (14)

Oil. IR (neat) 3425 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, two Me), 1.57 (m, H-8, 8′), 2.57 (dd, *J* = 13.8, 6.9 Hz, H-7b, 7′b), 2.66 (dd, *J* = 13.8, 7.2 Hz, H-7a, 7′a), 3.39 (dd, *J* = 12.6, 4.2 Hz, H-9a, 9′a), 3.80 (2 OMe), 3.81 (dd, *J* = 12.6, 2.0 Hz, H-9b, 9′b), 6.50-6.80 (6 ArH). ^{13}C NMR

($CDCl_3$, 75 MHz) δ 24.7 (2 CH_3), 37.1 (C-7, 7′), 42.8 (C-8, 8′), 55.6 (2 OMe), 61.8 (C-9, 9′), 101.2 (O-C-O), 111.2 (C-2, 2′), 113.8 (C-5, 5′), 121.8 (C-6, 6′), 132.3 (C-1, 1′), 143.6 (C-4, 4′), 146.2 (C-3, 3′). EI-MS (70 eV) *m/z* (rel. intensity) 402 (11) $[M]^+$, 137 (100).

Isolariciresinol-9,9′-acetonide (19)

Gum, $[\alpha]_D^{24}$ +32 ($CHCl_3$; *c* 2.9). IR (KBr) 3369 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, two Me), 1.80 (m, H-8′), 1.82 (m, H-8), 2.50 (dd, *J* = 12.0, 15.6 Hz, H-7b), 2.63 (dd, *J* = 4.4, 15.6 Hz, H-7a), 3.38 (d, *J* = 10.8 Hz, H-7′), 3.30-3.71 (4H, m, H-9, 9′), 3.77 (OMe), 3.82 (OMe), 6.25 (s, H-2), 6.50 (d, *J* = 1.5 Hz, H-2′), 6.53 (s, H-5), 6.59 (dd, *J* = 1.5, 8.0 Hz, H-6′), 6.78 (d, *J* = 8.0 Hz, H-5′). EI-MS (70 eV) *m/z* (rel. intensity) 400 (100) $[M]^+$.

Isotaxiresinol-9,9′-acetonide (21)

Gum, $[\alpha]_D^{24}$ +52 ($CHCl_3$; *c* 1.9). IR (KBr) 3360 cm^{-1}. ^1H NMR (CD_3COCD_3) δ 1.30 (s, two Me), 1.74 (m, H-8), 2.03 (m, H-8′), 2.62 (2H, m, H-7), 3.38 (d, *J* = 11.8 Hz, H-7′), 3.42-3.82 (m, H-9, 9′), 3.97 (s, OMe), 6.24 (s, H-2), 6.56 (dd, *J* = 8.0, 1.8 Hz, H-6′), 6.60 (d, *J* = 1.8 Hz, H-2′), 6.65 (s, H-5), 6.84 (d, *J* = 8.0 Hz, H-5′). ^{13}C NMR (CD_3COCD_3, 75 MHz) δ 24.2 (2 CH_3), 31.5 (C-7), 41.8 (C-7′), 47.6 (C-8), 49.1 (C-8′), 55.8 (OMe), 63.9 (C-9), 65.5 (C-9′), 100.4 (O-C-O), 111.9 (C-2), 114.8 (C-5), 115.6 (C-5′), 116.0 (C-2′), 120.6 (C-6′), 126.6 (C-1), 132.5 (C-6), 137.0 (C-1′), 143.3 (C-3′), 144.2 (C-4′), 144.9 (C-4), 145.5 (C-3). FAB-MS *m/z* 386 (100) $[M]^+$.

3′-*O*-Demethylepipinoresinol (23)

Gum, $[\alpha]_D^{24}$ +95.3 ($CHCl_3$; *c* 1.9). IR (neat) 3381 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.84 (m, H-8′), 3.16 (d, Hz, H-8), 3.72 (2H, m, H-9a), 3.78 (m, H-9′a), 3.81 (OMe), 4.03 (d, *J* = 10.0 Hz, H-9′b), 4.31 (d, *J* = 6.9 Hz, H-7′), 4.74 (d, *J* = 5.4 Hz, H-7), 6.70 (dd, *J* = 2.0, 8.0 Hz, H-6′), 6.75 (d, *J* = 8.0 Hz, H-5′), 6.78 (d, *J* = 7.8 Hz, H-5), 6.81 (dd, *J* = 1.8, 7.8 Hz, H-6), 6.87 (d, *J* = 2.0 Hz, H-2′), 6.96 (d, *J* = 1.8 Hz, H-2). ^{13}C NMR (CD_3COCD_3, 75 MHz) δ 49.9 (C-8), 54.7 (C-8′), 55.8 (OMe), 69.2 (C-9), 70.5 (C-9′), 81.7 (C-7), 87.6 (C-7′), 109.6 (C-2), 114.6 (C-5), 114.9 (C-5′), 117.0 (C-6), 118.8 (C-6′), 113.0 (C-2′), 130.3 (C-1), 133.0 (C-1′), 143.8 (C-3), 144.3 (C-3′), 146.0 (C-4), 147.7 (C-4′). EI-MS (70 eV) *m/z* (rel. intensity) 344 (20) $[M]^+$, 151 (100).

Taxiresinol 9-Acetate (28)

Gum. IR (neat) 3400, 1726 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.03 (s, Ac), 2.43 (m, H-8), 2.68 (m, H-8′), 2.80 (2H, m, H-7′), 3.85 (OMe), 3.69 (dd, *J* = 6.9, 8.0 Hz, H-9′b), 3.98 (dd, *J* = 6.4, 8.0 Hz, H-9′a), 4.15 (dd, *J* = 6.4, 10.2 Hz, H-9b), 4.32 (dd, *J* = 6.4, 10.2 Hz, H-9a), 4.69 (d, *J* = 6.3 Hz, H-7), 6.50-6.80 (6 ArH). ^{13}C NMR (CD_3COCD_3, 75 MHz) δ 20.9 (Ac), 33.1 (C-7′), 42.3 (C-8′), 48.8 (C-8), 55.8 (OMe), 62.6 (C-9), 72.6 (C-9′), 82.9 (C-7), 111.2 (C-2), 112.9 (C-5), 114.4 (C-2′), 115.1 (C-5′), 118.3 (C-6), 121.0 (C-6′), 131.7 (C-1′), 134.4 (C-1), 143.5 (C-4), 143.5 (C-4′), 144.0 (C-3′), 146.5 (C-3), 169.6 (Ac). FAB-MS *m/z* 388 $[M]^+$.

3′-*O*-Demethyltanegool (30)

Gum, $[\alpha]_D^{24}$ +66.4 (MeOH; *c* 1.1). IR (neat) 3433 cm^{-1}. ^1H NMR (CD_3COCD_3, 300 MHz) δ 1.87 (m, H-8), 2.53 (m, H-8′), 3.28 (2H, m, H-9), 3.73 (OMe), 3.91 (dd, *J* = 7.5, 8.7 Hz, H-9′a), 4.13 (dd, *J* = 4.5, 8.7 Hz, H-9′b), 4.51 (d, *J* = 7.5 Hz, H-7′), 4.52 (d, *J* = 7.5 Hz, H-7), 6.50-6.80 (6 ArH). FAB-MS *m/z* 352 $[M]^+$.

8′-Epitanegool (31)

Gum, $[\alpha]_D^{24}$ -69 (acetone; *c* 1.0) . IR (neat) 3432 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.23 (m, H-8), 2.58 (m, H-8′), 3.58 (2H, m, H-9), 3.69 (m, H-9′a), 3.89 (m, H-9′b), 3.76 (OMe), 3.77 (OMe), 4.42 (d, *J* = 4.5 Hz, H-7′), 4.45 (d, *J* = 5.1 Hz, H-7), 6.50-6.80 (6 ArH). FAB-MS *m/z* 376 $[M]^+$.

3,3′-Dimethoxy-4,4′,9-trihydroxy-7,9′-epoxylignan-7′-one (32)

Gum, $[\alpha]_D^{24}$ -60.4 (acetone; *c* 1.0). IR (neat) 3389, 1683 cm^{-1}. ^1H NMR (CD_3COCD_3, 300 MHz) δ 2.65 (m, H-8), 3.62 (d, *J* = 5.7, 10.8 Hz, H-9a), 3.72 (dd, *J* = 4.2, 10.8 Hz, H-9b), 3.75 (s, OMe), 3.79 (s, OMe), 4.04 (m, H-9′a), 4.07 (m, H-9b′), 4.09 (m, H-8′), 4.57 (d, *J* = 9.0 Hz, H-7), 6.68 (d, *J* = 8.0 Hz, H-5), 6.70 (dd, *J* = 2.0, 8.0 Hz, H-6), 6.75 (d, *J* = 8.0 Hz, H-5′), 6.88 (d, *J* = 2.0 Hz, H-2), 7.43 (dd, *J* = 2.0, 8.0 Hz, H-6′), 7.45 (d, *J* = 2.0 Hz, H-2′). ^{13}C NMR (CD_3COCD_3, 75 MHz) δ 48.8 (C-8′), 52.3 (C-8), 55.6 (OMe), 55.7 (OMe), 60.2 (C-9), 70.4 (C-9′), 83.4 (C-7), 109.1, 110.4, 113.8, 114.0, 119.7, 123.4, 129.1, 132.3, 145.3, 146.8, 146.9, 150.8, 197.7. FAB-MS *m/z* 374 $[M]^+$. HR-MS for $C_{20}H_{22}O_7$ requires 374.1366; found 374.1305.

3-*O*-Demethyldihydrodehydrodiconiferyl Alcohol (34)

$[\alpha]_D^{24}$ -10 (MeOH; *c* 1.0). IR (neat) 3208 cm^{-1}. ^1H NMR (CD_3COCD_3, 300 MHz) δ 1.77 (2H, m, H-8′), 2.53 (2H, t, *J* = 7.8 Hz, H-7′), 3.02 (m, H-8), 3.54 (2H, t, *J* = 6.4 Hz, H-9′), 3.75 (OMe), 3.83 (2H, m, H-9), 5.47 (d, *J* = 6.3 Hz, H-7), 5.47 (br s, H-2′), 5.47 (br s, H-6′), 6.77 (d, *J* = 8.1 Hz, H-5), 6.86 (dd, *J* = 1.8, 8.1 Hz, H-6), 7.02 (d, *J* = 1.8 Hz, H-2). ^{13}C NMR (CD_3COCD_3, 75 MHz) δ 31.6 (C-8′), 35.0 (C-7′), 54.4 (C-8), 55.7 (OMe), 61.0 (C-9′), 63.9 (C-9), 87.2 (C-7), 109.6 (C-2), 114.7 (C-2′), 115.4 (C-6′), 115.9 (C-5),

118.7 (C-6), 128.9 (C-1′), 133.8 (C-1), 135.4 (C-5′), 144.0 (C-3′), 146.3 (C-4′), 146.4 (C-4), 147.4 (C-3). FAB-MS *m/z* 346 $[M]^+$.

Taxumaiglucoside A Heptaacetate (55)

Oil, $[\alpha]_D^{28}$ +9.0 ($CHCl_3$; *c* 0.5). IR (neat) 1758, 1604 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.87-2.27 (21H, 7 Ac), 3.78 (2H, m, H-5′, 3a), 4.05 (m, H-3b), 4.12 (m, H-2), 4.31 (dd, *J* = 4.8, 12.0 Hz, H-6′a), 4.49 (dd, *J* = 2.4, 12.0 Hz, H-6′b), 4.71 (d, *J* = 7.8 Hz, H-1′), 5.01 (dd, *J* = 7.8, 9.0 Hz, H-2′), 5.12 (dd, *J* = 9.3, 9.3 Hz, H-4′), 5.17 (dd, *J* = 9.0, 9.3 Hz, H-3′), 5.82 (d, *J* = 7.2 Hz, H-1), 7.01 (2H, d, *J* = 8.0 Hz), 7.18 (2H, d, *J* = 8.0 Hz), 7.27 (2H, d, *J* = 8.0 Hz), 8.04 (2H, d, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.4-21.0 (7 Ac), 62.5 (C-6′), 63.1 (C-3), 68.5 (C-4′), 71.2 (C-2′), 71.8 (C-5′), 72.8 (C-3′), 74.7 (C-1), 78.2 (C-2), 100.9 (C-1′), 121.6 (C-3′, C-5″), 121.8 (C-6, C-8), 127.3 (C-1″), 128.3 (C-9, C-5), 131.2 (C-2″, C-6″), 133.5 (C-4), 150.8 (C-7), 154.5 (C-4″), 165.1 (C-7″), 169.1-170.3 (7 Ac). FAB-MS *m/z* 783 $[M + Na]^+$. HR-MS for $C_{36}H_{40}O_{18}$ requires 760.2215; found 760.2186.

Taxumaiglucoside B Heptaacetate (56)

Oil, $[\alpha]_D^{28}$ +4.0 ($CHCl_3$; *c* 0.5). IR (neat) 1759, 1605 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.84-2.27 (21H, 7 Ac), 3.78 (2H, m, H-5′, 3a), 3.86 (s, OMe), 4.05 (m, H-3b), 4.13 (m, H-2), 4.29 (dd, *J* = 4.8, 12.0 Hz, H-6′a), 4.49 (dd, *J* = 2.4, 12.0 Hz, H-6′b), 4.70 (d, *J* = 7.8 Hz, H-1′), 5.00 (dd, *J* = 7.8, 9.0 Hz, H-2′), 5.13 (dd, *J* = 9.3, 9.3 Hz, H-4′), 5.19 (dd, *J* = 9.0, 9.3 Hz, H-3′), 5.83 (d, *J* = 7.2 Hz, H-1), 7.01 (2H, d, *J* = 8.0 Hz), 7.18 (1H, d, *J* = 8.0 Hz, H-5″), 7.27 (2H, d, *J* = 8.0 Hz), 7.63 (1H, dd, *J* = 2.0, 8.0 Hz, H-6″), 7.66 (1H, d, *J* = 2.0 Hz, H-2″). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.6-21.1 (7 Ac), 56.1 (OMe), 62.5 (C-6′), 63.2 (C-3), 68.6 (C-4′), 71.3 (C-2′), 71.8 (C-5′), 72.8 (C-3′), 74.8 (C-1), 78.2 (C-2), 101.9 (C-1′), 113.5 (C-5″), 121.8 (C-8, C-6), 122.9 (C-6″), 127.3 (C-4), 128.0 (C-2″), 128.3 (C-5, C-9), 128.4 (C-1″), 143.9 (C-3″), 150.8 (C-7), 151.3 (C-4″), 165.3 (C-7″), 168.0-170.2 (7 Ac). FAB-MS *m/z* 813 $[M + Na]^+$. HR-MS for $C_{37}H_{42}O_{19}$ requires 790.2320; found 790.2119.

Taxumaiglucoside C Heptaacetate (57)

Oil, $[\alpha]_D^{28}$ +3.4 ($CHCl_3$; *c* 1.0). IR (neat) 1757, 1604 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.80-2.30 (7 Ac), 3.78 (m, H-5), 3.83 (s, OMe), 3.86 (m, H-3a), 4.03 (m, H-3b), 4.14 (m, H-2), 4.30 (dd, *J* = 4.8, 12.0 Hz, H-6′a), 4.45 (dd, *J* = 2.4, 12.0 Hz, H-6′b), 4.73 (d, *J* = 7.8 Hz, H-1′), 5.02 (dd, *J* = 7.8, 9.0 Hz, H-2′), 5.13 (dd, *J* = 9.3, 9.3 Hz, H-4′), 5.17 (dd, *J* = 9.0, 9.3 Hz, H-3′), 5.82 (d, *J* = 7.2 Hz, H-1), 6.85 (1H, d, *J* = 2.0 Hz, H-5), 6.87 (1H, d, *J* = 8.0 Hz, H-8), 6.97 (1H, dd, *J* = 2.0, 8.0 Hz, H-9), 7.16 (2H, d, *J* = 8.0 Hz), 8.05 (2H, d, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.4-21.1 (7 Ac), 55.9 (OMe), 62.6 (C-6′), 63.2 (C-3), 68.6 (C-4′), 71.2 (C-2′), 71.8 (C-5′), 72.9 (C-3′), 75.2 (C-1), 78.4 (C-2), 101.1 (C-1′), 111.4, 121.7, 123.0 (2 C), 127.3, 128.0, 128.3 (2 C), 131.3, 140.2, 151.2 (2 C), 165.3, 168.0-170.2 (7 Ac). FAB-MS *m/z* 813 $[M + Na]^+$. HR-MS for $C_{37}H_{42}O_{19}$ requires 790.2320; found 790.2294.

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Key Words

Taxus mairei; Taxaceae; Twigs; Lignans; Flavonoids; Phenolics; Terpenes; Steroids.

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