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Terpenes and lignans from leaves of *Chamaecyparis formosensis*

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Abstract

84 chemical constituents were isolated from the leaves of *Chamaecyparis formosensis*. These components include 18 sesquiterpenes, 40 diterpenes, 8 flavones, 7 lignans and 11 miscellaneous compounds. Among them 3 sesquiterpenes, 7 diterpenes and one lignan are new compounds, the structures of which were determined by chemical and spectral methods.

Keywords: Chamaecyparis formosensis; Cupressaceae; Leaves; Sesquiterpenes; Diterpenes; Flavones; Lignans; Sterols

1. Introduction

Chamaecyparis formosensis Matsumura, known as Taiwan red cypress (Li & Keng, 1994) is indigenous to the high mountain area of Taiwan. It is called red cypress since the bark appears to be slightly reddish brown color. The wood is frequently used in building and for expensive furniture. The plant is known to possess strong resistance against wood-decaying fungi (Saeki, Sumimoto, & Kondo, 1973; Harayama, Cho, & Inubushi, 1977). The chemical constitution of the root, bark, wood, pericarps and leaves of this plant has been investigated (Kafuku & Ichikawa, 1931; Nozoe, Cheng, & Toda, 1966; Fang, Lai, & Cheng, 1986; Fang, Sheu, & Cheng, 1986; Hsu, Fang, & Cheng, 1995). The studies of leaves are, however, limited to its essential oil (Kafuku & Ichikawa, 1931; Fang et al., 1986). We report herein a more detailed investigation of the constituents of leaves.

2. Results and discussion

The acetone extract of the leaves of *C. formosensis* was subjected to chromatography to give 84 components, including 18 sesquiterpenes, 40 diterpenes, 8 flavones, 7 lignans and 11 miscellaneous compounds (see Section 3). Among them, 73 components are known compounds, whose structures were readily identified by comparison of their physical and spectroscopic properties (m.p., [α], IR, UV, MS, ^{1}H and ^{13}C NMR spectra) with authentic samples.

The 84 various compounds (**1**–**84**) that were isolated are described in summary form in Section 3; 73 are known (see Section 3). Compounds **15**–**17**, **36**, **40**, **41**, **45**, **52**, **53**, **56** and **73**, however, have not been reported thus far. Their structures were determined by chemical and spectral methods. The molecular formula of **15** ($C_{13}H_{22}O_2$) was deduced from the exact mass measurement of its molecular ion, $[M]^+$ appearing at m/z 210.1614. The IR absorptions at 3448 and 1711 cm^{-1} were attributable to hydroxyl and carbonyl groups. The ^{13}C NMR spectrum showed 13 carbons, in which resonances at δ 65.0 (carbinyl), 208.5 (carbonyl), 124.8 and 135.9 (olefinic) were diagnostic. The ^{1}H NMR spectra showed four methyl groups at δ 0.95 (s), 0.99 (s), 1.57 (s, vinyl) and 2.12 (s, methyl ketone). The carbinyl proton resonance occurred at δ 3.91 (tdd, $J=10$, 6, 4 Hz), indicating its axial position on a cyclohexane ring. By assistance of the HMBC and HMQC spectral analyses, the structure of dinorsesquiterpene **15** was determined as 3-hydroxymegastigm-5-en-9-one. Com-

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pound **15** with (3*S*)-configuration is dextrorotatory, $[\alpha]_D^{25}$ +34.5 ($CHCl_3$; *c* 0.5), whereas the (3*R*)-enantiomer obtained enzymatically (Miyase, Ueno, Takizawa, Kobayashi, & Oguchi, 1988) is levorotatory, $[\alpha]_D^{23}$ −84.4 (MeOH; *c* 0.48). The (*R*)-enantiomer was also previously synthesized (Aakermann, Guillard, & Liaaen-Jensen, 1993), but no optical rotation was reported. Treatment of **15** with (±)-2-phenylbutanoic anhydride according to Horeau's method (Fiaud, Horeau, & Kagan, 1997) supported the (*S*)-configuration.

Compound **16** ($C_{13}H_{22}O_2$) gave rise to a molecular ion $[M]^+$ at *m*/*z* 210.1614. Compound **16** is a constitutional isomer of compound **15**; however, it showed an IR absorption at 1655 cm^{-1} and a UV absorption at 261 nm typical for an enone group. The corresponding carbon resonances for enone occurred at δ 130.9 (C-5), 164.7 (C-6) and 199.1 (C-4). The ^1H NMR spectrum also revealed the presence of a carbinyl proton (H-9) at δ 3.84 (m). Compound **16** with $[\alpha]_D^{25}$ +8.1 ($CHCl_3$; *c* 0.4) was thus determined to be (*S*)-9-hydroxymegastigm-5-en-4-one, whose C-9 chirality was established using Horeau's method (Fiaud et al., 1997).

Compound **17** ($C_{13}H_{24}O_2$), $[M]^+$ appearing at *m*/*z* 212.1771, was assigned as megastigm-5-ene-3,9-diol according to ^1H and ^{13}C NMR analyses. Compound **17** existed as a single isomer as shown by NMR spectra. The two carbinyl protons appeared at δ 3.77 (m, H-9) and 3.91 (tdd, J=10, 6, 4 Hz, H-3). Thus, H-3 was axially oriented and the C-3 hydroxyl group was equatorially oriented. Compound **17** was levorotatory, $[\alpha]_D^{25}$ −33.8 ($CHCl_3$; *c* 0.5), but, its absolute configuration was not rigorously determined.

The molecular formula $C_{21}H_{30}O_3$ of compound **36** was deduced from the exact mass measurement of its molecular ion $[M]^+$ at *m*/*z* 330.2183. The IR absorptions at 3327 and 1706 cm^{-1} were attributable to hydroxyl and carbonyl groups. The ^1H NMR spectrum indicated the presence of an isopropyl group (occurring at δ 1.25 (3 H, d), 1.26 (3 H, d) and 3.19 (1 H, sept)), three methyl groups on tertiary carbons (occurring at δ 1.08 (s), 1.11 (s) and 1.58 (s)) and a methoxy group on a phenyl ring (occurring at δ 3.76 (s)). Based on this information and the HMQC and HMBC spectral analyses, the structure of **36** was assigned as 3β-hydroxy-1-oxo-13-*O*-methyltotarol. The H-3 was axially oriented as it displayed at δ 3.60 as a doublet of doublets (J=12, 4.8 Hz). The HMBC spectrum showed correlation of C-13 (at δ 156.9) with H-11 (at δ 7.19), H-12 (at δ 6.75) and the MeO group (at δ_H 3.76). The position of the methoxy group on C-13 was thus established. A chemical correlation of **36** with 3β-hydroxy-1-oxototarol (**37**) (Kuo & Chen, 1994) was carried out to confirm the structural assignment. Indeed, treatment of **37** with diazomethane in Et_2O solution (25°C, 16 h) yielded an *O*-methylation product identical with compound **36**.

The ^1H NMR of compound **40** was similar to that of pisiferanol (**39**) (Hasegawa, Kojima, & Hirose, 1985), except for an additional signal at δ 3.76 (3 H, s) attributable to a methoxy group on a phenyl ring. Thus, compound **40** was assigned as 12-*O*-methylpisiferanol. An *O*-methylation product obtained by treatment of pisiferanol **39** with diazomethane in Et_2O was identical with compound **40**. The 9(20 → 10)*abeo*-abietane **40** also showed the two characteristic C-20 protons as an AB pattern at δ_H 2.53 (d, J=13.8 Hz) and 2.97 (d, J=13.8 Hz) in the ^1H NMR spectrum (Hasegawa et al., 1985).

Compound **41** ($C_{20}H_{30}O_3$) exhibited an ^1H NMR spectrum similar to that of pisiferanol **39** ($C_{20}H_{30}O_2$), except for the presence of an additional carbinyl proton at δ 3.69 (*m*). The ^{13}C NMR spectrum showed the corresponding secondary carbinyl carbon occurring at δ_C 76.7 and another tertiary carbinyl carbon occurring at δ 72.4. Compound **41** was assigned as 1β-hydroxypisiferanol. The diagnostic H-20α and H-20β resonances occurred at δ 2.51 (d, J=14 Hz) and 3.29 (d, J=14 Hz), respectively (Hasegawa et al., 1985). The occurrence of H-20β at a lower field, as compared to **40**, was due to the deshielding effect of the 1β-OH group. The NOESY spectrum showed the correlation of H-1α (at δ 3.69) with H-20α (at δ 2.51), supporting the assigned stereochemistry.

Compound **45** was determined as 10-deoxy-4,18-epoxy-12-methoxy-4,5-*seco*-pisiferan-19-ol from the spectral analyses. The exact mass of molecular ion $[M]^+$ at *m*/*z* 332.2340 was in agreement with a molecular formula $C_{21}H_{32}O_3$. In the ^1H NMR spectrum, two aromatic protons occurred as two singlets at δ 6.60 (H-11) and 6.93 (H-14) indicating their *para* positions. The phenyl ring bearing a C-12 methoxy group (at δ_H 3.77) and a C-13 isopropyl group was typical to pisiferanes. A methylene group at δ 2.00 (m, H-18) was attributable to an oxirane moiety, whereas another methylene group occurring as an AB type at δ 3.11 (d, J=10.6 Hz) and δ 3.62 (d, J=10.6 Hz) was attributable to a CH_2OH group. The structural assignment was supported by the ^{13}C, COSY and HMBC spectra, but, the stereochemistry at C-4 and C-10 remains unknown.

Compounds **51**–**53** are ester derivatives of labda-13(16),14-diene-8α,19-diol **50** as inferred from their ^1H and ^{13}C NMR spectra. Compound **51** was previously isolated from *Juniperus thurifera* (San Feliciano et al., 1988). Compound **51** showed proton resonances at δ 6.27 (d, J=16.0 Hz), 7.58 (d, J=16.0 Hz), 6.82 (d, J=8.4 Hz, 2 H) and 7.42 (d, J=8.4 Hz, 2 H) for an (*E*)-*p*-hydroxycinnamic ester. On the other hand, compound **52** displayed proton resonances at δ 5.79 (d, J=12.8 Hz), 6.81 (d, J=12.8 Hz), 6.76 (d, J=8.6 Hz,

2 H) and 7.56 (d, $J=8.6$ Hz, 2 H) attributable to a (*Z*)-*p*-hydroxycinnamic ester. The coupling constant (12.8 Hz) for the two olefinic protons in compound **52** was smaller than that in the *E*-isomer **51** (16 Hz).

Besides the pertinent proton resonances for the labdadiene moiety, compound **53** also exhibited five proton resonances at δ 6.25 (d, $J=15.9$ Hz), 7.56 (d, $J=15.9$ Hz), 6.89 (d, $J=8.1$ Hz), 7.00 (d, $J=1.7$ Hz) and 7.05 (dd, $J=8.1$, 1.7 Hz) attributable to an (*E*)-4-hydroxy-3-methoxycinnamate moiety. The stereochemistry of **53** was established by NOE experiments. For example, irradiation of the C-3′ methoxy group (at δ_H 3.90) caused an enhancement of H-2′ (at δ_H 7.00). Irradiation of the 10-Me group (at δ_H 0.82) caused enhancements of H-19 (at δ_H 3.98 and 4.27) and the 8β-Me group (at δ_H 1.13).

Compound **56a** ($C_{22}H_{34}O_4$) was obtained by acetylation of the parent alcohol. Compound **56a** contained a carboxylic group as inferred from the characteristic carbon resonance at δ_C 181.8 and IR absorptions at 3500–2500 and 1760 cm^{-1}. The signal at δ_C 170.3 was attributable to an acetyl group. The ^1H NMR spectrum showed three singlets at δ_H 0.72, 1.01 and 1.24 for three methyl groups on tertiary carbons. A vinyl methyl group occurred at δ_H 1.72, whereas an acetyl group occurred at δ_H 1.91. The conjugated diene moiety was indicated by the proton resonances at δ_H 4.85 (H-12), 4.87 (H-15), 5.16 (H-15) and 5.73 (H-14), as well as by the carbon resonances at δ 110.3 (C-15), 129.7 (C-12), 135.8 (C-13) and 148.6 (C-14). By comparison of the ^1H and ^{13}C spectra with those of *trans*-communic acid **54** (Thomas, 1966; Fang, Hsu, & Cheng, 1989), compound **56a** was assigned as 8α-acetoxylabda-12*E*,14-dien-19-oic acid. The C-10 methyl group appeared at a high field of δ_H 0.72 due to the shielding effect of the C-4 carboxyl group. By using a procedure of oxymercuration-demercuration (Barrero, Sanchez, Altarejos, Perales, & Torres, 1991), a methyl ester of *trans*-communic acid was previously converted to 8β-hydroxylabda-12,14-dien-19-oic acid methyl ester, of which C-10 methyl group occurred at a lower field of δ_H 0.80 due to the deshielding effect of the 8β-hydroxyl group.

Compound **73** was subjected to peracetylation (Ac_2O, pyridine) to give **73a**. The ^1H and ^{13}C NMR spectra of **73a** indicated the presence of five acetyl groups. Two diagnostic methyl groups appearing at δ 3.83 (s) and δ 1.17 (d, $J=6.1$ Hz) were attributable to an aromatic methoxy group and a methyl group of rhamnose. The exact mass measurement of molecular ion $[M]^+$ at *m*/*z* 702.2518 led to a molecular formula $C_{35}H_{42}O_{15}$. Thus, **73a** was inferred to contain an 18-carbon core structure of lignan by deduction of 1 methoxy carbon, 6 carbons from rhamnose and 10 carbons from 5 acetyl groups. A proton resonance at δ_H 4.68 (d, $J=1.4$ Hz) was ascribed to the axial anomeric proton (H-1″). Compound **73a** was determined to be 9′-(β-rhamnopyranosyl)-3-methoxy-3′:7,4′:8-diepoxy-neolignan-4,9-diol pentaacetate. Following analysis of the HMBC spectrum, the core structure of benzodioxane-type neolignan was established and individual protons and carbons were assigned. The 7,8-*trans* relationship was inferred from the relatively large coupling constant of 7.8 Hz between H-7 (at δ 4.87) and H-8 (at δ 4.17) (Fang, Lee, & Cheng, 1992). The *trans* isomers of such diepoxyneolignans usually exhibit larger coupling constants $J_{7,8}$ (ca. 8 Hz) than the *cis* isomers (ca. 3 Hz) (Fang et al., 1992). Compound **73a** likely has (7*R*,8*R*)-configuration as indicated by negative CD (θ) values at $\lambda=368$, 307 and 256 nm, a common feature of related benzodioxane systems, but this remains to be proven (Silva, Barbosa-Filho, Yoshida, & Gottlieb, 1989).

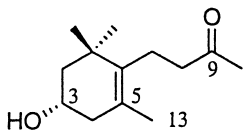
3. Experimental

3.1. General

Yanaco MP-500D melting point apparatus, JASCO DIP-1000 polarimeter, Perkin-Elmer 983G infrared spectrophotometer, Hitachi U-3210 ultraviolet-visible spectrophotometer, Bruker AM-300 spectrometer, Finnigan TSQ-46C mass spectrometer (EI-MS), JEOL SX-102A spectrometer (FAB-MS), JEOL JMS-HX 110 mass spectrometer (HR-MS) and Waters M501 HPLC with Lichrosorb Si-60 (7 μm) column (Waters R401 RI detector) 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.

3.2. Material

The leaves of *C. formosensis* Matsumura were collected from mountains in the north part of Taiwan. A voucher specimen is deposited in the Herbarium of National Taiwan University. The air-dried leaves (18 kg) were extracted with Me_2CO (60 l × 3). The extract was filtered through a column of activated charcoal, concentrated and partitioned between EtOAc and water (v/v = 1:1). The EtOAc-soluble part was concentrated (360 g), coated with silica gel (720 g) and chromatographed on a silica gel column (2.5 kg) by elution with gradients of hexane, EtOAc, Me_2CO and MeOH. 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 hexane (1.5 l) giving compounds **2**, **10**–**13**, **24**–**26**, **32**, **40**, **47**, **57** and **58**; (ii) the elution with gradients of EtOAc/hexane (1, 2, 3, 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90%, 1 l each) giving compounds **1**, **3**–**9**, **14**–**23**, **27**–**31**, **33**–**39**, **41**–**46**, **48**–



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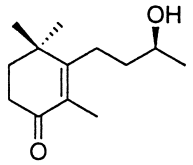

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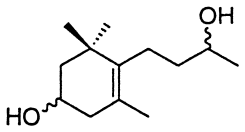

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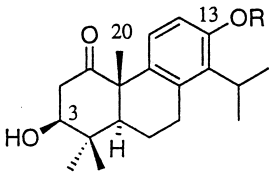
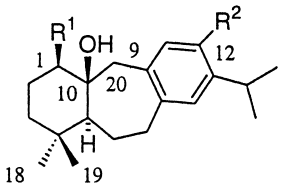
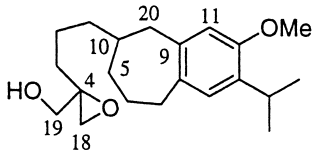


36 R = Me
37 R = H



39 R^1 = H, R^2 = OH
40 R^1 = H, R^2 = OMe
41 R^1 = R^2 = OH



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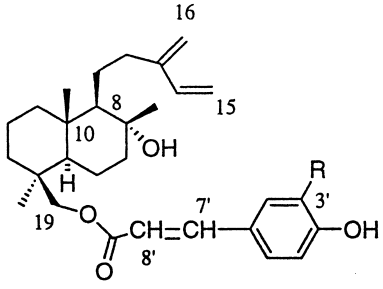
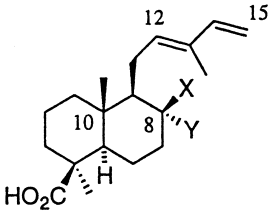
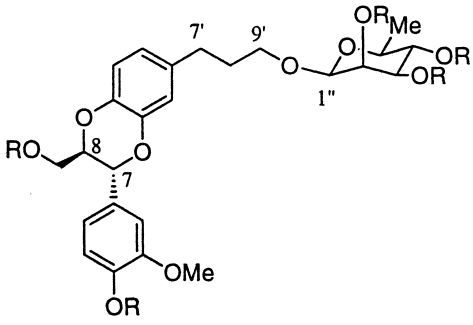


51 (7'*E*), R = H
52 (7'*Z*), R = H
53 (7'*E*), R = OMe



54 X, Y = CH_2
56a X = Me, Y = OAc



73 R = H
73a R = Ac

55, **67**–**71**, **74**–**79** and **81**–**84**; (iii) the elution with EtOAc (1 l) giving compound **59**; (iv) the elution with gradients of Me_2CO/EtOAc (10, 20, 30, 40, 50, 60, 70, 80 and 90%, 1 l each) giving compounds **56** (as the parent alcohol), **60**–**66**, **72** (as the parent triol) and **80** and (v) the elution with Me_2CO (0.8 l) followed by a gradient of Me_2CO/MeOH (1:1, 0.8 l) giving compound **73** (as the parent polyhydroxy compound). The total weight of these components was 238.5 g at this stage. Purification of the components collected from the fractions (i)–(iii) was carried out by using flash CC and HPLC. The fractions (iv) and (v) were subjected to acetylation (Ac_2O, pyridine, 25°C, 24 h), respectively, and the products were further separated by flash CC or HPLC.

The weight and percentage of each purified component (based on 238.5 g total weight of material collected from CC) are listed as follows: α-cadinol (Bottini & Garfagnoli, 1987) (**1**, 7.75 g, 3.25%), cadina-4(15),9-diene (Andersen et al., 1977) (**2**, 2.05 g, 0.86%), eudesm-4(15)-ene-1,6-diol (Gutierrez & Herz, 1988) (**3**, 596 mg, 0.25%), chaenocephalol (Box, Bardouille, & Chan, 1977) (**4**, 453 mg, 0.19%), eudesm-3-en-11-ol (Kutney & Singh, 1984) (**5**, 1.31 g, 0.55%), eudesm-4-en-11-ol (Beek, Kleis, Posthumus, & Veldhuizen, 1989) (**6**, 1.53 g, 0.64%), eudesm-4(15)-en-5-ol (Humber, Pinder, & Williams, 1967) (**7**, 1.36 g, 0.57%), cryptomeridol (Dolejs & Herout, 1961) (**8**, 549 mg, 0.23%), thujopsenol (Norin, 1961) (**9**, 358 mg, 0.15%), thujopsenic acid (Norin, 1961) (**10**, 501 mg, 0.21%), α-humulene (Peppard & Sharpe, 1980) (**11**, 1.62 g, 0.68%), β-sesquiphellandrene (Bohlmann & Suwita, 1979) (**12**, 1.07 g, 0.45%), 6,7-epoxycaryophyll-3(15)-ene (Warnhoof & Srinivason, 1973) (**13**,

692 mg, 0.29%), cedrol (Breitholle & Fallis, 1978) (**14**, 2.29 g, 0.96%), 3-hydroxymegastigm-5-en-9-one (**15**, 22 mg, <0.01%), 9-hydroxymegastigm-5-en-4-one (**16**, 19 mg, <0.01%), megastigm-5-en-3,9-diol (**17**, 16 mg, <0.01%), oplopanone (Takeda, Minato, & Ishikawa, 1966) (**18**, 859 mg, 0.36%), ferruginol (Fang, Sou, Chiu, & Cheng, 1993) (**19**, 763 mg, 0.32%), 12-*O*-methylferruginol (Matsumoto & Usui, 1979) (**20**, 739 mg, 0.31%), abieta-8,11,13-triene (Brieskorn, Fuchs, Bredenberg, Mcchesney, & Wenkert, 1964) (**21**, 1.00 g, 0.42%), *O*-methylpisiferic acid (Yatagai & Takahashi, 1980) (**22**, 6.80 g, 2.85%), pisiferic acid (Banerjee, Hurtado, Laya, Acevedo, & Alvárez, 1988) (**23**, 4.44 g, 1.86%), pisiferol (Matsumoto & Usui, 1982) (**24**, 2.96 g, 1.24%), 20-acetoxypisiferol (Kobayashi, Nishino, Tomita, & Fukushima, 1987) (**25**, 930 mg, 0.39%), pisiferal (Matsumoto, Endo, & Okimoto, 1983) (**26**, 692 mg, 0.29%), hinokione (Matsumoto, Usui, Kawasima, & Mitsuki, 1981) (**27**, 119 mg, 0.05%), hinokiol (Su, Fang, & Cheng, 1994) (**28**, 3.86 g, 1.62%), isohinokiol (Chow & Erdtman, 1962) (**29**, 382 mg, 0.16%), 12-*O*-methylisohinokiol (Kutney et al., 1992) (**30**, 119 mg, 0.05%), sugiol (Ara, Shaheen, Faizi, & Siddiqui, 1990) (**31**, 620 mg, 0.26%), sugiol methyl ether (Wenkert, Campello, McChesney, & Watts, 1974) (**32**, 239 mg, 0.10%), totarol (Ying & Kubo, 1991) (**33**, 4.25 g, 1.78%), 3β-hydroxytotarol (Campello & Fonseca, 1975) (**34**, 3.79 g, 1.59%), totarolone (Ying & Kubo, 1991) (**35**, 1.29 g, 0.54%), 3β-hydroxy-1-oxo-13-*O*-methyltotarol (**36**, 32 mg, 0.01%), 3β-hydroxy-1-oxototarol (Kuo & Chen, 1994) (**37**, 1.14 g, 0.48%), sempervirol (Fang, Lee, & Cheng, 1993) (**38**, 1.93 g, 0.81%), pisiferanol (Hasegawa et al., 1985) (**39**, 4.86 g, 2.04%), 12-*O*-methylpisiferanol (**40**, 835 mg, 0.35%), 1β-hydroxypisiferanol (**41**, 21 mg, <0.01%), 20β-hydroxypisiferanol (Ahn, Wada, & Marumo, 1986) (**42**, 382 mg, 0.16%), pisiferin (Hasegawa & Hirose, 1984) (**43**, 477 mg, 0.20%), 1β-hydroxyisopisiferin (Hasegawa et al., 1985) (**44**, 358 mg, 0.15%), 10-deoxy-4(18)-epoxy-12-methoxy-4,5-seco-pisiferan-19-ol (**45**, 19 mg, <0.01%,), phytol (Sims & Pettus, 1976) (**46**, 1.45 g, 0.61%), phytol acetate (Goodman, Oldfield, & Allerhand, 1973) (**47**, 1.17 g, 0.49%), sandaracopimaric acid (Edwards, Nicolson, & Rodger, 1960) (**48**, 1.26 g, 0.53%), isopimaric acid (Harris & Sanderson, 1948) (**49**, 405 mg, 0.17%), labda-13(16),14-diene-8α,19-diol (Thomas, 1966) (**50**, 404 mg, 0.17%), 8α-hydroxylabda-13(16),14-dien-19-yl (**E**)-4-hydroxycinnamate (San Feliciano et al., 1988) (**51**, 36 mg, 0.01%), 8α-hydroxylabda-13(16),14-dien-19-yl (*Z*)-4-hydroxycinnamate (**52**, 30 mg, 0.01%), 8α-hydroxylabda-13(16),14-dien-19-yl (*E*)-4-hydroxy-3-methoxycinnamate (**53**, 41 mg, 0.02%), *trans*-communic acid (Thomas, 1966; Fang et al., 1989) (**54**, 453 mg, 0.19%), *trans*-communol (Kitajima, Noda, Ida, Komori, & Kawasaki, 1982) (**55**, 525 mg, 0.22%), 8α-acetoxylabda-12,14-dien-19-oic acid (**56a**, 382 mg, 0.16%), *ent*-kaur-16-ene (Hogg & Knox, 1987) (**57**, 549 mg, 0.23%), beyer-15-ene (Kapadi, Somen, Sobti, & Dev, 1983) (**58**, 835 mg, 0.35%), catechin (Nonaka, Ezaki, Hayashi, & Nishioka, 1983) (**59**, 6.15 g, 2.58%), kaemferol (Kingston, 1971) (**60**, 1.41 g, 0.59%), kaemferol-3-*O*-α-L-rhamnopyranoside (Agrawal, 1989) (**61**, 3.20 g, 1.34%), quercetin (Chen, Wan, & Chen, 1988) (**62**, 1.29 g, 0.54%), quercetin-3-*O*-L-rhamnopyranoside (Looker, Holm, Minor, & Kagai, 1964) (**63**, 2.34 g, 0.98%), amentoflavone (Markham, Sheppard, & Geiger, 1987) (**64**, 2.91 g, 1.22%), sequoiaflavone (Markham, Franke, Molloy, & Webby, 1990) (**65**, 2.41 g, 1.01%), hinokiflavone (Dora & Edwards, 1991) (**66**, 2.24 g, 0.94%), pluviatolide (Ganeshpure & Stevenson, 1982) (**67**, 1.48 g, 0.62%), nortrachelogenin (Nishibe, Hisada, & Inagaki, 1971) (**68**, 1.79 g, 0.75%), 7-hydroxymatairesinol (Fang, Wei, & Cheng, 1985) (**69**, 739 mg, 0.31%), hinokinin (Formiga, 1976) (**70**, 572 mg, 0.24%), savinin (Fang, Jan, & Cheng, 1985) (**71**, 453 mg, 0.19%), cedrusin tetraacetate (Agrawal, Agrawal, & Rastogi, 1980) (**72a**, 24 mg, 0.01%), (7*R*,8*R*)-9′-(β-rhamnopyranosyl)-3-methoxy-3′:7,4′:8-diepoxyneolignan-4,9-diol pentaacetate (**73a**, 143 mg, 0.06%), umbelliferone (Chatterjee, Sarkar, & Shoolery, 1980) (**74**, 2.77 g, 1.16%), *cis*-2,4-dihydroxycinnamic acid (**75**, 739 mg, 0.31%), *trans*-4-hydroxy-3-methoxycinnamic acid (ferulic acid) (**76**, 382 mg, 0.16%), 4-hydroxycinnamic acid (**77**, 286 mg, 0.12%), 4-hydroxycinnamaldehyde (**78**, 382 mg, 0.16%), β-sitosterol (Holland, Diakow, & Taylor, 1978) (**79**, 5.91 g, 2.48%), sitosterol-3β-D-glucopyranoside (**80**, 310 mg, 0.13%) (Purushothaman, Sarada, & Saraswathy, 1987), stigmasterol (Holland et al., 1978) (**81**, 835 mg, 0.35%), (*Z*)-octadec-9-enoic acid (**82**, 6.82 g, 2.86%), octadec-9*Z*,12*Z*-dienoic acid (**83**, 5.70 g, 2.39%) and octadec-9*Z*,12*Z*,15*Z*-trienoic acid (**84**, 5.77 g, 2.42%).

The peracetates of compounds **61**, **63**, **65**, **66** and **80** were also prepared (Ac_2O, pyridine, 25°C, 24 h) and their structures were confirmed by spectral methods.

3.3. 3-Hydroxymegastigm-5-en-9-one (*15*)

Oil, $[\alpha]_D^{25}$ +34.5 ($CHCl_3$; *c* 0.5). TLC (25% Me_2CO in hexane) R_f 0.3. IR ν_{max}^{neat} cm^{-1}: 3448, 2932, 1711. ^1H NMR ($CDCl_3$): δ 0.95 (3 H, s, H-11), 0.99 (3 H, s, H-12), 1.41 (1 H, m, H-2), 1.57 (3 H, s, H-13), 1.63 (2 H, m, H-7), 1.66 (1 H, m, H-4), 1.74 (1 H, m, H-2), 1.95 (1 H, m, H-8), 2.12 (3 H, s, H-10), 2.22 (1 H, m, H-8), 2.47 (1 H, m, H-4), 3.91 (1 H, tdd, *J*=10, 6, 4 Hz, H-3). ^{13}C NMR ($CDCl_3$): δ 19.5 (C-13), 21.7 (C-7), 28.2 (C-10), 29.2 (C-11), 29.4 (C-12), 37.7 (C-1), 42.1 (C-8), 44.2 (C-4), 48.3 (C-2), 65.0 (C-3), 124.8 (C-5), 135.9 (C-6), 208.5 (C-9). EI-MS (70 eV) *m*/*z* (rel. int.): 210 [M^+] (18), 192 (8), 177 (15), 159 (45), 134 (63), 119 (100).

3.4. 9-Hydroxymegastigm-5-en-4-one (**16**)

Oil, $[\alpha]_D^{25}$ +8.1 ($CHCl_3$; *c* 0.4). TLC (25% Me_2CO in hexane) R_f 0.3. IR ν_{max}^{neat} cm^{-1}: 3423, 2962, 1655. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.14 (6 H, s, H-11, H-12), 1.23 (3 H, d, $J=6.4$ Hz, H-10), 1.56 (2 H, m, H-8), 1.75 (3 H, s, H-13), 1.78 (2 H, m, H-7), 2.19 (2 H, m, H-2), 2.44 (2 H, m, H-3), 3.84 (1 H, m, H-9). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.5 (C-13), 23.5 (C-10), 26.8 (C-2), 26.9 (C-11), 27.0 (C-12), 34.2 (C-3), 36.4 (C-1), 37.4 (C-7), 37.9 (C-8), 68.4 (C-9), 130.9 (C-5), 164.7 (C-6), 199.1 (C-4). EI-MS (70 eV) *m/z* (rel. int.): 210 [M^+] (22), 195 (80), 177 (33), 165 (50), 152 (100), 137 (77), 121 (42), 109 (78).

3.5. Megastigm-5-en-3,9-diol (**17**)

Oil, $[\alpha]_D^{25}$ −33.8 ($CHCl_3$; *c* 0.5). TLC (30% Me_2CO in hexane) R_f 0.3. IR ν_{max}^{neat} cm^{-1}: 3396, 2920. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.01 (3 H, s, H-11), 1.04 (3 H, s, H-12), 1.19 (3 H, s, H-10), 1.36 (1 H, m, H-2), 1.48 (2 H, m, H-8), 1.60 (3 H, s, H-13), 1.68 (1 H, m, H-2), 1.80 (1 H, m, H-4), 2.20 (2 H, m, H-7), 2.23 (1 H, m, H-4), 3.77 (1 H, m, H-9), 3.91 (1 H, tdd, $J=10.2$, 5.7, 4 Hz, H-3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.7 (C-13), 23.4 (C-10), 24.4 (C-7), 28.5 (C-11), 29.7 (C-12), 37.9 (C-1), 39.7 (C-8), 42.3 (C-4), 48.6 (C-2), 65.3 (C-3), 68.7 (C-9), 124.1 (C-5), 136.9 (C-6). EI-MS (70 eV) *m/z* (rel. int.): 212 [M^+] (17), 194 (8), 179 (11), 161 (40), 153 (18), 136 (62), 121 (100).

3.6. 3β-hydroxy-1-oxo-13-O-methyltotarol (**36**)

Solid, m.p. 179–180.6°C, $[\alpha]_D^{25}$ +3.5 (MeOH; *c* 1.3). TLC (25% EtOAc in hexane) R_f 0.33. IR ν_{max}^{neat} cm^{-1}: 3327, 1706. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.08 (3 H, s, H-19), 1.11 (3 H, s, H-18), 1.25 (3 H, d, $J=7.2$ Hz, H-16), 1.26 (3 H, d, $J=7.2$ Hz, H-17), 1.50 (1 H, m, H-5), 1.58 (3 H, s, H-20), 1.78 (1 H, m, H-6), 2.00 (1 H, m, H-6), 2.64 (1 H, dd, $J=4.8$, 11.2 Hz, H-2α), 2.70 (1 H, m, H-7), 2.90 (1 H, m, H-7), 3.10 (1 H, dd, $J=11.2$, 12 Hz, H-2β), 3.19 (1 H, sept, $J=7.2$ Hz, H-15), 3.60 (1 H, dd, $J=4.8$, 12 Hz, H-3), 3.76 (s, OMe), 6.75 (1 H, d, $J=8.8$ Hz, H-12), 7.19 (1 H, d, $J=8.8$ Hz, H-11). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.2 (C-19), 18.8 (C-6), 20.2 (C-17), 20.4 (C-16), 25.2 (C-20), 27.7 (C-15), 28.7 (C-18), 29.4 (C-7), 38.9 (C-4), 45.1 (C-2), 48.9 (C-5), 53.6 (C-10), 55.0 (OMe), 78.4 (C-3), 109.1 (C-12), 128.4 (C-11), 132.7 (C-9), 133.1 (C-8), 134.0 (C-14), 156.9 (C-13), 210.4 (C-1). EI-MS (70 eV) *m/z* (rel. int.): 330 [M^+] (50), 287 (45), 257 (100), 244 (20), 216 (25), 173 (35). HR-MS for $C_{21}H_{30}O_3$ requires 330.2187; found 330.2183.

3.7. 12-O-Methylpisiferanol (**40**)

Oil. $[\alpha]_D^{26}$ +28 (MeOH; *c* 2.5). TLC (5% EtOAc in hexane) R_f 0.35. IR ν_{max}^{neat} cm^{-1}: 3550, 1605, 1582, 1500. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.86 (3 H, s, H-18), 0.90 (3 H, s, H-19), 1.15 (3 H, d, $J=7$ Hz, H-16), 1.19 (3 H, d, $J=7$ Hz, H-17), 1.16-1.70 (8 H, m), 1.67–1.84 (1 H, m), 1.88-2.10 (1 H, m), 2.53 (1 H, d, $J=13.8$ Hz, H-20), 2.70 (2 H, m, H-7), 2.97 (1 H, d, $J=13.8$ Hz, H-20), 3.23 (1 H, sept, $J=7$ Hz, H-15), 3.76 (3 H, s, OMe), 6.59 (1 H, s, H-11), 6.91 (1 H, s, H-14). ^{13}C NMR ($CDCl_3$): δ 18.7, 21.6, 22.6, 23.0, 24.1, 26.4, 32.3, 34.4, 35.4, 42.1, 42.5, 51.4, 55.6, 58.0, 70.8, 114.5, 126.3, 133.9, 135.2, 135.7, 155.0. EI-MS (70 eV) *m/z* (rel. int.): 316 [M^+] (37), 298 (8), 190 (100), 175 (18), 163 (8).

3.8. 1β-Hydroxypisiferanol (**41**)

Needles, $[\alpha]_D^{25}$ +30.5 (MeOH, *c* 0.35). TLC (35% Me_2CO in hexane) R_f 0.33. IR ν_{max}^{neat} cm^{-1}: 3535, 3357, 2934, 2870. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (3 H, s, H-19), 0.94 (3 H, s, H-18), 1.20 (2 H, m, H-2), 1.21 (3 H, d, $J=6.8$ Hz, H-16), 1.23 (3 H, d, $J=6.8$ Hz, H-17), 1.51 (1 H, m, H-6), 1.68 (1 H, m, H-5), 2.04 (2 H, m, H-3), 2.15 (1 H, m, H-6), 2.51 (1 H, d, $J=14$ Hz, H-20), 2.70 (2 H, m, H-7), 3.15 (1 H, sept, $J=6.8$ Hz, H-15), 3.29 (1 H, d, $J=14$ Hz, H-20), 3.69 (1 H, m, H-1), 6.56 (1 H, s, H-11), 6.91 (1 H, s, H-14). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.7 (C-19), 22.5 (C-16), 22.8 (C-17), 23.6 (C-3), 25.9 (C-6), 26.7 (C-15), 32.1 (C-18), 33.9 (C-4), 34.6 (C-2), 34.9 (C-7), 47.7 (C-20), 51.7 (C-5), 72.4 (C-10), 76.7 (C-1), 118.9 (C-11), 126.4 (C-14), 132.8 (C-13), 133.6 (C-9), 136.3 (C-8), 150.9 (C-12). EI-MS (70 eV) *m/z* (rel. int.): 318 [M]$^+$ (35), 236 (25), 176 (70), 84 (100). HR-MS for $C_{20}H_{30}O_3$ requires 318.2187; found 318.2185.

3.9. 10-Deoxy-4(18)-epoxy-12-methoxy-4,5-seco-pisiferan-19-ol (**45**)

Gum, $[\alpha]_D^{25}$ +25.8 ($CHCl_3$; *c* 0.03). TLC (30% EtOAc in hexane) R_f 0.32. IR ν_{max}^{neat} cm^{-1}: 3342, 1605, 1580, 1268, 840. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.83 (2 H, m, H-3), 1.15 (3 H, d, $J=6.8$ Hz, H-16), 1.19 (3 H, d, $J=6.8$ Hz, H-17), 1.27 (3 H, m, H-5, H-6), 1.40 (2 H, m, H-1), 1.60 (1 H, m, H-10), 2.00 (3 H, m, H-5, H-18), 2.13 (2 H, m, H-2), 2.61 (1 H, d, $J=13.1$ Hz, H-20α), 3.09 (1 H, d, $J=13.1$ Hz, H-20β), 2.70 (2 H, m, H-7), 3.11 (1 H, d, $J=10.6$ Hz, H-19), 3.24 (1 H, sept, $J=6.8$ Hz, H-15), 3.62 (1 H, d, $J=10.6$ Hz, H-19), 3.77 (3 H, s, OMe), 6.60 (1 H, s, H-11), 6.93 (1 H, s, H-14). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.8 (C-2), 22.5 (C-16), 22.9 (C-17), 24.0 (C-6), 26.4 (C-15), 26.9

(C-1), 27.8 (C-3), 35.4 (C-7), 38.9 (C-5), 41.8 (C-18), 50.4 (C-20), 55.5 (OMe), 58.4 (C-10), 68.9 (C-19), 70.3 (C-4), 114.2 (C-11), 126.5 (C-14), 133.0 (C-8), 135.6 (C-13), 135.7 (C-9), 155.0 (C-12). EI-MS (70 eV) *m/z* (rel. int.): 332 $[M]^+$ (8), 314 (3), 190 (100), 175 (28), 161 (15), 149 (20), 133 (18), 81 (22), 69 (25), 55 (40). HR-MS for $C_{21}H_{32}O_3$ requires 332.2343; found 332.2340.

3.10. 8α-Hydroxylabda-13(16),14-dien-19-yl (Z)-4-hydroxycinnamate (**52**)

Solid, m.p. 206–208°C, $[\alpha]_D^{25}$ +6.5 (MeOH; *c* 1.65). TLC (35% EtOAc in hexane) R_f 0.30. IR ν_{max}^{neat} cm^{-1}: 3483, 3300, 1680, 1620, 1590, 1500, 1260, 1175. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.79 (3 H, s, H-20), 0.92 (3 H, s, H-18), 0.97–1.08 (3 H, m), 1.12 (3 H, s, H-17), 1.22–1.26 (1 H, m), 1.32–1.45 (4 H, m), 1.53–1.58 (1 H, m), 1.63–1.75 (4 H, m), 1.86 (1 H, dd, *J* = 9.0, 2.7 Hz, H-9), 2.26 (1 H, td, *J* = 10.8, 7.1 Hz, H-12), 2.31 (1 H, td, *J* = 11.8, 7.1 Hz, H-12), 3.92(1 H, d, *J* = 11.1 Hz, H-19), 4.18 (1 H, d, *J* = 11.1 Hz, H-19), 4.99 (2 H, br s, H-16), 5.04 (1 H, d, *J* = 10.7 Hz, H-15), 5.27(1 H, d, *J* = 17.6 Hz, H-15), 5.79 (1 H, d, *J* = 12.8 Hz, H-8′), 6.33 (1 H, dd, *J* = 10.7, 17.6 Hz, H-14), 6.76 (2 H, d, *J* = 8.6 Hz), 6.81 (1 H, d, *J* = 12.8 Hz, H-7′), 7.56 (2 H, d, *J* = 8.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.9 (C-20), 18.0 (C-2), 36.2 (C-3), 36.9 (C-4), 21.0 (C-6), 23.8 (C-17), 24.6 (C-11), 27.4 (C-18), 34.9 (C-12), 38.9 (C-10), 39.5 (C-1), 44.5 (C-7), 56.6 (C-5), 61.6 (C-9), 66.9 (C-19), 74.5 (C-8), 113.5 (C-15), 115.1 (2 C), 115.7 (C-16), 116.7, 126.9, 132.2 (2 C), 138.7 (C-14), 143.8, 147.2 (C-13), 157.3, 167.2. EI-MS (70 eV) *m/z* (rel. int.): 452 $[M]^+$ (0.5), 434 (1), 288 (2.5), 270 (4), 189 (20), 147 (100). HR-MS for $C_{29}H_{40}O_4$ requires 452.2916; found 452.2920.

3.11. 8α-Hydroxylabda-13(16),14-dien-19-yl (E)-4-hydroxy-3-methoxycinnamate (**53**)

Solid, m.p. 110–112°C, $[\alpha]_D^{25}$ +6.2 (MeOH; *c* 0.7). TLC (35% EtOAc in hexane) R_f 0.32. IR ν_{max}^{neat} cm^{-1}: 3490, 3310, 1675. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.82 (3 H, s, H-20), 1.01 (3 H, s, H-18), 0.97–1.08 (3 H, m), 1.13 (3 H, s, H-17), 1.22–1.26 (1 H, m), 1.35–1.50 (4 H, m), 1.53–1.65 (2 H, m), 1.70–1.92 (4 H, m), 2.20–2.42 (2 H, m), 3.90 (3 H, s, OMe), 3.98 (1 H, d, *J* = 11 Hz, H-19), 4.27 (1 H, d, *J* = 11 Hz, H-19), 4.99 (2 H, br s, H-16), 5.04 (1 H, d, *J* = 10.7 Hz, H-15), 5.27 (1 H, d, *J* = 17.6 Hz, H-15), 6.25 (1 H, d, *J* = 15.9 Hz), 6.33 (1 H, dd, *J* = 10.7, 17.6 Hz, H-14), 6.89 (1 H, d, *J* = 8.1 Hz), 7.00 (1 H, d, *J* = 1.7 Hz), 7.05 (1 H, dd, *J* = 1.7, 8.1 Hz), 7.56 (1 H, d, *J* = 15.9 Hz, H-7′). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.9 (C-20), 18.0 (C-2), 20.8 (C-6), 23.7 (C-17), 24.7 (C-11), 27.5 (C-18), 35.0 (C-12), 36.4 (C-3), 37.2 (C-4), 38.9 (C-10), 39.6 (C-1), 44.8 (C-7), 55.9 (OMe), 56.7 (C-5), 61.7 (C-9), 66.8 (C-19), 74.0 (C-8), 109.5, 113.5, 114.7, 115.6, 122.9, 126.9, 138.7, 144.6 (2 C), 146.8, 147.3, 147.9, 167.5. UV λ_{max}^{MeOH} nm (ε): 220 (13 200). EI-MS (70 eV) *m/z* (rel. int.): 482 $[M]^+$ (1), 384 (0.5), 288 (1), 271 (2), 202 (2), 177 (100). HR-MS for $C_{30}H_{42}O_5$ requires 482.3021; found 482.3025.

3.12. 8α-Acetoxylabda-12,14-dien-19-oic acid (**56a**)

Gum, TLC (40% EtOAc in hexane) R_f 0.34. IR ν_{max}^{neat} cm^{-1}: 3500–2500, 1760, 1600, 887. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.72 (3 H, s, H-20), 1.01 (3 H, s, H-18), 1.24 (3 H, s, H-17), 1.24–1.62 (8 H, m), 1.63–1.85 (2 H, m), 1.89 (1 H, m), 1.72 (3 H, s, H-16), 1.91 (3 H, s, OAc), 1.98–2.08 (2 H, m), 2.24 (1 H, m), 4.85 (1 H, t, *J* = 6.4 Hz, H-12), 4.87 (1 H, dd, *J* = 10.4, 4.4 Hz, H-15), 5.16 (1 H, dd, *J* = 17.2, 4.4 Hz, H-15), 5.73 (1 H, dd, *J* = 10.4, 17.2 Hz, H-14). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.8 (C-16), 15.1 (C-20), 18.7 (C-2), 21.0 (C-17), 23.5 (C-11), 26.9 (C-6), 28.5 (C-18), 29.0 (OAc), 35.1 (C-3), 36.4 (C-7), 37.5 (C-1, C-4), 40.6 (C-10), 49.8 (C-5), 50.2 (C-9), 51.9 (C-8), 110.3 (C-15), 129.7 (C-12), 135.8 (C-13), 148.6 (C-14), 170.3 (OAc), 181.8 (C-19). EI-MS (70 eV) *m/z* (rel. int.): 362 $[M]^+$ (78), 302 (100), 287 (34), 257 (18), 175 (65), 121 (70), 81 (80).

3.13. (7R,8R)-9′-(β-Rhamnopyranosyl)-3-methoxy-3′:7,4′:8-diepoxyneolignan-4,9-diol pentaacetate (**73a**)

Gum, $[\alpha]_D^{25}$ −25 ($CHCl_3$; *c* 4.0). TLC (35% Me_2CO in hexane) R_f 0.3. CD (MeOH, nm): $[\theta]_{368.2}$ −346, $[\theta]_{326.8}$ +45, $[\theta]_{306.8}$ −79, $[\theta]_{272.1}$ −26, $[\theta]_{256.4}$ −61, $[\theta]_{244.4}$ −3, $[\theta]_{236.0}$ +31, $[\theta]_{218.0}$ −36. IR ν_{max}^{neat} cm^{-1}: 2939, 1747, 1607, 1594, 1507, 1452. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.17 (3 H, d, *J* = 6.1 Hz, H-6″), 1.86 (2 H, m, H-8′), 1.94 (3 H, s), 1.99 (6 H, s, 2 Ac), 2.09 (3 H, s), 2.26 (3 H, s), 2.59 (2 H, t, *J* = 6.8 Hz, H-7′), 3.40 (1 H, m, H-9′), 3.62 (1 H, m, H-9′), 3.82 (1 H, m, H-5″), 3.83 (3 H, s, OMe), 3.94 (1 H, dd, *J* = 4.4, 12 Hz, H-9), 4.17 (1 H, m, H-8), 4.29 (1 H, dd, *J* = 3.3, 12 Hz, H-9), 4.66 (1 H, d, *J* = 1.4 Hz, H-1″), 4.87 (1 H, d, *J* = 7.8 Hz, H-7), 5.01 (1 H, dd, *J* = 9.9, 9.9, Hz, H-4″), 5.20 (1 H, dd, *J* = 1.4, 3.5 Hz, H-2″), 5.29 (1 H, dd, *J* = 3.5, 9.9 Hz, H-3″), 6.69 (1 H, dd, *J* = 1.9, 8.2 Hz, H-6′), 6.76 (1 H, d, *J* = 1.9 Hz, H-2′), 6.85 (1 H, d, *J* = 8.2 Hz, H-5′), 6.92 (1 H, br d, *J* = 8.0 Hz, H-5), 6.95 (1 H, br s, H-2), 7.02 (1 H, d, *J* = 8.0 Hz, H-6). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.2 (C-6″), 20.4 (Ac), 20.5 (Ac), 20.6 (3 Ac), 30.7 (C-8′), 31.3 (C-7′), 55.8 (OMe), 62.7 (C-9), 66.1 (C-5″), 67.1 (C-9′), 69.0 (C-3″), 69.8 (C-2″), 70.9 (C-4″), 75.2 (C-8), 76.2 (C-7), 97.3 (C-1″), 110.9 (C-2), 116.7 (C-2′), 116.8 (C-5′), 119.7 (C-5), 121.7 (C-6′), 122.9 (C-6), 134.7 (C-1), 134.9 (C-1′), 140.2 (C-4), 140.9 (C-4′), 142.9 (C-3′), 151.4 (C-3),

168.6 (OAc), 169.9 (2 Ac), 170.0 (Ac), 170.3 (Ac). FAB-MS (NBA) m/z: 702 $[M]^+$. HR-MS for $C_{35}H_{42}O_{15}$ requires 702.2511; found 702.2518.

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