



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. © 1999 Elsevier Science Ltd. All rights reserved.

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 com-

ponents, 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., $[\alpha]$, IR, UV, MS, ^1H 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** ($\text{C}_{13}\text{H}_{22}\text{O}_2$) was deduced from the exact mass measurement of its molecular ion, $[\text{M}]^+$ 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 (carbiny), 208.5 (carbonyl), 124.8 and 135.9 (olefinic) were diagnostic. The ^1H 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 carbiny proton resonance occurred at δ 3.91 (tdd, $J=10, 6, 4\text{ Hz}$), 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, $[\alpha]_D^{25} + 34.5$ (CHCl₃; *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** (C₁₃H₂₂O₂) 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 $[\alpha]_D^{25} + 8.1$ (CHCl₃; *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** (C₁₃H₂₄O₂), [M]⁺ appearing at *m/z* 212.1771, was assigned as megastigm-5-ene-3,9-diol according to ¹H and ¹³C 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, $[\alpha]_D^{25} - 33.8$ (CHCl₃; *c* 0.5), but, its absolute configuration was not rigorously determined.

The molecular formula C₂₁H₃₀O₃ 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 3 β -hydroxy-1-oxo-13-*O*-methyltatarol. 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 3.76). The position of the methoxy group on C-13 was thus established. A chemical correlation of **36** with 3 β -hydroxy-1-oxotatarol (**37**) (Kuo & Chen, 1994) was carried out to confirm the structural assignment. Indeed, treatment of **37** with diazomethane in Et₂O

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 Et₂O 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 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** (C₂₀H₃₀O₃) exhibited an ¹H NMR spectrum similar to that of pisiferanol **39** (C₂₀H₃₀O₂), except for the presence of an additional carbinyl proton at δ 3.69 (*m*). The ¹³C NMR spectrum showed the corresponding secondary carbinyl carbon occurring at δ 76.7 and another tertiary carbinyl carbon occurring at δ 72.4. Compound **41** was assigned as 1 β -hydroxypisiferanol. The diagnostic H-20 α and H-20 β 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-20 β at a lower field, as compared to **40**, was due to the deshielding effect of the 1 β -OH group. The NOESY spectrum showed the correlation of H-1 α (at δ 3.69) with H-20 α (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 C₂₁H₃₂O₃. 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 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 CH₂OH group. The structural assignment was supported by the ¹³C, 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-8 α ,19-diol **50** as inferred from their ¹H and ¹³C 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 labadiene 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 8 β -Me group (at δ_{H} 1.13).

Compound **56a** (C₂₂H₃₄O₄) 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 ¹³C spectra with those of *trans*-communic acid **54** (Thomas, 1966; Fang, Hsu, & Cheng, 1989), compound **56a** was assigned as 8 α -acetyl- λ -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 8 β -hydroxyl- λ -12*E*,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 8 β -hydroxyl group.

Compound **73** was subjected to peracetylation (Ac₂O, pyridine) to give **73a**. The ¹H and ¹³C 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 C₃₅H₄₂O₁₅. 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).

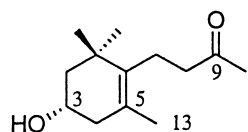
3. Experimental

3.1. General

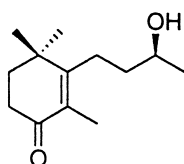
Yanaco MP-500D melting point apparatus, JASCO DIP-1000 polarimeter, Perkin-Elmer 983G infrared spectrophotometer, Hitachi U-3210 ultraviolet-visible spectrophotometer, Bruker AM-300 spectrometer, Finnigan TSQ-46C mass spectrometer (EI-MS), JEOL SX-102A spectrometer (FAB-MS), JEOL JMS-HX 110 mass spectrometer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

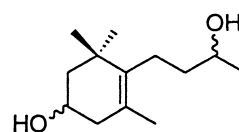
The leaves of *C. formosensis* Matsumura were collected from mountains in the north part of Taiwan. A voucher specimen is deposited in the Herbarium of National Taiwan University. The air-dried leaves (18 kg) were extracted with Me₂CO (60 l $\times$ 3). The extract was filtered through a column of activated 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, Me₂CO 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–**



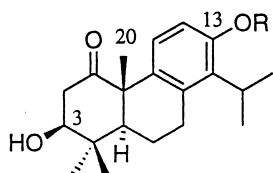
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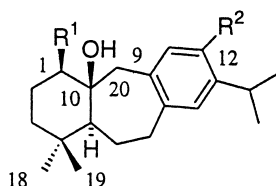
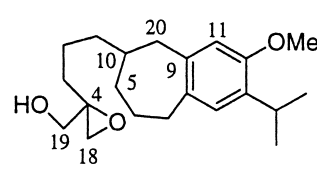


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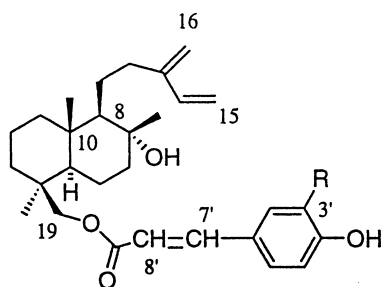


36 R = Me

37 R = H

39 R¹ = H, R² = OH40 R¹ = H, R² = OMe41 R¹ = R² = OH

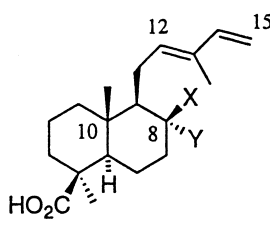
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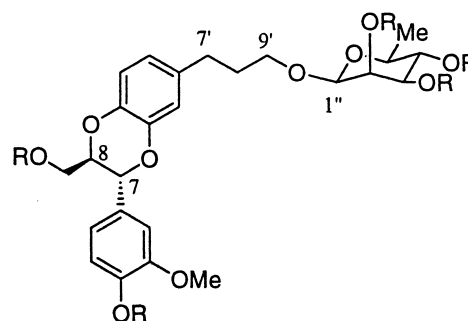
51 (7'E), R = H

52 (7'Z), R = H

53 (7'E), R = OMe

54 X, Y = CH₂

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 Me₂CO/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 Me₂CO (0.8 l) followed by a gradient of Me₂CO/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 (Ac₂O, 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 col-

lected from CC) are listed as follows: α -cadinol (Bottini & Garfagnoli, 1987) (**1**, 7.75 g, 3.25%), cadi-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 & Srinivasan, 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, & Álvarez, 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%), pisiferol (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%), 3 β -hydroxytotarol (Campello & Fonseca, 1975) (**34**, 3.79 g, 1.59%), totarolone (Ying & Kubo, 1991) (**35**, 1.29 g, 0.54%), 3 β -hydroxy-1-oxo-13-*O*-methyltotarol (**36**, 32 mg, 0.01%), 3 β -hydroxy-1-oxototarol (Kuo & Chen, 1994) (**37**, 1.14 g, 0.48%), semperviol (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%), 1 β -hydroxypisiferanol (**41**, 21 mg, <0.01%), 20 β -hydroxypisiferanol (Ahn, Wada, & Marumo, 1986) (**42**, 382 mg, 0.16%), pisiferin (Hasegawa & Hirose, 1984) (**43**, 477 mg, 0.20%), 1 β -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-8 α ,19-diol (Thomas, 1966) (**50**, 404 mg, 0.17%), 8 α -hydroxylabda-13(16),14-dien-19-yl (*E*)-4-hydroxycinnamate (San Feliciano et al., 1988) (**51**, 36 mg, 0.01%), 8 α -hydroxylabda-13(16),14-dien-19-yl (*Z*)-4-hydroxycinnamate (**52**, 30 mg, 0.01%), 8 α -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%), 8 α -

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 -sitossterol (Holland, Diakow, & Taylor, 1978) (**79**, 5.91 g, 2.48%), sitosterol-3 β -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 (Ac₂O, pyridine, 25°C, 24 h) and their structures were confirmed by spectral methods.

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

Oil, $[\alpha]_D^{25} + 34.5$ (CHCl₃; *c* 0.5). TLC (25% Me₂CO in hexane) *R*_f 0.3. IR $\nu_{\text{max}}^{\text{neat}}$ cm⁻¹: 3448, 2932, 1711. ¹H NMR (CDCl₃): 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). ¹³C NMR (CDCl₃): 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 $\nu_{\text{max}}^{\text{neat}} \text{ cm}^{-1}$: 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 $\nu_{\text{max}}^{\text{neat}} \text{ cm}^{-1}$: 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. 3 β -hydroxy-1-oxo-13-O-methyltatarol (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 $\nu_{\text{max}}^{\text{neat}} \text{ cm}^{-1}$: 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-2 α), 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-2 β), 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 $\text{C}_{21}\text{H}_{30}\text{O}_3$ 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 $\nu_{\text{max}}^{\text{neat}} \text{ cm}^{-1}$: 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. 1 β -Hydroxypisiferanol (41)

Needles, $[\alpha]_D^{25} + 30.5$ (MeOH, c 0.35). TLC (35% Me_2CO in hexane) R_f 0.33. IR $\nu_{\text{max}}^{\text{neat}} \text{ cm}^{-1}$: 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 $\text{C}_{20}\text{H}_{30}\text{O}_3$ 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 $\nu_{\text{max}}^{\text{neat}} \text{ cm}^{-1}$: 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-20 α), 3.09 (1 H, d, $J=13.1$ Hz, H-20 β), 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. 8 α -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. 8 α -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. 8 α -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. (7*R*,8*R*)-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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