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Chemical Constituents of the Pericarp of *Platycladus orientalis*

Yueh-Hsiung Kuo*[a,b] (郭悅雄) and Wen-Chin Chen[a] (陳文卿)
[a]*Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.*
[b]*National Research Institute of Chinese Medicine, Taipei, Taiwan, R.O.C.*

In previous papers, we have reported two new compounds, 15-hydroxypinusolidic acid and platydiol, from the pericarp of *Platycladus orientalis*. In addition to the above compounds, the isolation and identification of twenty-one compounds from the same source are described. Their structures were determined on the basis of spectral evidence as well as direct comparison with authentic samples. These compounds included four fatty alcohols and acids, three monolignols, one sesquiterpene, nine diterpenes, two steroids, one flavone, and one sugar. Among these, docosyl 3-hydroxyferulate is a new compound. And docosyl *trans*- and *cis*-ferulates were isolated in pure form.

INTRODUCTION

Platycladus is a monotypic genus. Many chemical components from *P. orientalis* Firanco (= Biota orientalis Endl.) (側柏) (Cupressaceae) (柏科) have been extensively investigated; sesquiterpenoids and diterpenoids from its heartwood,[1-5] flavonoids from its leaves,[6] bisnor- and trinorlabdane-type diterpenoids from its seeds,[7] and two monolignol derivatives from its pollen.[8] Because we are interested in labdane and norlabdane type diterpenoids, we have investigated the components of the pericarp of this species, and found two new compounds including one monoterpene (platydiol)[9] and one diterpene (15-hydroxypinusolic acid).[10] Now we report all of the components from the same extract.

RESULTS AND DISCUSSION

Air dried pericarps of *P. orientalis* were extracted at room temperature with acetone and methanol, succesively. The combined acetone and methanol extracts were separated by repeated SiO_2 chromatography. Eleven components were isolated, including ginnol (**1**),[11] α-cedrol (**2**),[12] 1-hexa- and 1-octacosanol (**3**), docosyl *trans*-ferulate (**4**), *cis*- and *trans*-communic acids (**5**),[13] sandaracopimaric acid (**6**),[14,15] isopimaric acid (**7**),[14,15] 14,15-bisnor-13-oxo-8(17),11(*E*)-labdadien-19-oic acid (**8**),[16] fatty acid (**9**), 15-norlabda-8(17),12(*E*)-diene-14-carboxaldehyde-19-oic acid (**10**),[17] and bornesitol (**11**),[18] in that eluting order from acetone extract. And methanol extract gave twenty components, including **2**, **4**, docosyl *cis*-ferulate (**12**), **5**, **6**, β-sitosterol (**13**),[19] palmitic acid (**14**), pinusolide (**15**),[20] pinusolidic acid (**16**),[21] 5-hydroxy-7,4′-dimethoxyflavone (**17**),[22] 8,15-pimaradien-18-oic acid (**18**),[23] 15-hydroxypinusolidic acid (**19**),[10] Docosyl *trans*-3-hydroxyferulate (**20**), platydiol (**21**),[10] 7-oxo-8,15-pimaradiene-18-oic acid (**22**),[24] β-sitostoryl-1-*O*-β-glucopyranoside (**23**),[18] and **11**.

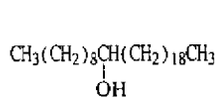
Balde has isolated three major and two minor ferulic acid esters[25] from haxane extract of *Pavetta owarienisis*, from which a mixture of docosyl *trans*- and *cis*-ferulates was obtained. Docosy *trans*- and *cis*-ferulates were observed from *Teucrium divaricutum* by Ulubelen, but the melting points of both compounds have not described.[26] The pure form of docosyl *trans*-ferulate (**4**) was separated from acetone extract after recrystallization with hexane. A mixture of docosy *trans*- and *cis*-ferulates was found from the methanol extract, but recrystallization with hexane, pure docosyl *cis*-ferulate (**12**) was obtained. Both melted at 57-58 °C but with different IR and ^{1}H NMR spectra. Hydrogenation of both compounds yielded the same docosyl dihydroferulate (**24**) [mp 54-55 °C; EI-MS *m/z* 504; δ 2.59, 2.88 (each 2H, t, J = 7.4 Hz)].

Compound **20** is a new monolignol, which melted at 60-61 °C and was deduced to have the molecular formula $C_{32}H_{54}O_5$, on the basis of its HR-MS. It showed an UV λ_{max} at 384 nm and a reversible bathochromic shift indicated the presence of a phenolic hydroxyl group. Bands at 3401, 1709 cm^{-1} in the IR spectrum are indicative of a hydroxyl group and a conjugated ester, respectively. The bands at 1605, 1514 and 721 cm^{-1} suggest the presence of an aromatic and of long chain groups. The mass spectrum showed the molecular peak at *m/z* 518 (20%) and the other major peaks correspond to hydroxyferulic acid (*m/z* 210) (100%)

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

and hydroxyforuloyl (*m/z* 193) (72%) fragments. The ^{1}H NMR spectrum of **20** exhibits signals characteristic of 3-hydroxyferuloyl moiety: a phenolic methy signal at δ 3.89, two *trans* olefinic protons [δ 6.25 and 7.53 (each 1H, d, J = 15.9 Hz)], two *meta* phenyl protons [δ 6.64 and 6.80 (each 1H, brs)], and two D_2O exchangeable phenolic protons [δ 5.34 and 5.64]. The presence of an aliphatic alcohol moiety was indicated by the triplet signal at δ 0.66 (J = 6.9 Hz) (terminal methyl), the broad singlet at δ 1.22 for CH_2 and the downfield triplet at δ 4.16 (J = 6.6 Hz) corresponding to a methylene adjacent to an oxycarbonyl function. H-7 (δ 7.53) expresses NOE correlation with both phenyl protons (see structure **20**). The above result gave a conclusion that compound **20** is a docosyl 3,4,5-trioxygenatedcinnamate. Two phenyl protons present different chemical shifts that indicated trioxygenation is not a symmetry. The phenyl proton at δ 6.80 has NOE correlation with the methoxyl group, therefore the structure of **4** can be elucidated as docosyl *trans*-3-hydroxyferulate. Acetylation of **20** with Ac_2O in pyridine afforded a diacetate **25** [δ 2.27 (6H, s)]. By the treatment of NaOMe in MeOH, compound **20** yielded two products, 1-docosanol and **26** [mp 160-161 °C; δ 3.78 and 3.90 (each 3H, s)] were isolated.

Twenty-three compounds contained eleven different skeletons: four fatty alcohols and acids (**1**, **3**, **9** and **14**), three monolignols (**4**, **12**, and **20**), one monoterpene (**21**), one sesquiterpene (**2**), ten diterpenes (**5**, **6**, **7**, **8**, **10**, **15**, **16**, **18**, **19**, and **20**; including six labdanes, four pimaranes, one



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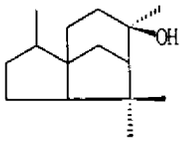

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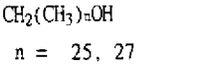

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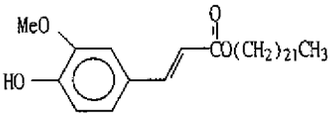

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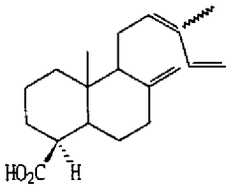
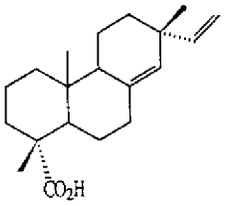


5 *cis* and *trans*



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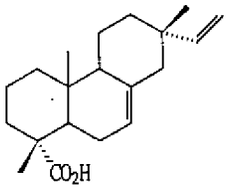

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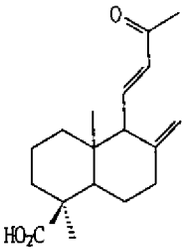

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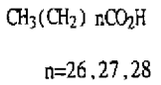

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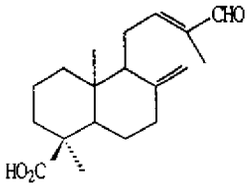

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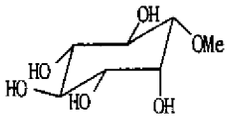

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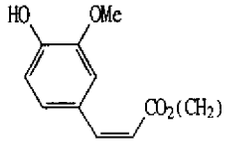

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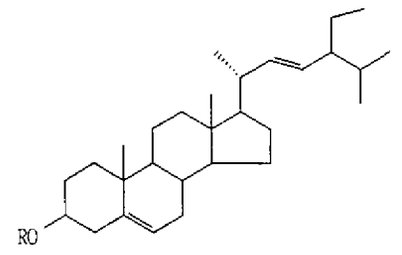
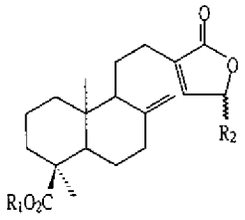
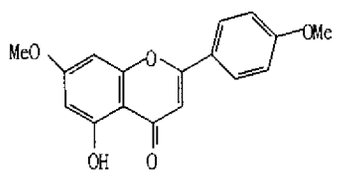


13 R = H
25 R = glc

14



15 R_1 = CH_3, R_2 = H
16 R_1 = R_2 = H
19 R_1 = H, R_2 = OH



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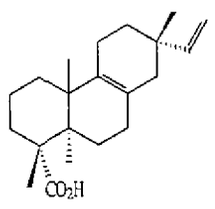

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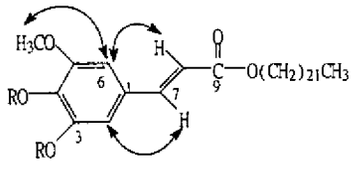
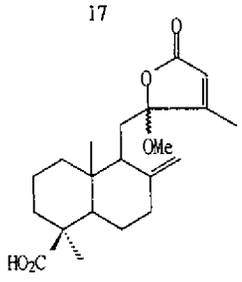


20 R = H (Key NOE ⟷)
28 R = Ac



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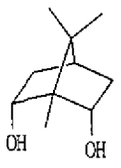

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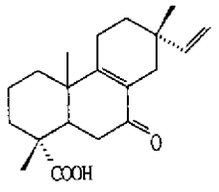

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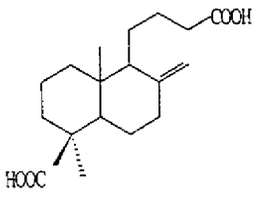

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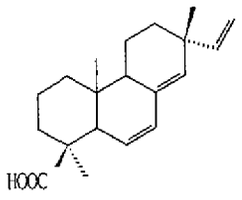

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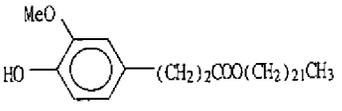

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norlabdane, and two bisnorlabdanes), one sugar (**11**), two steroids (**13** and **23**), and one flavone (**17**), from which three new compounds were isolated and elucidated. And pure forms of docosyl *trans*- and *cis*-ferulates (**4** and **12**) were obtained.

EXPERIMENTAL SECTION

General Methods

Melting points were determinated on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. ^{1}H- and ^{13}C-NMR spectra were run on a Bruker AM 300 in $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard. Chemical shifts are given in δ-values and coupling constants (*J*) are given in hertz (Hz). EI-MS and UV spectra were taken on a JEOL-JMS-100 and Hitachi RMS-4 spectrometers, respectively.

Extraction and Isolation

The air dried pericarps of *P. orientalis* (4.2 Kg) were extracted at room temperature with acetone (60 L, 3d × 4). The residues were sucessively extracted with methanol (60

L, 5d × 3). Two extracts were evaprated in vacuo to yield brown viscous residiues, 170 g from acetone extract and 105 g from ethanol extract. Components were separated by a column chromatography on silica gel and elution with hexane + ethyl acetate gradients. The components from acetone extract were eluted in that order as **1** (2.1 g) (2% EtOAc in hexane), **2** (7.2 g) (5% EtOAc in hexane), **3** (2.1 g) (10% EtOAc in hexane), **4** (2.0 g) (20% EtOAc in hexane), **5** (3.0 g) (30% EtOAc in hexane), **6** (4.2 g) (30% EtOAc in hexane), **7** (0.5 g) (30% EtOAc in hexane), **8** (0.5 g) (30% EtOAc in hexane), **9** (1.8 g) (30% EtOAc in hexane), **10** (80 mg) (50% EtOAc in hexane) and **11** (2.6 g) (80% EtOAc in hexane). Methanol extract was separated as six fractions. The first fraction (10% EtOAc in hexane) gave **2** (3.0 g) and **4** (1.2 g); the second fraction (20% EtOAc in hexane) yielded **12** (190 mg), **5** (2.7 g), **6** (1.9 g), **13** (2.8 g); the third fraction (30% EtOAc in hexane) gave **14** (170 mg), **15** (410 mg), **16** (2.8 g), **17** (299 mg), **18** (285 mg); the fourth fraction (50% EtOAc in hexane) afforded **19** (301 mg), **20** (410 mg), **21** (1.1 g), **22** (1.0 g); the fifth fraction (80% EtOAc in hexane) yielded **23** (2.0 g), and the sixth fraction (100% EtOAc) afforded **11** (2.4 g). Physical data of some compounds are omitted.

Ginnol (1)

Mp 83-84 °C; IR (KBr) ν_{max}: 3314, 1133, 733 cm^{-1}; EI-MS *m/z* (%): 423 [(M-H)$^+$, 2], 297 (80), 209 (20), 157 (30), 111 (35), 83 (100).

α-Cedrol (2)

Mp 85-86 °C; IR (KBr) ν_{max}: 3629, 1366, 1246, 1147, 963 cm^{-1}; EI-MS *m/z* (%): 222 (M$^+$, 5), 207 (M$^+$-CH_3, 17), 150 (100), 135 (30).

Docosyl *trans*-Ferulate (4)

Mp 57-58 °C; IR (KBr) ν_{max}: 3549, 3451, 1677, 1619, 1595, 1514, 1223, 1180, 1032, 983 cm^{-1}; EI-MS *m/z* (%): 502 (100), 194 (80), 177 (60); ^{1}H NMR ($CDCl_3$) δ: 0.85 (3H, t, *J* = 6.9 Hz -CH_3), 1.23 (about 38 H, brs), 1.67, 4.10 (each 2H, t, *J* = 6.6 Hz), 3.89 (3H, s), 5.96 (1H, brs, -OH), 6.27, 7.58 (each 1H, d, *J* = 15.9 Hz), 6.89 (1H, d, *J* = 8.2 Hz), 7.00 (1H, d, *J* = 1.5 Hz), 7.04 (1H, dd, *J* = 1.5, 8.2 Hz).

***trans*- and *cis*-Communic Acids (5)**

Mp 74-78 °C; IR (KBr) ν_{max}: 3200-2500, 3080, 1685, 1637, 1600, 1262, 1177, 986, 889 cm^{-1}; *trans*-Communic acid: ^{1}H NMR ($CDCl_3$) δ: 0.64, 1.23, 1.73 (each 3H, s), 4.43, 4.83 (each 1H, brs), 4.86 (1H, d, *J* = 11.7 Hz), 5.03 (1H, d, *J* = 11.7 Hz), 5.38 (1H, t, *J* = 7.0 Hz), 6.31 (1H, dd, *J* = 17.4, 11.7 Hz); *cis*-Communic acid: ^{1}H NMR ($CDCl_3$) δ: 0.64, 1.23, 1.73 (each 3H, s), 4.43, 4.83 (each 1H, brs), 5.10 (1H, d, *J* = 10.9 Hz), 5.17 (1H, d, *J* = 16.9 Hz), 5.29 (1H, t, *J* = 7.0 Hz), 6.79 (1H, dd, *J* = 16.9, 10.9 Hz).

Sandaracopimaric Acid (6)

Mp 166-168 °C; IR (KBr) ν_{max}: 3200-2500, 1688, 1630, 1271, 997, 910, 829 cm^{-1}; EI-MS *m/z* (%): 302 (M$^+$, 23), 287 (36), 257 (14), 167 (20), 121 (100), 105 (48).

Isopimaric Acid (7)

Mp 159-161 °C; IR (KBr) ν_{max}: 3200-2500, 1700, 1635, 1382, 1277, 1000, 906, 834 cm^{-1}; EI-MS *m/z* (%): 302 (M$^+$, 100), 287 (70), 214 (77), 187 (60), 119 (68), 105 (72); ^{1}H NMR ($CDCl_3$) δ: 0.84, 0.89, 1.25 (each 3H, s), 4.85 (1H, dd, *J* = 10.6, 1.2 Hz), 4.90 (1H, dd, *J* = 17.5, 1.2 Hz), 5.20 (1H, brs), 5.78 (1H, dd, *J* = 17.5, 10.6 Hz).

14,15-Bisnor-13-oxo-8(17),11(*E*)-labdadien-19-oic Acid (8) Methyl Ester

Purified by methylation with diazomethane. Methyl ester: Amorphous; IR (KBr) ν_{max}: 3050, 1722, 1675, 1642, 1227, 1154, 980, 891 cm^{-1}; EI-MS *m/z* (%): 304 (M$^+$, 10), 265 (20), 136 (42), 121 (100), 109 (53); ^{1}H NMR ($CDCl_3$) δ: 0.68, 1.18, 2.25, 3.61 (each 3H, s), 4.39, 4.78 (each 1H, brs), 6.05 (1H, d, *J* = 15.8 Hz), 6.82 (1H, dd, *J* = 15.8, 10.2 Hz).

15-Norlabda-8(17),12(*E*)-diene-14-carboraldehyde-19-oic Acid (10) Methyl Ester

Purified by methylation with diazomethane. Methyl ester: Amorphous; IR (KBr) ν_{max}: 3035, 2730, 1719, 1682, 1638, 1280, 1150, 1031, 985, 889 cm^{-1}; EI-MS *m/z* (%): 318 (M$^+$, 5), 260 (20), 121 (100), 105 (48), 91 (63); ^{1}H NMR ($CDCl_3$) δ: 0.57, 1.19, 1.74, 3.62 (each 3H, s), 4.38, 4.85 (each 1H, brs), 6.41 (1H, t, *J* = 6.1), 9.33 (1H, s).

Bornesitol (11) Pentaacetate

Purified by acetylation. Pentaacetate: Mp 140-141 °C; IR (KBr) ν_{max}: 1730, 1725, 1350, 1215, 1030 cm^{-1}; EI-MS *m/z* (%): 405 [(M+H)$^+$, 13], 345 (82), 182 (73), 140 (71), 43 (100); ^{1}H NMR ($CDCl_3$) δ: 1.97, 1.98, 2.00, 2.04, 2.04, 3.34 (each 3H, s), 3.57 (1H, dd, *J* = 6.5, 3.6 Hz), 5.17 (3H, m), 5.35 (2H, m).

Docosyl *cis*-Ferulate (12)

Mp 57-58 °C; IR (KBr) ν_{max}: 3427, 1707, 1623, 1592, 1511, 1283, 1140, 825 cm^{-1}; EI-MS *m/z* (%): 502 (M$^+$, 100), 194 (92), 177 (62); ^{1}H NMR ($CDCl_3$) δ: 0.86 (3H, t, *J* = 6.8 Hz), 1.23 (about 38H, brs), 1.66, 4.10 (each 2H, t, *J* = 6.8

Hz), 3.91 (3H, s), 5.79, 6.77 (each 1H, d, J = 12.9 Hz), 6.86 (1H, d, J = 8.1 Hz), 7.08 (1H, dd, J = 8.1, 1.1 Hz), 7.74 (1H, d, J = 1.1 Hz).

β-Sitosterol (13)

Mp 136-137 °C; IR (KBr) ν_{max}: 3430, 1660, 1385, 1365, 1051, 958, 881 cm^{-1}.

Pinusolide (15)

Mp 81-82 °C; IR (KBr) ν_{max}: 3086, 1740, 1714, 1644, 1604, 1209, 1072, 893, 854 cm^{-1}; EI-MS *m/z* (%): 346 (M^+, 10), 314 (M^+, 12), 286 (51), 121 (100); ^1H NMR ($CDCl_3$) δ: 0.42, 1.09, 3.52 (each 3H, s), 4.66 (2H, d, J = 1.6 Hz), 4.40, 4.80 (each 1H, brs), 7.05 (1H, t, J = 1.6 Hz).

Pinusolidic Acid (16)

Mp 104-106 °C; IR (KBr) ν_{max}: 3200-2500, 3050, 1749, 1690, 1642, 1032, 892, 829 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.60, 1.24 (each 3H, s), 4.78 (2H, d, J = 1.4 Hz), 4.58, 4.92 (each 1H, brs), 7.10 (1H, t, J = 1.4 Hz).

5-Hydroxy-7,4′-dimethoxyflavone (17)

Mp 167-168 °C (yellow needles); IR (KBr) ν_{max}: 3432, 1662, 1601, 1505, 1335, 1269, 1187, 1027, 832 cm^{-1}; EI-MS *m/z* (%): 298 (M^+, 100), 283 (65), 280 (45), 167 (45).

8,15-Pimaradien-18-oic Acid (18) Methyl Ester

Purified by methylation with diazomethane. Methyl ester: Mp 70-71 °C; IR (KBr) ν_{max}: 3040, 1723, 1634, 1246, 1184, 1121, 1041, 908, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.96, 0.98, 1.18, 3.66 (each 3H, s), 4.85 (1H, dd, J = 17.3, 1.5 Hz), 4.92 (1H, dd, J = 10.7, 1.5 Hz), 5.76 (1H, dd, J = 17.3, 10.9 Hz).

Docosyl *trans*-3-hydroxyferulate (20)

Mp 60-61 °C; IR (KBr) ν_{max}: 3401, 1709, 1605, 1370, 1274, 1206, 1096, 891 cm^{-1}; UV λ_{max} (MeOH) (log ε): 240 (4.22), 320 (3.91), 348 (3.74) nm; EI-MS *m/z* (%): 519 [$(M+H)^+$, 65], 518 (20), 490 (18), 210 (100), 193 (72), 166 (22).

7-Oxo-8,15-pimaradien-18-oic Acid (22) Methyl Ester

Purified by methylation with diazomethane. Methyl ester: Amorphous; IR (KBr) ν_{max}: 3074, 1720, 1657, 1611, 1239, 1164, 1110, 910 cm^{-1}; EI-MS *m/z* (%): 330 (M^+, 23), 315 (13), 289 (38), 255 (85), 229 (50), 189 (17); ^1H NMR ($CDCl_3$) δ: 1.01, 1.12, 1.27, 3.65 (each 3H, s), 2.30-2.50 (2H, m, H-6), 4.86 (1H, dd, J = 17.4, 1.3 Hz), 4.96 (1H, dd, J = 10.8, 1.3 Hz), 5.70 (1H, J = 17.4, 10.8 Hz).

β-Sitosteryl-1-*O*-β-glucopyranoside (23) Pentaacetate

Purified by acetylation. Pentaacetate: Mp 178-180 °C; FAB (+)/NBA-MS *m/z*: 767.3 (M^++H+Na, 4); ^1H NMR ($CDCl_3$) δ: 0.65, 0.96, 1.98, 2.00, 2.03, 2.05 (each 3H, s), 0.75 (3H, t, J = 5.7 Hz), 0.80, 0.81 (each 3H, d, J = 6.2 Hz), 0.92 (3H, d, J = 6.2 Hz), 3.47 (1H, m), 3.65 (1H, m), 4.08 (1H, dd, J = 12.3, 2.5 Hz), 4.24 (1H, dd, J = 12.3, 4.9 Hz), 4.57 (1H, d, J = 7.9 Hz), 4.93 (1H, dd, J = 9.3, 7.9 Hz), 5.05 (1H, t, J = 9.3 Hz), 5.19 (1H, t, J = 9.3 Hz), 5.34 (1H, brd, J = 5.0 Hz).

Hydrogenation of 4 and 12

Compound **4** or **12** (20 mg each) in 30 mL of ethyl acetate was hydrogenated in the presence of 10% Pd-C (10 mg). After 7 h, the catalyst was removed by filtration and washed several times with ethyl acetate. With combined filtration and washings, both reactions gave the same product **24** [Mp 54-55 °C; IR (KBr) ν_{max}: 3510, 1723, 1610, 1516, 1276, 1235, 1181, 1026, 855, 822 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.9 Hz), 1.25 (about 38H, brs), 1.58 (2H, quin, J = 6.7 Hz), 2.59, 2.88 (each 2H, t, J = 7.4 Hz), 4.06 (2H, t, J = 6.7 Hz), 6.69 (1H, d, J = 7.8 Hz), 6.71 (1H, s), 6.83 (1H, d, J = 7.8 Hz)].

Acetylation of 20

Compound **20** (15 mg) was allowed to react with Ac_2O (0.5 mL) and pyridine (0.5 mL) at room temperature overnight. The usual work-up gave **25** (15 mg) [Amorphous; IR (KBr) ν_{max}: 1776, 1720, 1638, 1592, 1501, 1274, 1206, 1096, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.66 (3H, t, J = 6.9 Hz), 1.23 (about 38H, brs), 1.57 (2H, quin, J = 6.6 Hz), 2.26, 2.26, 3.86 (each 3H, s), 4.19 (2H, t, J = 6.6 Hz), 6.37, 7.58 (each 1H, d, J = 16.0 Hz), 6.98 (2H, s)].

Transesterification of 20

Compound **20** (30 mg) and NaOMe (10 mg) were dissolved in 5 mL of MeOH, and the reaction mixture was set under stirring for 8 h at room temperature. The solution was acidified with 1 N HCl to pH 4, and then excess of H_2O (50 mL) was poured into it. The aqueous solution was extracted with ethyl acetate (30 mL × 3), and the organic layer was washed with aqueous 3% $NaHCO_3$ and saturated brine water. The crude product was separated by SiO_2 chromatography and afforded two products, 1-dodecanol (14 mg) and **26** (10 mg) [Mp 160-161 °C; IR (KBr) ν_{max}: 3251, 1766, 1701, 1630, 1591, 1500, 1281, 1210, 1095, 986, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 3.78, 3.90 (each 3H, s), 5.46, 5.69 (each 1H, brs, exchangeable with D_2O), 6.26, 7.55 (each 1H, d, J = 16.0 Hz), 6.63, 6.98 (1H, d, J = 1.7 Hz)].

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Key Words

Platycladus orientalis; Cupressaceae; Diterpene; Steroid; Flavonoid; Monoligonol; Docosyl 3-hydroxyferulate.

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