Phytochemistry, Vol. 31, No. 10, pp. 3659-3661, 1992
Printed in Great Britain.

0031-9422/92 \$5.00+0.00

LIGNANS FROM LEAVES OF *JUNIPERUS CHINENSIS*

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(*Received* 3 *January* 1992)

Key Word Index—*Juniperus chinensis*; Cupressaceae; leaves; lignans; 2-arylpropane-1,3-diol; benzodioxane neolignans.

Abstract—Umbelliferone, 13 lignans and an unusual compound 2-(3,4-methylenedioxyphenyl)propane-1,3-diol, were isolated from the leaves of *Juniperus chinensis*. The lignans include *meso*-secoisolariciresinol, 3,4-methylenedioxy-3′,4′-dimethoxylignan-9′,9-olide, hibalactone, isohibalactone, 7-oxohinokinin, 7-hydroxyhinokinin, 7-acetyloxyhinokinin, (+)-xanthoxylol, dihydrodehydrodiconiferyl alcohol, 3-methoxy-8,4′-oxyneoligna-3′,4,7,9,9′-pentol and three new compounds, viz., (8*S*)-3-methoxy-8,4′-oxyneoligna-3′,4,9,9′-tetraol, (7*S*,8*S*)-3-methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9,9′-triol and the corresponding (7*R*,8*S*)-isomer.

INTRODUCTION

Juniperus chinensis, is a common ornamental tree [1]. There is only one previous report regarding the isolation of hinokiflavone and kayaflavone from the leaves [2, 3]. We investigated further the chemical constituents of these leaves and report herein on their lignan components.

RESULTS AND DISCUSSION

The acetone-soluble part of the leaves of *J. chinensis* was extracted with ethyl acetate and the extract subjected to chromatography to give compounds **1–15**. The most abundant component, **1**, was identified as umbelliferone by comparison with an authentic sample [4]. The exact mass $[M]^+$ at *m/z* 196.073 revealed a molecular fomula of $C_{10}H_{12}O_4$ for **2**. The ^{13}C NMR spectrum indicated six aromatic carbons, a methylenedioxy at δ101 (*t*), a methine at δ49 (*d*) and a signal at δ65 (*t*) equivalent to two oxymethylene protons ($-CH_2O-$). Along with the analysis of its ^1H NMR spectrum, **2** is assigned as 2-(3,4-methylenedioxyphenyl)propane-1,3-diol. The branched skeleton of **2** is unique compared with the 1-phenylpropyl subunit commonly found in lignans.

The molecular symmetry of **3** ($C_{20}H_{22}O_6$), $[M]^+$ at *m/z* 362, is characterized by its ^{13}C NMR spectrum, which exhibited only 10 signals. By comparison of the IR and ^1H NMR spectra with the literature, the structure was determined to be either secoisolariciresinol [5] or its *meso*-form. Since compound **3** is optically inactive, it is assigned as *meso*-secoisolariciresinol [6]. Compound **4** showed an IR absorption at 1766 cm^{-1} attributable to a γ-lactone. The mass spectrum shows a parent peak at *m/z* 370 and two fragments at *m/z* 151 (base peak) and 135 derived, respectively, from the dimethoxybenzyl and methylenedioxybenzyl units. Compound **4** ($C_{21}H_{22}O_6$) is assigned as 3,4-methylenedioxy-3′,4′-dimethoxylignan-9′,9-olide [7, 8]. Since two C-9′ protons are non-equivalent, showing at δ3.88 (*dd*, $J = 9.2, 4.9$ Hz) and at δ4.10 (*dd*, $J = 9.2, 6.7$ Hz), the lignan lactone **4** should have the *trans*-configuration [8]. Compound **5** ($C_{20}H_{16}O_6$), mp 147°, was readily recognised as hibalactone by comparison with an authentic sample [9]. Compound **6**, $[M]^+$ at *m/z* 352, was identified as an isomer of **5**, isohibalactone [10, 11]. Compound **6** having a *Z*-configuration displayed the H-7 resonance at a higher field of δ6.57, while the corresponding resonance of its *E*-isomer **5** appeared at δ7.44 due to the deshielding effect of the neighbouring carbonyl group. Compound **7** ($C_{20}H_{16}O_7$), mp 109.5°, was identified as 7-oxohinokinin, a lignan we first isolated from *Calocedrus formosana* [12]. Compound **8** ($C_{20}H_{18}O_7$), mp 124.5–126°, and compound **9** ($C_{22}H_{20}O_8$), mp 121.5–122.5°, are assigned as 7-hydroxyhinokinin [13] and 7-acetyloxyhinokinin [14], respectively, based on comparison of the IR, mass and NMR spectra with the literature. The structures of **8**, also known as sventenin, and **9** are further proved by chemical correlations. The ketone **7** was selectively reduced with $Zn(BH_4)_2$ to give an exclusive product of the alcohol **8**, which was subsequently subjected to acetylation (Ac_2O, pyridine) to afford the derivative **9**. The reduction is believed to occur with the 1,3-dicarbonyl groups chelating to a Zn^{2+} ion, followed by hydride attack at the less hindered α-face [15, 16]. Thus, **8** and **9** should have the 7*S*-configurations with the hydroxy and acetoxy groups on the β-faces.

The ^1H NMR spectrum of **10** showed a methoxy signal at δ3.83 (*s*), a methylenedioxy signal at δ5.92 (*s*), six aromatic protons at δ6.7–6.9, and two oxybenzyl protons (ArCHOR) at δ4.38 (*d*, $J = 7.2$ Hz) and 4.79 (*d*, $J = 5.2$ Hz). The molecular formula $C_{20}H_{20}O_6$ is inferred from the parent peak at *m/z* 356 and the moieties of ArCO and $ArCH_2$, where Ar represents a hydroxymethoxybenzene or a methylenedioxy group, are indicated by four intense peaks at *m/z* 151, 149, 137 and 135. The ^{13}C NMR spectrum of **10** further supported its structure as either xanthoxylol [17] or the C-7,7′ epimer, pluviatiol [18]. Compound **10** had mp 140–142°, close to that of xanthoxylol (mp 140.5–141.5°) but different from that of pluviatiol

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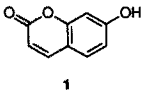

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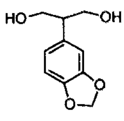

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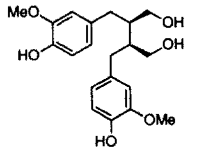

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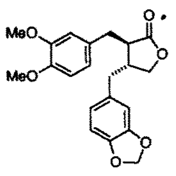

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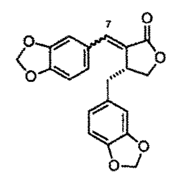
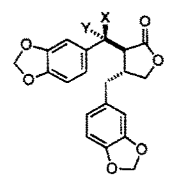
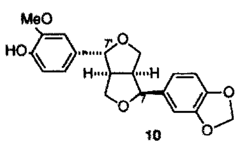


5 (*E*)
6 (*Z*)



7 X,Y = O
8 X = OH, Y = H
9 X = OAc, Y = H



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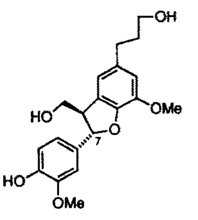

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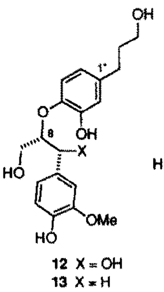
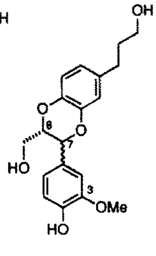


12 X = OH
13 X = H



14 (*trans*)
15 (*cis*)

(mp 161.5–162.5°). The ^{1}H NMR spectra of **10** and its acetate derivative reveal that the position of H-7 is unchanged (δ4.82, *d*, $J = 5$ Hz) but the H-7′ of the acetate is shifted to a lower field (δ4.45) compared with that of **10** (at δ4.38, *d*, $J = 7$ Hz). The structure of **10** is thus assigned as (7*S**,7′*R**,8*S**,8′*S**)-4′-hydroxy-3′-methoxy-3,4-methylenedioxy-7,9′:7′,9-diepoxylignane. However, **10** showed a positive $[\alpha]_D$ rather than the laevorotatory xanthoxylol isolated from *Xanthoxyllum piperitum* [17]. The absolute configuration remains unknown.

Compound **11** was identified as the well-known neolignan, dihydrodehydodiconiferyl alcohol [19, 20], by comparison with an authentic sample ([α], IR, mass spectrum, ^{1}H and ^{13}C NMR). The *trans*-configuration has been determined [21] and the coupling constant between H-7 and H-8 is 6.4 Hz. Compounds **12–15** were also shown to be neolignans by spectral evidence. Compound **12** ($C_{19}H_{24}O_7$) was identified as 3-methoxy-8,4′-oxyneoligna-3′,4,7,9,9′-pentol [22]. The oxybenzyl proton (H-7) appeared at δ4.97 as a doublet with a relatively small coupling constant ($J_{7,8} = 4.6$ Hz), indicating the *erythro* form. The exact mass of the $[M]^+$ at *m/z* 348.158 leads to a molecular formula $C_{19}H_{24}O_6$ for **13**. It was identified as 3-methoxy-8,4′-oxyneoligna-3′,4,9,9′-tetraol, a mono-deoxy derivative of **12**, based on spectral comparison [23]. Compounds **14** and **15** are shown to be the *trans* and *cis* isomers ($C_{19}H_{22}O_6$) of a benzodioxane neolignan, 3-methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9,9′-triol. The coupling constant between H-7 and H-8 in the *trans*-isomer **14** is larger (8.0 Hz) than that in the *cis*-isomer **15** ($J_{7,8} = 2.7$ Hz). Treatment of 3-(3,4-dihydroxyphenyl)propan-1-ol and 3-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-ol with Ag_2O for 16 hr in tetrahydrofuran gave a major oxidative coupling product identical to **14**. This experiment supports the regio- and stereostructure of **14** [24, 25]. The CD spectra of compounds **13–15** all showed positive signs for maxima at 228, 249 and 245 nm, indicating that they have the 8*S*-configuration according to the study of related benzodioxane system [26]. Thus, compounds **12–15** are deduced to have the (7*R*,8*S*)-, (8*S*)-, (7*S*,8*S*)- and (7*R*,8*S*)-configurations, respectively.

EXPERIMENTAL

Plant material. Leaves of *J. chinensis* L. var. *kaizuka* Hort. were collected from plants growing in the surroundings of the Department of Chemistry, National Taiwan University. A voucher specimen is deposited in the herbarium of our university. Leaves (1.83 kg) were soaked in Me_2CO (7 l) for one week. The Me_2CO ext was concd to give 90 g of a residue, which was dil. with H_2O and extd × 3 with EtOAc. The combined EtOAc exts were concd to give an oil (25.5 g), which was absorbed on 31 g of silica gel and then chromatographed on a column packed wtih 250 g of silica gel. By elution with gradients of hexane, EtOAc and Me_2CO, compounds **6** (12 mg), **7** (63 mg), **9** (15 mg), **10** (24 mg), **8** (18 mg), **4** (12 mg), **5** (1.5 g), **2** (45 mg), **14** (26 mg), **15** (20 mg), **13** (20 mg), **12** (30 mg), **3** (8 mg), **11** (25 mg) and **1** (2.3 g) were obtained in ascending order of polarity.

Compound **1**. Mp 229–230°. *Compound* **3**. $[\alpha]_D^{25}$ 0° ($CHCl_3$; *c* 0.7). ^{13}C NMR (Me_2CO-d_6) δ35.8 (*t*), 44.4 (*d*), 55.8 (*q*), 61.0 (*t*), 113.0 (*d*), 115.1 (*d*), 122.1 (*d*), 133.3 (*s*), 145.1 (*s*), 147.8 (*s*). *Compound* **4**. $[\alpha]_D^{25}$ −25° ($CHCl_3$; *c* 0.1). *Compound* **5**. Mp 147°. $[\alpha]_D^{25}$ −25° (Me_2CO; *c* 2.8). *Compound* **6**. Mp 145–146°. $[\alpha]_D^{25}$ −155° ($CHCl_3$; *c* 0.85). *Compound* **7**. Mp 109.5°. $[\alpha]_D^{25}$ +10° ($CHCl_3$; *c* 0.82). *Compound* **8**. Mp 124.5–126°. $[\alpha]_D^{25}$ −43° ($CHCl_3$; *c* 0.44). ^{13}C NMR ($CDCl_3$) δ36.2 (*t*, C-7′), 39.4 (*d*, C-8′), 52.8 (*d*, C-8), 71.8 (*t*, C-9′), 72.7 (*d*, C-7), 100.9 (*t*), 101.1 (*t*), 105.7 (*d*), 108.0 (*d*, 2 C), 108.6 (*d*), 118.3 (*d*), 121.5 (*d*), 131.5 (*s*), 135.0 (*s*), 146.1 (*s*), 146.8 (*s*), 147.6 (*s*), 147.7 (*s*), 178.4 (*s*). *Compound* **9**. Mp 121.5–122.5°. $[\alpha]_D^{25}$ −29° ($CHCl_3$; *c* 0.1). ^{13}C NMR ($CDCl_3$) δ20.9 (*q*), 37 5 (*t*), 39.3 (*d*), 50 9 (*d*, C-8), 72.0 (*t*), 73.5 (*d*), 101.0 (*t*), 101.3 (*t*), 105.8 (*d*), 108.2 (*d*), 108.4 (*d*), 108.6 (*d*), 118.6 (*d*), 121.6 (*d*), 131.1 (*s*), 131.2 (*s*), 146.3 (*s*), 147.4 (*s*), 147.8 (*s*), 148.0 (*s*), 169.0 (*s*), 175.8 (*s*). *Compound* **10**. Mp 140–142°. $[\alpha]_D^{25}$ +122° ($CHCl_3$; *c* 5.8). ^{13}C NMR ($CDCl_3$) δ50.1 (*d*, C-8′), 54.5 (*d*, C-8), 55.9 (*q*), 69.6 (*t*, C-9′), 70.9 (*t*, C-9), 82.0 (*d*, C-7′), 87.7 (*d*, C-7), 100.9 (*t*), 106.4 (*d*), 108.1 (*d*), 108.6 (*d*), 114.2 (*d*), 118.7 (*d*), 119.2 (*d*), 132.3 (*s*), 133.0 (*s*), 145.3 (*s*), 146.6 (*s*), 146.7 (*s*), 147.6 (*s*). Acetate of **10**. $[\alpha]_D^{25}$ +84.4° ($CHCl_3$; *c* 0.5). *Compound* **11**. $[\alpha]_D^{25}$ −18° (MeOH; *c* 0.6). ^{13}C NMR (MeOH-d_4) δ32.9 (*t*), 35.8 (*t*), 55.4 (*d*, C-8), 56.3 (*q*), 56.7 (*q*), 62.2 (*t*, C-9′), 65.0 (*t*, C-9), 89.0 (*d*, C-7), 110.6 (*d*), 114.1 (*d*), 116.3 (*d*), 117.9 (*d*), 119.8 (*d*), 129.9 (*s*), 134.3 (*s*), 136.8 (*s*), 145.1 (*s*), 147.5 (*s*), 148.2 (*s*), 149.3 (*s*). *Compound* **12**. $[\alpha]_D^{25}$ +11.7° (Me_2CO; *c* 3.0). ^{13}C NMR ($CDCl_3$) δ32.1 (*t*, C-7′), 35.3 (*t*, C-8′), 56.2 (*q*), 61.6 (*t*, C-9′), 61.8 (*t*, C-9), 73.7 (*d*, C-7), 87.9 (*d*, C-8), 111.3 (*d*), 115.3 (*d*), 117.0 (*d*), 119.9 (*d*), 120.4 (*d*), 120.8 (*d*), 133.3 (*s*), 138.8 (*s*), 145.2 (*s*), 146.7 (*s*), 148.0 (*s*), 149.8 (*s*).

2-(3,4-*methylenedioxyphenyl*)*Propane*-1,3-*diol* (**2**). Oily solid. IR ν_{max}^{neat} cm^{-1}: 3356 (OH), 1602. 1481, 933, ^{1}H NMR ($CDCl_3$): δ2.91 (1 H, *m*), 3.54 (2H, *br s*, OH), 3.7–3.9 (4H), 5.88 (2H, *s*), 6.62 (1H, *dd*, $J = 7.9$, 1.5 Hz), 6.68 (1H, *d*, $J = 1.5$ Hz), 6.72 (1H, *d*, $J = 7.9$ Hz). ^{13}C NMR (75 MHz): δ49.3 (*d*, C-2), 65.4 (*t*, C-1, 3), 100.9 (*t*, OCH_2O), 108.2 (*d*), 108.4 (*d*), 121.1 (*d*, C-6′), 133.2 (*s*, C-1), 146.4 (*s*), 147.7 (*s*). EIMS (70 eV) *m/z* (%) 196 $[M]^+$ (100), 165

(95), 148 (71), 135 (92), 121 (13), 107 (96), 89 (14), 79 (96), 77 (64). Exact mass $[M]^+$ for $C_{10}H_{12}O_4$ requires 196.0736; Found 196.0727.

(8S)-3-*Methoxy-8,4′-oxyneoligna-3′,4,9,9′-tetraol* (**13**). Oil, $[\alpha]_D^{25}$ +0.11° (MeOH; *c* 1.7). IR ν_{max}^{neat} cm^{-1}: 3399, 1600, 1510, 1272, 1034. UV$_{max}^{MeOH}$ nm: 278 (ε 8213), 217 (ε 21 576). CD (MeOH): $[\theta]_{296.5}$ −210, $[\theta]_{270}$ 0, $[\theta]_{227.5}$ +3 663. ^{1}H NMR (Me_2CO-d_6): δ1.76 (*m*, two H-8′), 2.55 (*t*, *J* = 7.7 Hz, two H-7′), 2.90 (*dd*, *J* = 13.7, 7.1 Hz, H-7), 2.99 (*dd*, *J* = 13.7, 6.1 Hz, H-7), 3.54 (*t*, *J* = 6.4 Hz, two H-9′), 3.63 (*dd*, *J* = 11.5, 6.4 Hz, H-9), 3.72 (*dd*, *J* = 11.5, 3.3 Hz, H-9), 3.78 (*s*, OMe), 4.20 (*m*, H-8), 6.55 (*dd*, *J* = 8.1, 2.1 Hz, H-6′), 6.69 (*d*, *J* = 2.1 Hz, H-2′), 6.71 (*d*, *J* = 8.1 Hz, H-5′), 6.74 (*d*, *J* = 8.1 Hz, H-5), 6.80 (*br d*, *J* = 8.1 Hz, H-6), 6.89 (*br s*, H-2). ^{13}C NMR (Me_2CO-d_6): 31.9 (*t*, C-7′), 35.2 (*t*, C-8′), 37.4 (*t*, C-7), 55.9 (*q*, OCH_3), 61.5 (*t*, C-9′), 63.4 (*t*, C-9), 84.5 (*d*, C-8), 113.6 (*d*, C-2), 115.4 (*d*, C-5), 116.5 (*d*, C-2′), 118.8 (*d*, C-6), 119.7 (*d*, C-6′), 122.5 (*d*, C-5′), 129.7 (*s*), 138.0 (*s*), 144.6 (*s*), 146.0 (*s*), 147.9 (*s*), 149.2 (*s*). EIMS (70 eV) *m/z* (%) 348 $[M]^+$ (8), 181 (13), 167 (18), 137 (100). Exact mass $[M]^+$ for $C_{19}H_{24}O_6$ requires 348.1573; Found 348.1578.

(7S,8S)-3-*Methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9,9′-triol* (**14**). Oil, $[\alpha]_D^{25}$ +0.34° (MeOH; *c* 1.4). IR ν_{max}^{neat} cm^{-1}: 3395, 2935, 1590, 1500, 1271, 1124, 1034. UV λ_{max}^{MeOH} nm: 277 (ε 19 174), 227 (ε 33 753). CD (MeOH): $[\theta]_{333}$ −2196, $[\theta]_{302}$ −1845, $[\theta]_{269.5}$ +4359, $[\theta]_{258}$ +210, $[\theta]_{248.5}$ +4270. EIMS (70 eV) *m/z* (%) 346 $[M]^+$ (37), 328 (18), 180 (53), 179 (30), 162 (53), 152 (26), 137 (100), 124 (57). ^{1}H NMR (Me_2CO-d_6): δ1.77 (2H, *m*), 2.58 (2H, *t*, *J* = 7.4 Hz), 3.55 (2H, *t*, *J* = 6.5 Hz), 3.47 (*br d*, *J* = 12 Hz, H-9), 3.69 (*br d*, *J* = 12 Hz, H-9), 3.85 (3H, *s*), 4.04 (*ddd*, *J* = 8.0, 2.6, 2.4 Hz, H-8), 4.92 (*d*, *J* = 8.0 Hz, H-7), 6.69 (*dd*, *J* = 8.1, 1.9 Hz, H-6′), 6.72 (*d*, *J* = 1.9 Hz, H-2′), 6.79 (*d*, *J* = 8.1 Hz, H-5′), 6.86 (*d*, *J* = 8.1 Hz, H-5), 6.93 (*dd*, *J* = 8.1, 1.8 Hz, H-6), 7.09 (*d*, *J* = 1.8 Hz, H-2). ^{13}C NMR (Me_2CO-d_6): δ32.0 (*t*, C-7′), 35.6 (*t*, C-8′), 56.3 (*q*), 61.7 (*t*, C-9′), 61.9 (*t*, C-9), 77.1 (*d*, C-7), 79.4 (*d*, C-8), 111.9 (*d*, C-2), 115.7 (*d*, C-5), 117.3 (*d*, C-5′), 117.5 (*d*, C-2′), 121.5 (*d*, C-6), 122.0 (*d*, C-6′), 129.4 (*s*), 136.1 (*s*), 142.6 (*s*), 144.6 (*s*), 147.9 (*s*), 148.5 (*s*). Exact mass $[M]^+$ for $C_{19}H_{22}O_6$ requires 346.1416; Found 346.1408.

(7R,8S)-3-*Methoxy-3′,7-epoxy-8,4′-oxyneoligna-4,9,9′-triol* (**15**). Oil, $[\alpha]_D^{23}$ −2.6° (MeOH; *c* 1.7). IR ν_{max}^{neat} cm^{-1}: 3389, 2933, 1699, 1587, 1499, 1268, 1157, 1122, 1035. UV λ_{max}^{MeOH} nm: 280 (ε 7319), 227 (ε 15 703). CD (MeOH): $[\theta]_{327.5}$ −1761, $[\theta]_{303.5}$ −107, $[\theta]_{271.5}$ +450, $[\theta]_{258.5}$ +281, $[\theta]_{245}$ +417. EIMS (70 eV) *m/z* (%) 346 $[M]^+$ (40), 328 (18), 269 (4), 241 (5), 237 (5), 209 (5), 180 (37), 179 (23), 162 (68), 152 (24), 137 (100), 124 (69). ^{1}H NMR (Me_2CO-d_6): δ1.78 (2 H, *m*), 2.60 (2 H, *t*, *J* = 7.4 Hz), 3.55 (2 H, *t*, *J* = 6.5 Hz), 3.43 (2H, *m*, H-9), 3.78 (3H, *s*), 4.46 (*ddd*, *J* = 7.8, 2.8, 2.6 Hz, H-8), 5.24 (*d*, *J* = 2.8 Hz, H-7), 6.71 (*dd*, *J* = 8.1, 1.9 Hz, H-6′), 6.77 (*d*, *J* = 1.9 Hz, H-2′), 6.79 (*d*, *J* = 8.1 Hz, H-5′), 6.84 (*d*, *J* = 8.1 Hz, H-5), 6.88 (*dd*, *J* = 8.1, 1.8 Hz, H-6), 7.23 (*d*, *J* = 1.8 Hz, H-2): ^{13}C NMR (Me_2CO-d_6): δ32.0 (*t*, C-7′), 35.5 (*t*, C-8′), 56.2 (*q*), 59.7 (*t*, C-9′), 61.7 (*t*, C-9), 76.5 (*d*, C-7), 78.4 (*d*, C-8), 111.1 (*d*, C-2), 115.7 (*d*, C-5), 117.6 (*d*, C-5′), 117.8 (*d*, C-2′), 120.2 (*d*, C-6), 122.2 (*d*, C-6′), 129.1 (*s*), 136.6 (*s*), 141.2 (*s*), 144.1 (*s*), 147.4 (*s*), 148.3 (*s*). Exact mass $[M]^+$ for $C_{19}H_{22}O_6$ requires 346.1416; Found 346.1396.

Acknowledgement—We are grateful to the National Science Council (Republic of China) for financial support.

REFERENCES

1. Ying, S. S. (1985) *Coloured Illustrated Flora of Taiwan* Vol. 1, p. 168. National Taiwan University, Taipei.
2. Hsu, C. M. (1960) *Chemical Constituents of the Medicinal Plants in Taiwan* Vol. 1, 174. National Research Institute for Chinese Medicine, Taipei.
3. Sawada, T. (1958) *Yakugaku Zasshi* **78**, 1020.
4. Fang, J. M., Lang, C. I., Chen, W. L. and Cheng, Y. S. (1991) *Phytochemistry* **30**, 2793.
5. Fonseca, S. F., Campello, J. D. P., Barata, L. E. S. and Ruveda, E. A. (1978) *Phytochemistry* **17**, 499.
6. Agrawal, P. K. and Rastogi, R. P. (1982) *Phytochemistry* **21**, 1459.
7. McDoniel, P. B. and Cole, J. R. (1972) *J. Pharm. Sci.* **61**, 1992.
8. Lopes, L. M. X., Yoshida, M. and Gottlieb, O. R. (1983) *Phytochemistry* **22**, 1516.
9. Fang, J. M., Jan, S. T. and Cheng, Y. S. (1985) *Phytochemistry* **24**, 1863.
10. Burden, R. S., Crombie, L. and Whiting, D. A. (1969) *J. Chem. Soc. C* 2470.
11. Banerji, J., Das, B., Chatterjee, A. and Shoolery, J. N. (1984) *Phytochemistry* **23**, 2323.
12. Fang, J. M., Liu, M. Y. and Cheng, Y. S. (1990) *Phytochemistry* **29**, 3048.
13. Martinez, E. A., Funes, J. L. B., Gonzalez, A. G. and Luis, F. R. (1969) *Anal. Quim.* **65**, 809.
14. Gonzalez, A. G., Martinez, E. A., Iniguez, M. A. M. and Luis, F. R. (1971) *Anal. Quim.* **67**, 441.
15. Gensler, W. J., Johnson, F. and Sloan, A. D. B. (1960) *J. Am. Chem. Soc.* **82**, 6074.
16. Nakata, T. and Oishi, T. (1980) *Tetrahedron Letters* **21**, 1641.
17. Abe, F., Yahara, S., Kubo, K., Nonaka, G., Okabe, H. and Nishioka, I. (1974) *Chem. Pharm. Bull.* **22**, 2650.
18. Corrie, J. E. T., Green, G. H., Ritchie, E. and Taylor, W. C. (1970) *Aust. J. Chem.* **23**, 133.
19. Popoff, T. and Theander, O. (1975) *Phytochemistry* **14**, 2065.
20. Agrawal, P. K., Agarwal, S. K. and Rastogi, R. P. (1980) *Phytochemistry* **19**, 1260.
21. Agrawal, P. K., Rastogi, R. P. and Osterdahl, B.-G. (1983) *Org. Magn. Res.* **21**, 119.
22. Popoff, T. and Theander, O. (1977) *Acta. Chem. Scand.* **B**, 329.
23. Cavalcante, S. H., Yoshida, M. and Gottlieb, O. R. (1985) *Phytochemistry* **24**, 1051.
24. Merlini, L., Zanarotti, A., Pelter, A., Rochefort, M. P. and Hansel, R. (1980) *J. Chem. Soc., Perkin Trans I* 775.
25. Arnoldi, A., Arnone, A. and Merlini, L. (1984) *Heterocycles* **22**, 1537.
26. Silva, M. S., Barbosa-Filho, J. M., Yoshida, M. and Gottlieb, O. R. (1989) *Phytochemistry* **28**, 3477.