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THREE NEW PHENOLIC COMPOUNDS FROM THE
ROOTS OF *SOPHORA LEACHIANA*

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ABSTRACT.—By further investigation of the root constituents of *Sophora leachiana*, eight phenolic compounds, including two new flavanones **1** and **2** and a new chromone **3**, were isolated. The structures were established by means of spectroscopic analysis.

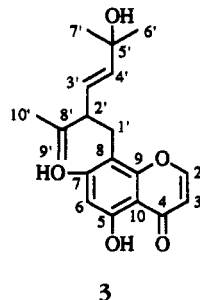
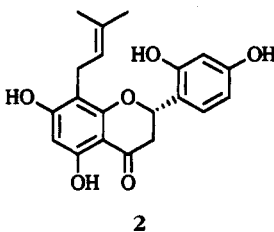
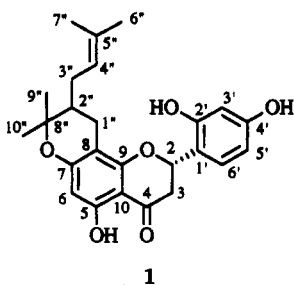
In previous papers, we reported the structures of flavanones with a C₁₀ alkyl side chain, exclusively a lavandulyl group, named leachianones A–E (1–3), in the roots of *Sophora leachiana* Peck (Leguminosae). By further study of the chemical constituents of the roots, eight phenolic compounds with a C₅ or a C₁₀ alkyl unit, including two new flavanones (leachianones F [**1**] and G [**2**]) and a new chromone (leachianone H [**3**]), were isolated by means of repeated purification of a C₆H₆ and an EtOAc extract with Si gel cc and preparative tlc. In the present paper, the structural determinations of these compounds are described.

RESULTS AND DISCUSSION

C₆H₆ and EtOAc partition residues of an Me₂CO extract of *S. leachiana* were chromatographed separately on Si gel cc using a C₆H₆/Me₂CO system as eluent. Further purification of each extract by Si

gel cc and preparative tlc gave eight phenolic compounds. Three of them, **1**–**3** are novel natural products.

Compound **1**, leachianone F, was obtained as a yellow oil and gave positive reactions to Mg–HCl, FeCl₃, and the Gibbs test. In the hrms, [M]⁺ m/z 424.1862, its empirical formula was confirmed to be C₂₅H₂₈O₆ (calcd 424.1885). In the ¹H-nmr spectrum, three one-proton doublets at δ 2.77 (*J*=17, 3 Hz), 3.11 (*J*=17, 13 Hz), and 5.72 (*J*=13, 3 Hz), assigned to the protons at C-3 and C-2 in a flavanone skeleton, were observed. A C₁₀ alkyl unit and three OH groups were deduced by the following data: δ 1.20, 1.42 (3H each, s, Me), 1.59, 1.69 (3H each, s, Me attached to a double bond), 1.71 (1H, m, CH), 1.84, 2.77 (1H each, m, CH₂), 2.18, 2.73 (1H each, dd, *J*=17, 10 and 17, 5 Hz, CH₂), 5.18 (1H, m, CH=), 8.40, 8.67 (1H each, br s, OH) and 11.94 (1H, s, chelated OH). The ¹H-nmr spectrum also showed an ABX spin



system attributable to a B ring at δ 6.44 (dd, $J=8, 2$ Hz), 6.48 (d, $J=2$ Hz) and 7.34 (d, $J=8$ Hz). In the eims spectrum, a significant fragment ion at m/z 136 (B_1) indicated the B-ring moiety to have a 2',4'-dihydroxyl substitution.

A hydrogen-bonded OH group in flavanones substituted at C-6 with a Me or a γ,γ -dimethylallyl group is shifted to lower field compared to one substituted at C-8 (4). The chelated OH group of **1** was found at δ 11.94, and the shift value was closely similar to that (δ 11.91) of kenusanone J (5,2',4'-trihydroxy-6'',6''-dimethyl-dihydropyrano[2'',3'':7,8]flavanone) (5). By comparison of the ^1H - and ^{13}C -nmr spectral data with those of leachianone B (2), **1** clearly had the same partial structure of the A ring as leachianone B. Taking into account the cd data (Experimental), the configuration at C-2 was determined to be *S* (6). The structure of leachianone F was, consequently, concluded to be **1**, which is a partially cyclized derivative of sophoraflavanone G (1).

Compound **2**, leachianone G, was obtained as a colorless powder and showed positive reactions to Mg-HCl, FeCl₃, and the Gibbs test. Its empirical formula was found to be C₂₀H₂₀O₆ by the hrms, observed $[\text{M}]^+$ m/z 356.1284; calcd 356.1260. The ^1H -nmr spectrum exhibited three one-proton double doublets at δ 2.77 ($J=17, 3$ Hz), 3.11 ($J=17, 13$ Hz), and 5.69 ($J=13, 3$ Hz) which were assignable to H-3 and H-2 of a flavanone skeleton. The signals corresponding to a γ,γ -dimethylallyl group [δ 1.61, 1.63 (3H each, s, Me), 3.24 (2H, br d, $J=7$ Hz, CH₂), and 5.22 (1H, t-like m, CH=)] and two OH groups [δ 8.90 (br s), 12.18 (1H, s, chelated OH)] were also found in the spectrum. The fragment ions at m/z 165 and 136 due to the retro-Diels-Alder cleavage in the eims indicated that two OH groups and the γ,γ -dimethylallyl group exist on the A ring and two OH groups are on the B ring. In the ^1H -nmr spectrum, three protons at δ 6.45 (dd,

$J=8, 2$ Hz), 6.49 (d, $J=2$ Hz), and 7.35 (d, $J=8$ Hz) suggested that the B ring had a 2',4'-dihydroxyl substitution. The chemical shift of the 5-OH allowed a partial structure of the A ring to have an 8-(γ,γ -dimethylallyl)-5,7-dihydroxyl substitution (4). The cd data indicated that the configuration at C-2 was *S* (Experimental). The structure of leachianone G was, thus, determined to be (2*S*)-5,7,2',4'-tetrahydroxy-8-(γ,γ -dimethylallyl)flavanone (**2**).

Compound **3** was obtained as a colorless oil, gave $[\text{M}]^+$ at m/z 330 in the eims, and showed a positive result to FeCl₃. In the ^1H -nmr spectrum, two one-proton doublets due to a set of cis olefinic protons [δ 6.20 ($J=6$ Hz) and 8.15 ($J=6$ Hz)], a one-proton singlet in a nucleus (δ 6.32), and two OH protons [δ 9.55 and 12.76 (chelated)] were superimposable upon the corresponding signals of exiguachromone A (7) and sophorachromone A (8) (which were chromone derivatives isolated from *Sophora exigua* and *Sophora tomentosa*, respectively) except for signals associated with an alkyl side chain. The ^1H -nmr spectrum showed the presence of a C₁₀ unit: three methyls [δ 1.29 (Me \times 2) and 1.71 (attached to a double bond)], a methylene attached to a benzene ring (δ 2.73), a methine (δ 2.94), an olefinic methylene (δ 4.75), a set of trans olefinic protons [δ 5.35 (d, $J=16$ Hz) and 5.60 (dd, $J=16, 8$ Hz)]. These signals were assignable to a derivative of a lavandulyl group as found in leachianone D (3), and the group could be characterized as a 5-hydroxy-2-isopentenyl-5-methyl-*trans*-hex-3-enyl residue. Therefore, the overall structure of **3** was concluded to be 8-(5-hydroxy-2-isopentenyl-5-methyl-*trans*-hex-3-enyl)-5,7-dihydroxychromone, which was named leachianone H.

The other five compounds were determined to be sophoraflavanone H (9), sophoraflavanone B (10), kievitone (11), wightone (12), and 2'-hydroxylupalbigenin (13) by means of spectroscopic

analysis. These compounds have a common C₅ unit(s) side chain, and were isolated for the first time from the roots of *S. leachiana*. In earlier reports, the phenolic compounds found in the plant were flavonoids with a C₁₀ unit: in particular, a lavandulyl group or its derivative. *S. leachiana* had not been described in the classification of the genus *Sophora* by Tsoong and Ma (14,15), who divided the genus into two subgenera (*Sophora* and *Styphnolobium*) using morphological aspects. The subgenus *Sophora* was further classified into three sections and *Styphnolobium* into four. Considering the close similarities of the chemical constituents obtained in the present experiment between *S. leachiana* and *Sophora moorcroftiana*, which is located in the subgenus *Sophora* sect. *Pseudosophora*, *S. leachiana* may be classified in the same section as *S. moorcroftiana* as well as *Sophora alopecuroides* and *Sophora lehmannii*, based on the chemosystematics.

EXPERIMENTAL

PLANT MATERIAL—The roots of *S. leachiana* were collected at Medford, Oregon in June 1992. Voucher specimens are deposited at the Herbarium of Gifu Pharmaceutical University.

EXTRACTION AND ISOLATION OF COMPOUNDS 1-3.—Dried and ground roots (580 g) of *S. leachiana* were extracted with Me₂CO and MeOH, successively. The Me₂CO solution was concentrated under reduced pressure, and the residue was poured into H₂O. The suspended solution was partitioned with C₆H₆, EtOAc, and *n*-BuOH, successively. After concentration, the EtOAc residue (45 g) and the C₆H₆ residue (15 g) were separately subjected to Si gel cc (a C₆H₆/Me₂CO system) and further purified by preparative tlc [CHCl₃-MeOH (10:1)] to give **1** (40 mg), **2** (15 mg), and **3** (2 mg) in addition to sophoraflavanone B (5 mg), kievitone (13 mg), wightone (8 mg), and 2'-hydroxylupalbinogenin (3 mg) from the EtOAc residue, and sophoraflavanone H (1.3 g) from the C₆H₆ residue.

Leachianone F [1].—A yellow oil: *R*_f 0.37 [CHCl₃-MeOH (10:1)]; cd Δε₂₈₇ -11.5, Δε₃₁₀ +1.5; eims *m/z* (rel. int.) [M]⁺ 424 (78), 409 (31), 406 (93), 391 (42), 337 (61), 283 (57), 219 (32), 177 (23), 165 (100), 135 (44), 123 (19); ¹H nmr (400 MHz, Me₂CO-*d*₆) δ 1.20 (3H, s, H-9''), 1.42 (3H, s, H-10''), 1.59 (3H, br s, H-7''), 1.69 (3H, br

s, H-6''), 1.71 (1H, m, H-2''), 1.84 (1H, m, H-3''), 2.18 (1H, dd, *J*=17, 10 Hz, H-1''), 2.27 (1H, m, H-3''), 2.73 (1H, dd, *J*=17, 5 Hz, H-1''), 2.77 (1H, dd, *J*=17, 3 Hz, H-3), 3.11 (1H, dd, *J*=17, 13 Hz, H-3), 5.18 (1H, m, H-4''), 5.72 (1H, dd, *J*=13, 3 Hz, H-2), 5.83 (1H, s, H-6), 6.44 (1H, dd, *J*=8, 2 Hz, H-5'), 6.48 (1H, d, *J*=2 Hz, H-3'), 7.34 (1H, d, *J*=8 Hz, H-6'), 8.40, 8.67 (1H each, br s, OH), 11.94 (1H, s, chelated OH); ¹³C nmr (100 MHz, Me₂CO-*d*₆) δ 17.9 (C-7''), 21.2 (C-10''), 22.5 (C-1''), 25.9 (C-9''), 30.0 (C-3''), 41.7 (C-2''), 42.6 (C-3), 75.7 (C-2), 80.1 (C-8''), 97.1 (C-6), 101.9 (C-3'), 103.3 (C-10), 103.5 (C-8), 107.9 (C-5'), 117.6 (C-1'), 123.3 (C-4''), 128.6 (C-6'), 133.5 (C-5''), 156.3 (C-2'), 159.5 (C-4'), 161.4 (C-9), 162.4 (C-5), 163.1 (C-7), 197.9 (C-4) (assignment of C-9'' and C-10'' is interchangeable).

Leachianone G [2].—A colorless powder: *R*_f 0.25 [CHCl₃-MeOH (10:1)]; cd Δε₂₈₇ -13.5, Δε₃₁₀ +1.8; eims *m/z* (rel. int.) [M]⁺ 356 (48), 338 (62), 323 (16), 295 (57), 283 (47), 170 (17), 205 (31), 192 (24), 177 (43), 165 (100), 136 (22); ¹H nmr (270 MHz, Me₂CO-*d*₆) δ 1.61, 1.64 (3H each, s, Me-4'', -5''), 2.77 (1H, dd, *J*=17, 3 Hz, H-3eq), 3.11 (1H, dd, *J*=17, 13 Hz, H-3ax), 3.24 (2H, br d, *J*=7 Hz, H-1''), 5.22 (1H, t-like m, H-2''), 5.69 (1H, dd, *J*=13, 3 Hz, H-2), 6.04 (1H, s, H-6), 6.45 (1H, dd, *J*=8, 2 Hz, H-5'), 6.49 (1H, d, *J*=2 Hz, H-3'), 7.35 (1H, d, *J*=8 Hz, H-6'), 8.90 (br s, OH), 12.18 (1H, s, 5-OH); ¹³C nmr (67.5 Hz, Me₂CO-*d*₆) δ 18.0 (C-5''), 22.4 (C-1''), 26.1 (C-4''), 42.7 (C-3), 75.5 (C-2), 96.4 (C-6), 103.4 (C-10), 103.6 (C-3'), 108.0 (C-5') 108.4 (C-8), 117.8 (C-1'), 123.9 (C-2'), 128.8 (C-6'), 131.3 (C-3'), 156.4 (C-2'), 159.6 (C-4'), 161.7 (C-9), 163.1 (C-5), 164.9 (C-7), 198.2 (C-4).

Leachianone H [3].—A colorless oil: eims *m/z* (rel. int.) [M]⁺ 330 (1), 191 (100), 165 (6); ¹H nmr (Me₂CO-*d*₆) δ 1.29 (6H, br s, Me-6'' and Me-7''), 1.73 (3H, br s, Me-10''), 2.73 (2H, m, H-1''), 2.94 (1H, m, H-2''), 4.75 (2H, m, H-9''), 5.35 (1H, d, *J*=16 Hz, H-4''), 5.60 (1H, dd, *J*=16, 8 Hz, H-3''), 6.20 (1H, d, *J*=6 Hz, H-3), 6.32 (1H, s, H-6), 8.15 (1H, d, *J*=6 Hz, H-2), 9.55 (1H, br s, OH), 12.76 (1H, s, 5-OH).

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