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Studies on the Constituents of Ophiopogonis Tuber. V.[1] Isolation of a Novel Class of Homoisoflavonoids and Determination of Their Structures (1)

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New homoisoflavonoidal compounds, methylophiopogonanone A (Ia), methylophiopogonanone B (IIa), methylophiopogonone A (IIIa) and methylophiopogonone B (IVa), were isolated from ophiopogonis tubers (tubers of *Ophiopogon japonicus* Ker-Gawler var. *genuinus* Maxim., Liliaceae) and their structures were shown to be 5,7-dihydroxy-6,8-dimethyl-3-(3,4-methylenedioxybenzyl)-chroman-4-one, 5,7-dihydroxy-6,8-dimethyl-3-(4-methoxybenzyl)-chroman-4-one, 5,7-dihydroxy-6,8-dimethyl-3-(3,4-methylenedioxybenzyl)-chromone and 5,7-dihydroxy-6,8-dimethyl-3-(4-methoxybenzyl)-chromone, respectively. Methylophiopogonones A and B are members of a new class of naturally occuring homoisoflavonoidal compounds having a double bond at C_{2-3}.

Keywords——Ophiopogonis tuber; *Ophiopogon japonicus*; Liliaceae; homoisoflavonoid; methylophiopogonanone A, B; methylophiopogonone A, B; column chromatography; UV; NMR; mass spectra

The structures of spirostanol glycosides, ophiopogonins A, B, B′, C, C′, D and D′,[1,3] isolated from Ophiopogonis tubers (tubers of *Ophiopogon japonicus* Ker–Gawler var. *genuinus* Maxim., Liliaceae), were previously reported to be ruscogenin glycosides and diosgenin glycosides.

Several species of Liliaceae are known to be sources of phenolic compounds having unique structural properties, and this group of natural products has been given the name of homoisoflavonoids. The number of carbons in the homoisoflavonoid skeleton is sixteen, while that in the isoflavonoid skeleton is fifteen. The sixteenth carbon is considered to be derived from the methoxyl carbon of 2′-methoxychalcone, which is regarded as a significant precursor on the basis of an experimental study used an isotopic labelled compound.[4]

Interestingly, all naturally occurring homoisoflavonoidal compounds have so far been isolated from the subfamily "scilloideae" only; *Eucomis bicolor*, *E. comosa*, *E. autumnalis*[5] and *Scilla scilloides*.[6] The skeletons of these known homoisoflavonoids can be classified into four types (V)—(VIII).[7]

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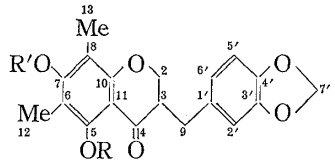
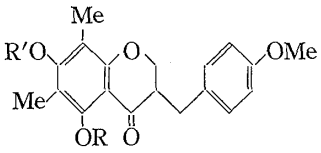
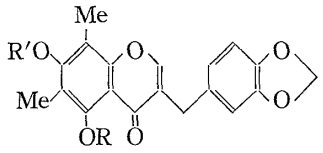


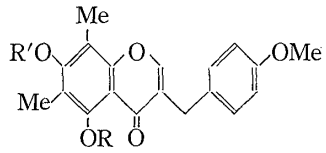
Ia: R=R′=H
Ib: R=H, R′=Me
Ic: R=H, R′=Ac
Id: R=R′=Ac



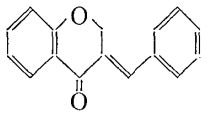
IIa: R=R′=H
IIb: R=H, R′=Me
IIc: R=H, R′=Ac
IId: R=R′=Ac



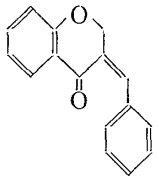
IIIa: R=R′=H
IIIb: R=H, R′=Me



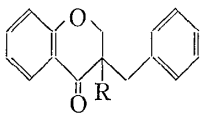
IVa: R=R′=H
IVb: R=H, R′=Me



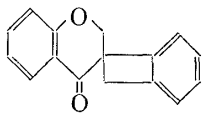
V: (*E*)-, (*trans*)



VI: (*Z*)-, (*cis*)



VII: R=H, OH



VIII

Chart 1

Further investigation of the non-glycosidic fraction of Ophiopogonis tuber has resulted in the isolation of a novel type of homoisoflavonoidal compounds, named methylophiopogonanones A (Ia) and B (IIa), methylophiopogonones A (IIIa) and B (IVa), ophiopogonanone A, ophiopogonones A and B, isoophiopogonone A, desmethylisoophiopogonone B, substances A and B. The present paper is mainly concerned with Ia, IIa, IIIa and IVa.

It is noteworthy that the plant source belongs to the subfamily "ophiopogonoideae" (monodoideae) from which homoisoflavonoidal compounds have not been isolated, and some of these newly isolated compounds can be considered to be a new class of homoisoflavonoids. The isolation procedure for the eleven new homoisoflavonoids obtained from the ether-soluble portion of the methanolic extract of the tuber is shown in Chart 2. The proton magnetic resonance (PMR) spectral data are summarized in Table I.

Methylophiopogonanone A (Ia)

Ia, $C_{19}H_{18}O_6$ (M.W. 342), $[\alpha]_D$ −72.0° ($CHCl_3$), was obtained as colorless needles of mp 166—167° from carbon tetrachloride. The molecular formula was supported by mass spectrometry. The infrared (IR) spectrum showed absorption bands at 3280 (OH), 1630 (C=O) and 935 (methylenedioxy) cm^{-1}, and the ultraviolet (UV) spectrum exhibited absorption maxima at 214 (log ε 4.73) and 298 (4.87)nm.

Since the PMR spectrum of Ia indicated the presence of a methylenedioxy group at δ 5.94 (2H, singlet) and two methyl groups attached to an aromatic nucleus at 2.04 and 2.08 (3H each, singlets), the carbon skeleton of Ia was assumed to be that of a homoisoflavonoidal compound; the spectral properties are very similar to those of the compounds reported by Tamm *et al.*[5] Acetylation of Ia with acetic anhydride and pyridine gave a monoacetate (Ic) whose PMR spectrum showed a 3H singlet at δ 2.35 and a diacetate (Id) (OAc at δ 2.38 and 2.44), while methylation of Ia with ethereal diazomethane afforded a monomethyl ether (Ib) (OMe at δ 3.74).

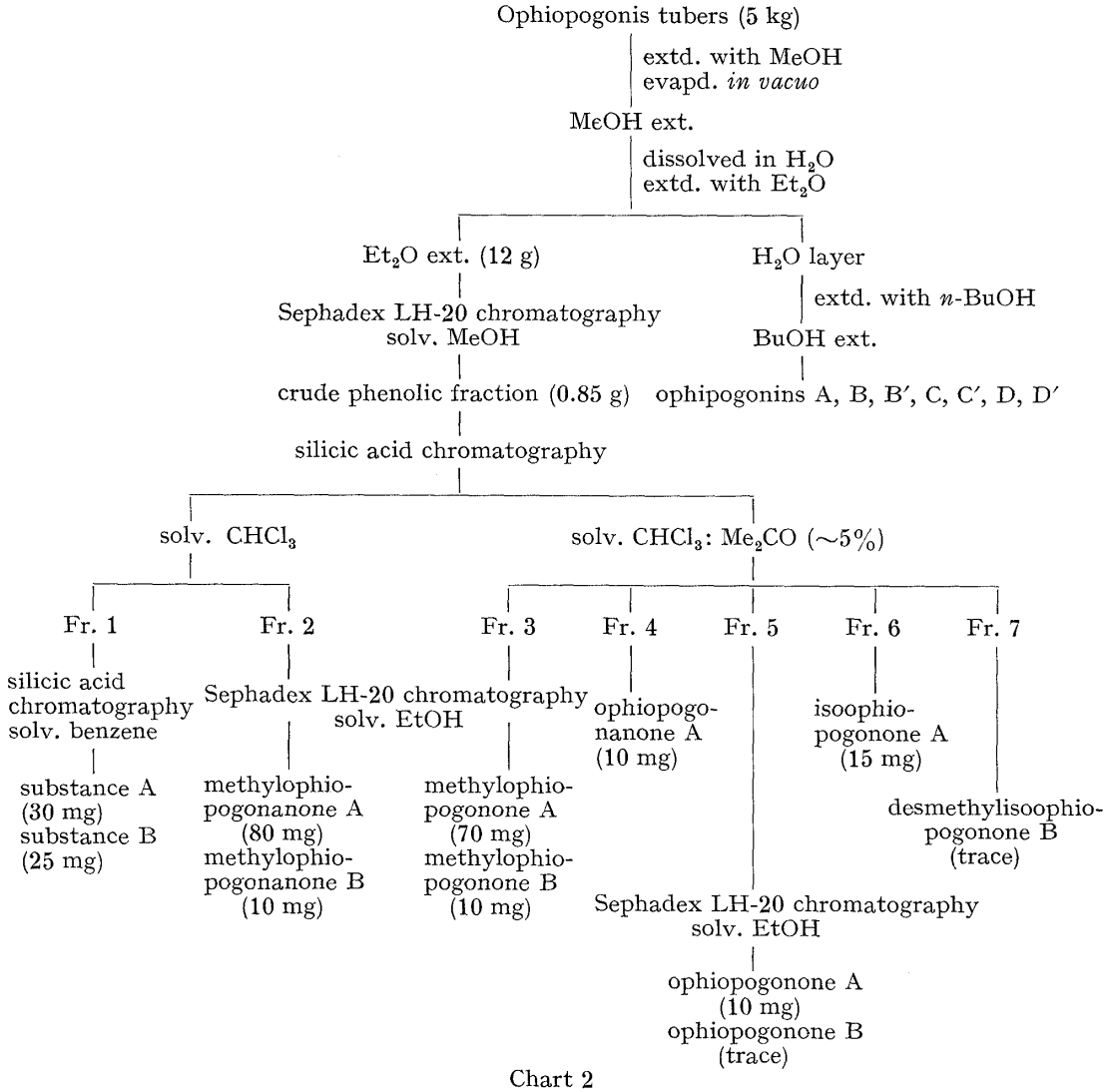


Chart 2

In addition, the occurrence of the UV absorption shifts upon addition of NaOAc and $AlCl_3$[8] indicated the presence of hydroxyls at C-7 and C-5 of a homoisoflavanone skeleton, respectively. The PMR spectrum of Ia showed ABC signals attributable to the protons of the γ-dihydropyrone moiety of a homoisoflavanone; H_{2ax} was observed as a double doublet at δ 4.12 (J=12 and 7 Hz), H_{2eq} as a double doublet at δ 4.32 (J=12 and 3 Hz) and H_{3ax} at δ 2.72—3.00 as a multiplet. The other PMR signals are two hydroxylic signals at δ 5.45 and 12.37 (chelated, assignable to C-5, s) exchangeable with D_2O, ABC-type aromatic proton signals, and benzylmethylene at δ 2.64 (1H, dd, J=10 and 10 Hz) and 3.20 (1H, d, J=10 Hz). Since two hydroxyl groups were suggested to be located at C-7 and C-5 in ring A, the methylenedioxy group should be located in ring B. The PMR spectrum of Ia showed a characteristic ABC couplig pattern of the C-2′, C-5′ and C-6′ protons of flavonoids, and the position of the methylenedioxy group in ring B was also suggested by the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum. Consequently, the structure of methylophiopogonanone A should be Ia, 5,7-dihydroxy-6,8-dimethyl-3-(3,4-methylenedioxybenzyl)-chroman-4-one. This is supported by the ^{13}C-NMR data summarized in Table II and by the results of mass spectrometry, shown in Chart 3.

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Methylophiopogonanone B (IIa)

Although the crude solid showed a homogeneous spot on a TLC plate, it was indicated to be a mixture of methylophiopogonanones A (Ia) and B (IIa) by the PMR spectrum. IIa was separated from Ia by Sephadex LH-20 chromtography, eluting with ethanol.

TABLE I. PMR Spectral Data for Homoisoflavonoidal Compounds (δ Value, 90 MHz)

Compound	C(2)	C(3)	C(5)	C(7)	C(6)	C(8)
Ia	4.12 d.d (12, 7) 4.32 d.d (12, 3)	2.72—3.00 m	12.37	5.45	2.04	2.08
Ib	4.12 d.d (12, 7) 4.35 d.d (12, 3)	2.78—3.05 m	12.09	3.74	2.04	2.08
Ic	4.15 d.d (12, 7) 4.38 d.d (12, 3)	2.78—3.05 m	12.08	2.35	1.92	1.97
Id	4.17 d.d (12, 7) 4.41 d.d (12, 3)	2.65—2.96 m	2.44	2.38	1.96	2.03
IIa	4.09 d.d (12, 7) 4.31 d.d (12, 3)	2.72—3.08 m	12.34		2.03	2.08
IIb	4.10 d.d (12, 7) 4.32 d.d (12, 3)	2.74—3.04 m	12.09	3.73 or 3.79	2.04	2.08
IIc	4.13 d.d (12, 7) 4.36 d.d (12, 3)	2.80—3.10 m	12.11	2.36	1.93	1.98
IId	4.16 d.d (12, 7) 4.40 d.d (12, 3)	2.65—3.05 m	2.45	2.38	1.96	2.03
IIIa[a]	8.06		13.03		2.15	2.23
IIIb	7.61		12.71	3.78	2.19	2.23
IVa[a]	8.01		13.06		2.12	2.20
IVd	7.58		12.71	3.79 or 3.82	2.23	2.26

Compound	C(9)	C(2′,5′,6′)	C(2′,6′)	C(3′,5′)	C(7′)	C(7′)
Ia	2.64 d.d (10, 10) 3.20 d (10)	6.65—6.82 m				5.94
Ib	2.66 d.d (10, 10) 3.22 d (10)	6.62—6.86 m				5.96
Ic	2.68 d.d (10, 10) 3.20 d (10)	6.62—6.74 m				5.95
Id	2.56 d.d (10, 10) 3.16 d.d (10, 3)	6.56—6.70 m				5.96
IIa	2.66 d.d (10, 10) 3.20 d (10)		7.15 d(9)	6.87 d(9)	3.80	
IIb	2.67 d.d (10, 10) 3.20 d (10)		7.17 d(9)	6.84 d(9)	3.79 or 3.73	
IIc	2.69 d.d (10, 10) 3.22 d (10)		7.14 d(9)	6.84 d(9)	3.80	
IId	2.70 d.d (10, 10) 3.18 d.d (10, 3)		7.13 d(9)	6.85 d(9)	3.82	
IIIa[a]	3.71	6.76—6.90 m				5.97
IIIb	3.71	6.75 br. s				5.92
IVa[a]	3.71		7.28 d(9)	6.86 d(9)	3.76	
IVb	3.76		7.19 d(9)	6.86 d(9)	3.82 or 3.79	

a) These compounds were measured in acetone-d_6 and the others were measured in $CDCl_3$. Figures in parentheses are coupling constants (J) in Hz.
Hydroxyl signals of all compounds were confirmed by the addition of D_2O.
d=doublet, m=multiplet; those not cited are singlets.

Table II. ^{13}C-NMR Spectral Data for Homoisoflavonoidal Compounds (δ: ppm from TMS, in DMSO-d_6)

	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
Ia	69.0	45.5	198.2	158.8[a]	103.4[b]	162.4[a]	102.3[b]	31.8	157.4[a]	100.8
IIa	68.9	45.6	198.2	158.8[a]	103.4[b]	162.4[a]	102.3[b]	31.2	157.4[a]	101.2
IIIa	154.2	121.5	181.0	156.0[a]	106.9[b]	159.7[a]	104.2[b]	29.9	153.0[a]	100.7

	C(12)	C(13)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(7′)
Ia	8.1[c]	7.6[c]	132.0	109.2[d]	147.4[e]	145.9[e]	108.1[d]	122.1	101.2
IIa	8.0[c]	7.6[c]	130.1	130.1	113.8	157.9	113.8	130.1	55.0
IIIa	8.0	8.0	133.0	109.1[d]	147.2[e]	145.5[e]	108.0[d]	121.5	101.6

a), *b*), *c*), *d*), *e*): assignments may be reversed.
Concentration 0.12 mM/ml using 10 mm tubes; temperature 25°.
FT NMR conditions: spectral width 6.25 kHz, pulse flipping angle 45° or 90°, acquistion time 0.5 sec, number of data poinnts 4096, transient time 1—2 sec, number of transients 2000—3000.

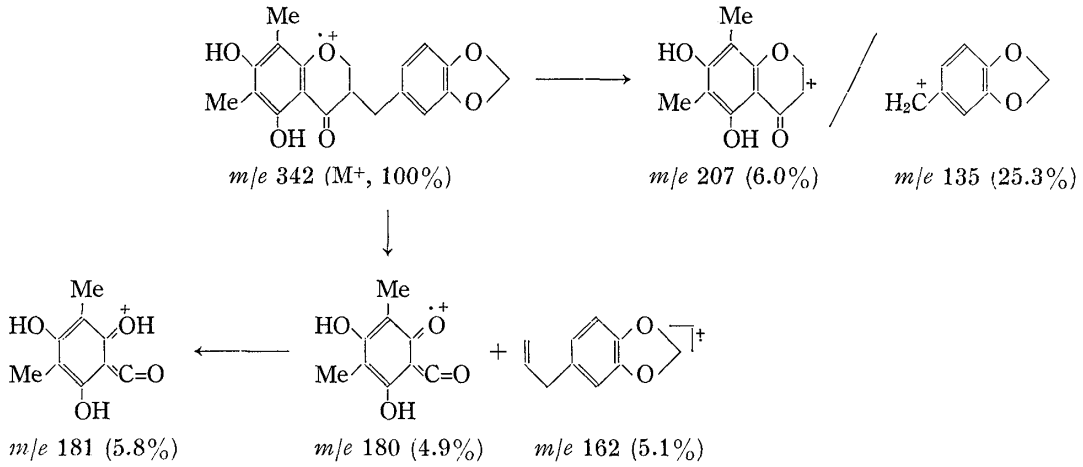

Chart 3. Mass Spectrum of Methylophiopogonanone A (Ia)

IIa, $C_{19}H_{20}O_5$ (M. W. 328), $[\alpha]_D$ −53.0° (dioxane), was obtained as colorless needles of mp 159—160° from carbon tetrachloride. The molecular formula was supported by its mass spectrum. The IR spectrum showed absorption bands at 3430 (OH) and 1634 (C=O) cm^{-1} and UV absorption maxima appeared at 220 (4.62) and 298 (4.53) nm. The PMR spectrum indicated the presence of a methoxyl group at δ 3.80 (3H, s) and four aromatic protons in an A_2B_2 system at δ 6.87 and 7.15 with J=9 Hz (*ortho*-coupling). Two aromatic C-methyl groups were seen at δ 2.03 and 2.08 (3H each, s) benzylmethylene appeared at δ 2.66 (1H, dd, J=10 and 10 Hz) and 3.20 (1H, d, J=10 Hz) and γ-dihydropyrone protons were observed at 2.72—3.08 (1H, m, H_{3ax}), 4.09 (1H, dd, J=12 and 7 Hz, H_{2ax}) and 4.31 (1H, dd, J=12 and 3 Hz, H_{2eq}). The mass spectrum of IIa showed a fragment ion at *m/e*: 121 (*p*-methoxybenzylium or tropylium ion) and the fragmentation pattern resembled that of Ia. Although methylation of IIa with ethereal diazomethane afforded a monomethyl ether (IIb) whose PMR spectrum showed methoxyl signals at δ 3.73 and 3.79 (3H each, s) and a hydroxyl at 12.09 (1H, s), acetylation of IIa with acetic anhydride and pyridine gave a monoacetate (IIc) (OAc at δ 2.36) and a diacetate (IId) (OAc at δ 2.38 and 2.45). Besides these results, the occurrence of UV absorption shifts on the addition of sodium acetate and aluminum trichloride indicated the presence of hydroxyls at C-7 and C-5, and the structure should thus be IIa, 5,7-dihydroxy-6,8-

dimethyl-3-(4-methoxybenzyl)-chroman-4-one. This was supported by the ^{13}C-NMR spectrum.

Methylophiopogonone A (IIIa)

IIIa, $C_{19}H_{16}O_6$ (M. W. 340) was obtained as pale yellow needles of mp 210—211° from ethanol. The IR spectrum of IIIa showed absorption bands at 3520 (OH), 1650, 1626 (C=O) and 926 (methylenedioxy) cm^{-1} and UV absorption maxima appeared at 231 (shoulder, 4.47), 266 (4.62), 297 (sh., 4.20) and 340 (inflexion, 3.87) nm. The PMR spectrum indicated the presence of a methylenedioxy group at δ 5.97 (2H, s), two methyl groups attached to an aromatic nucleus at δ 2.15 and 2.23 (3H each, s) aromatic proton signals centered at δ 6.83 (3H, m) and a chelated hydroxylic signals at δ 13.03 (1H, s). Since the mass spectrum of IIIa showed peaks at *m/e*: 181 (fragment derived from ring A) and 135 (fragment from ring B), and the fragmentation pattern of IIIa closely resembled that of Ia, the substitution pattern of rings A and B was thought to be the same as that of Ia. The remaining signals at δ 3.71 (2H, s) and 8.06 (1H, s) were assigned to the C-9 and C-2 protons, respectively. The signals of the C-2 and C-9 protons of the type-V compounds were observed at δ *ca.* 5.2 (doublet) and δ *ca.* 7.8 (triplet), whereas those of the type-VI compounds were seen at δ *ca.* 4.9 (doublet) and δ *ca.* 6.8 (triplet).[5] Consequently, IIIa was assumed to be a new type of homoisoflavone derivative having a double bond at the C-2 carbon. Treatment of IIIa with ethereal diazomethane afforded a monomethyl ether (IIIb) whose PMR spectrum showed a 3H singlet at δ 3.78 and a 1H singlet at δ 12.71 (chelated OH, assignable to C-5). The UV spectrum indicated the presence of 5- and 7-hydroxyl groups, since marked bathochromic shifts were observed on the addition of $AlCl_3$ and NaOAc, respectively. Hydrogenation of IIIa in the presence of prereduced 10% Pd–C gave a product which was identical with Ia (mixed mp, TLC, UV, IR and PMR spectra). In conclusion, the structure of methylophiopogonone A should be IIIa, 5,7-dihydroxy-6,8-dimethyl-3-(3,4-methylenedioxybenzyl)-chromone. This was supported by the ^{13}C-NMR spectrum.

Methylophiopogonone B (IVa)

Methylophiopogonones A (IIIa) and B (IVa) were obtained as a mixture showing a homogeneous spot on a TLC plate. IVa was separated from IIIa by Sephadex LH-20 column chromatography, eluting with ethanol.

IVa, $C_{19}H_{18}O_5$ (M. W. 326), was obtained as pale yellow needles of mp 219—220° from ethanol. The IR spectrum showed bands at 3450 (OH), 1645 and 1628 (C=O) cm^{-1} and UV absorption maxima appeared at 221 (inf., 4.29), 266 (4.31), 305 (3.74) and 329 (inf., 3.47) nm. The PMR spectrum of IVa showed two aromatic C-methyl groups at δ 2.12 and 2.20 (3H each, s) and benzylmethylene protons at δ 3.71 (2H, s), a methoxyl group at δ 3.76 (3H, s), four aromatic protons in an A_2B_2 system at δ 6.86 and 7.28 (2H each, d, J=9 Hz), an olefinic proton at δ 8.01 (1H, s) and a hydroxyl group at δ 13.06 (1H, s, exchangeable with D_2O). The mass spectrum showed the peak of *p*-methoxybenzylium ion at *m/e*: 121 and the other fragments resembled those of IIIa. Treatment of IVa with ethereal diazomethane afforded a monomethyl ether (IVb) whose PMR spectrum showed methoxyl groups at δ 3.79 and 3.82 (3H each, s, C-7 or C-4′) and a hydroxyl group at 12.71 (1H, s, exchangeable with D_2O).

The UV spectrum of IVa indicated the presence of free 5- and 7-hydroxyls since marked bathochromic shifts were observed on the addition of $AlCl_3$ and NaOAc, respectively. Hydrogenation of IVb in the presence of prereduced 10% Pd–C gave a product which was identical with IIb (TLC, UV and PMR spectra). On the basis of these results, the structure of methylophiopogonone B is IVa (5,7-dihydroxy-6,8-dimethyl-3-(4-methoxybenzyl)-chromone). Confirmation of the structures of these compounds was obtained by total synthesis; the details will be published shortly.

It should be noted that methylophiopogonones A and B are members of a new class of naturally occurring homoisoflavonoidal compounds, since they have a double bond at C_{2-3}.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus (hot-stage type) and are uncorrected. The UV spectra were recorded with a Hitachi EPS-3 spectrophotometer, IR spectra with a JASCO IRA-1 unit, PMR spectra with a Hitachi R-22 (90 MHz) spectrometer and ^{13}C-NMR spectra with a JEOL PFT-100 spectrometer. Mass spectra were measured with a Hitachi RMS-4 instrument. The optical rotations were measured with a Yanagimoto OR-50.

Extraction and Isolation of Homoisoflavonoids——Ophiopogonis tubers (dried tubers of *Ophiopogon japonicus* KER-GAWLER var. *genuinus* MAXIM.) were crushed and treated as shown in Chart 3. The ether extract was subjected tc rapid column chromatography on Sephadex LH-20 with MeOH. The crude phenolic fraction was rechromatographed on silicic acid, eluting with $CHCl_3$ (Fr. 1, 2) and $CHCl_3$–Me_2CO (~5%) (Fr. 3—7). Fr.1 was rechromatographed on silicic acid, eluting with benzene, to give substances A and B.

Fr. 2, 3 and 5 were each subjected to Sephadex LH-20 chromatography, eluting with EtOH, to afford methylophiopogonanone A (Ia) and methylophiopogonanone B (IIa) from Fr. 2, methylophiopogonone A (IIIa) and methylophiopogonone B (IVa) from Fr. 3, and ophiopogonone A and ophiopogonone B from Fr. 5. Fr. 4 gave ophiopogonanone A, Fr. 6 gave isoophiopogonone A and Fr. 7 afforded desmethylisoophiopogonone B.

Methylophiopogonanone A (Ia)——Colorless needles (from CCl_4) mp 166—167°, $[\alpha]_D^{19}$ −72.0° (c=1.0, $CHCl_3$). λ_{max}^{EtOH} nm (log ε): 214 (4.73), 298 (4.87). $\lambda_{max}^{EtOH+AcONa}$ nm: 345. $\lambda_{max}^{EtOH+AlCl_3}$ nm: 322. ν_{max}^{KBr} cm^{-1}: 3280, 1630, 935. *m/e*: 342 (M$^+$, 100%), 207 (6.0%), 181 (5.8%), 180 (4.9%), 162 (5.1%), 135 (25.5%). *Anal.* Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.30; H, 5.30.

Methylophiopogonanone B (IIa)——Colorless needles (from CCl_4). mp 159—160°. $[\alpha]_D^{17}$ −53.0° (c=1.0, dioxane). λ_{max}^{EtOH} nm (log ε): 220 (4.62), 298 (4.53). $\lambda_{max}^{EtOH+AcONa}$ nm: 344. $\lambda_{max}^{EtOH+AlCl_3}$ nm: 323. ν_{max}^{KBr} cm^{-1}: 3430, 1634. *m/e*: 328 (M$^+$, 100%), 207 (4.5%), 206 (2.0%), 181 (3.8%), 180 (3.8%), 152 (7.4%), 121 (65.9%). *Anal.* Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.15; H, 6.19.

Methylophiopogonone A (IIIa)——Pale yellow needles (from EtOH) mp 210—211°. λ_{max}^{EtOH} nm (log ε): 231 (sh., 4.47), 266 (4.62), 297 (sh., 4.20), 340 (inf., 3.87). $\lambda_{max}^{EtOH+AcONa}$ nm: 278, 345. $\lambda_{max}^{EtOH+AlCl_3}$ nm: 322, 392. ν_{max}^{KBr} cm^{-1}: 3520, 1650, 1626, 926. *m/e*: 340 (M$^+$, 100%), 181 (18.2%), 135 (7.9%). *Anal.* Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.75. Found: C, 66.98; H, 4.72.

Methylophiopogonone B (IVa)——Pale yellow needles (from EtOH) mp 219—220°. λ_{max}^{EtOH} nm (log ε): 221 (inf., 4.29), 266 (4.31), 305 (3.74), 329 (inf., 3.47). $\lambda_{max}^{EtOH+AcONa}$ nm: 342. $\lambda_{max}^{EtOH+AlCl_3}$ nm: 277, 322, 366. ν_{max}^{KBr} cm^{-1}: 3450, 1645, 1628. *m/e*: 326 (M$^+$, 100%), 181 (38.7%), 146 (18.7%), 121 (11.3%). *Anal.* Calcd for $C_{19}H_{18}O_5$: C, 69.92; H, 5.56. Found: C, 70.06; H, 5.67.

Methylation of Ia, IIa, IIIa and IVa with Ethereal CH_2N_2——Methanolic solutions of Ia, IIa, IIIa and IVa were each treated with an excess of ethereal diazomethane at 0° and allowed to stand for 1 hr. The solvent was removed under reduced pressure and the residue was crystallized from EtOH.

Methylophiopogonanone A Monomethyl Ether (Ib)——Colorless needles, mp 93—95°, $[\alpha]_D^{19}$ −60.0° (c=1.0, $CHCl_3$). λ_{max}^{EtOH} nm (log ε): 216 (4.34), 287 (4.24). $\lambda_{max}^{EtOH+AlCl_3}$ nm: 220, 310. ν_{max}^{KBr} cm^{-1}: 3450, 1625, 928. *m/e*: 356 (M$^+$). *Anal.* Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.64; H, 5.67.

Methylophiopogonanone B Monomethyl Ether (IIb)——Colorless needles, mp 94—95°, $[\alpha]_D^{24}$ −21.0° (c=1.0, $CHCl_3$). λ_{max}^{EtOH} nm (log ε): 220 (4.24), 285 (4.06). $\lambda_{max}^{EtOH+AlCl_3}$ nm: 313. ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1694, 1629, 1615. *m/e*: 342 (M$^+$).

Methylophiopogonone A Monomethyl Ether (IIIb)——Colorless needles, mp 142—143°, λ_{max}^{EtOH} nm (log ε): 230 (4.53), 245 (4.53), 265 (4.55), 341 (3.60). $\lambda_{max}^{EtOH+AlCl_3}$ nm: 276, 380. ν_{max}^{KBr} cm^{-1}: 3450, 1642, 1600, 931. *m/e*: 354 (M$^+$). *Anal.* Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.48; H, 5.12.

Methylophiopogonone B Monomethyl Ether (IVb)——Colorless needles, mp 128—129°. λ_{max}^{EtOH} nm (log ε): 230 (4.50), 245 (4.53), 265 (4.58), 341 (3.88). $\lambda_{max}^{EtOH+AlCl_3}$ nm: 277, 405. ν_{max}^{KBr} cm^{-1}: 3450, 1625. *m/e*: 340 (M$^+$). *Anal.* Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.71; H, 6.00.

Acetylation of Ia and IIa with Ac_2O and Pyridine——Ia and IIa were each acetylated with acetic anhydride and pyridine in the usual manner. Each product was purified by column chromatography on silicic acid, eluting with benzene.

Methylophiopogonanone A Monoacetate (Ic)——Colorless needles (from EtOH), mp 171—172°, $[\alpha]_D^{19}$ −15.0° (c=0.3, $CHCl_3$). λ_{max}^{EtOH} nm (log ε): 212 (4.10), 283 (3.99). $\lambda_{max}^{EtOH+AlCl_3}$ nm: 319. ν_{max}^{KBr} cm^{-1}: 3400, 1740, 1630, 920. *m/e*: 384 (M$^+$). *Anal.* Calcd for $C_{21}H_{20}O_7$: C, 65.61; H, 5.24. Found: C, 65.42; H, 5.37.

Methylophiopogonanone A Diacetate (Id)——Colorless needles (from EtOH), mp 107—109°, $[\alpha]_D^{29}$ −21.3° (c=1.0, $CHCl_3$). λ_{max}^{EtOH} nm (log ε): 219 (4.47), 263 (4.02). ν_{max}^{KBr} cm^{-1}: 1760, 1680, 1610, 920. *m/e*: 426 (M$^+$). *Anal.* Calcd for $C_{23}H_{22}O_8$: C, 64.78; H, 5.20. Found: C, 64.92; H, 5.18.

Methylophiopogonanone B Monoacetate (IIc)——Colorless needles (from EtOH), mp 134—135°, $[\alpha]_D^{24}$ −36.4° (c=0.14, $CHCl_3$). λ_{max}^{EtOH} nm (log ε): 224 (4.41), 278 (4.21). $\lambda_{max}^{EtOH+AlCl_3}$ nm: 318. λ_{max}^{KBr} cm^{-1}: 3440, 1750, 1630, 1620, *m/e*: 370 (M$^+$). *Anal.* Calcd for $C_{21}H_{22}O_6$: C, 68.09; H, 5.99. Found: C, 67.98; H, 5.97.

Methylophiopogonanone B Diacetate (IId)——Colorless needles (from EtOH), mp 123—124°. $[\alpha]_D^{24}$ −57.1° (c=0.14, $CHCl_3$). λ_{max}^{EtOH} nm (log ε): 222 (4.60), 263 (4.13). ν_{max}^{KBr} cm^{-1}: 1760, 1685, 1610. *m/e*: 412 (M$^+$). *Anal.* Calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 67.05; H, 5.90.

Hydrogenation of Methylophiopogonone A (IIIa) with Pd-C (Formation of Ia)——An ethanolic solution of IIIa (50 mg) was hydrogenated in the presence of prereduced 10% Pd-C (50 mg). After removal of the solvent, the residue was purified by column chromatography on silicic acid using benzene. The product was crystallized from CCl_4 to afford colorless needles, mp 167—168°. This material was identical with methylophiopogonanone A (Ia) on the basis of its TLC behavior and UV and PMR spectra.

Hydrogenation of Methylophiopogonone B Monomethyl Ether (IVb)——IVb (20 mg) was hydrogenated in the presence of 10% Pd-C (20 mg) in EtOH. The product was crystallized from EtOH to afford colorless needles, mp 95—96°. This material was shown to be identical with methylophiopogonanone B monomethyl ether (IIb) by means of TLC, and UV and PMR spectroscopy.

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