Water-Soluble Constituents of Fennel. V. [1] Glycosides of Aromatic Compounds

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From the water-soluble portion of the methanol extract of the herbal medicine fennel, the fruit of *Foeniculum vulgare* MILLER (Umbelliferae), four new phenylpropanoid glycosides, three new benzyl alcohol derivative glycosides, one new phenylethanoid and its glycoside were obtained. They were characterized by spectral investigation.

Key words fennel; *Foeniculum vulgare* fruit; aromatic compound glycoside; Umbelliferae

We previously reported the isolation and characterization of alkyl, anethole glycol and monoterpenoid glycosides[1,2] from the water-soluble fraction of fennel, the fruit of *Foeniculum vulgare* MILLER (Umbelliferae). In this paper, we treat glycosides bearing aromatic moiety, which were obtained from a similar water-soluble fraction as described in the Experimental section.

Sixteen glycosides (**1**—**8**, **10**—**15**, **17**, **18**) and one phenolic compound (**16**) thus isolated are listed in the table for their ^{13}C-NMR spectra and in the chart for the structures. All the glycosides were β-D-glucopyranosides as evidenced from the data in the table. The molecular formulae of all compounds in this investigation were indicated from the accurate mass number of $[M+H]^+$ or $[M+Na]^+$ ion peaks in the high-resolution positive FAB-MS.

Glycosides **1** to **4** were identified as syringin, sinapyl alcohol 4,3′-di-*O*-β-D-glucopyranoside, zizybeoside I and icariside F_2.[2d] Glycosides **5** and **6** were identified as benzyl β-D-glucopyranoside[3] and isosalicin (2-hydroxybenzyl β-D-glucopyranoside).[4] Glycoside **7** was identified as methylsyringin[5] by comparison of the ^{1}H- and ^{13}C-NMR data with those of **1** and from the results of heteronuclear multiple-bond correlation (HMBC) experiment.

Glycoside **8** ($C_{16}H_{22}O_8$, mp 145—147 °C, $[\alpha]_D^{21}$ −48.0°) showed the presence of one tetrasubstituted benzene ring, one methoxyl, one methylene and one terminal-methylene group. Enzymatic hydrolysis of **8** gave a D-glucose and an aglycone (**9**, $C_{10}H_{12}O_3$, an amorphous powder) which showed an $[M+H]^+$ ion peak at *m/z* 181. Its ^{1}H- and ^{13}C-NMR spectral data indicated that **9** has a 3,5-dihydroxyestragole[6] structure. This was also supported by the analysis of the HMBC spectrum of **8** which showed three-bond correlations from the H_2-1′ proton to the C-2 and C-6 carbons. Thus, **8** was represented as 3,5-dihydroxyestragole 3-*O*-β-D-glucopyranoside.

Glycoside **10** ($C_{15}H_{22}O_9$, mp 175—177 °C, $[\alpha]_D^{21}$ −20.7°) showed the presence of one 3,5-dimethoxyl-1,4-substituted benzene ring and one hydroxymethyl group. By comparison of its NMR data with those of **1** and **7**, and from the observed nuclear Overhauser effect (NOE) interaction between the hydroxymethyl proton and H-2 in the nuclear Overhauser enhancement and exchange spectroscopy (NOESY) spectrum, **10** was characterized as 3,5-dimethoxy-4-hydroxybenzyl alcohol 4-*O*-β-D-glucopyranoside.

Glycoside **11** ($C_{16}H_{22}O_7$, an amorphous powder, $[\alpha]_D^{23}$ −60.0°) was indicated to be a glucoside of *p*-hydroxycinnamyl alcohol methylether. The positions of the glucosyl and methoxyl units were at C-4 and C-3′, respectively, from the observed NOE interactions between the anomeric proton and H-3, and between the methoxyl proton and H_2-3′ in its NOESY spectrum. Thus, **11** was characterized as 3′-*O*-methyl-*p*-hydroxycinnamyl alcohol 4-*O*-β-D-glucopyranoside.

As HPLC for glycoside **12** ($C_{16}H_{22}O_7$, an amorphous powder, $[\alpha]_D^{21}$ −52.0°) showed a single peak, but the compound was revealed to be a mixture of two isomeric compounds in the ratio of about 3 : 1 by the analysis of ^{1}H- and ^{13}C-NMR spectral data. Both compounds contained one 1,4-substituted benzene ring and one 2-hydroxypropyl group, suggesting they were a mixture of glucosides of 1′-(4-hydroxyphenyl)-2′-propanol. The position of the glucosyl unit was found to be C-4 from the observed NOE interaction between the anomeric proton and H-3 in the NOESY spectrum. Thus, **12** was characterized as a mixture of an epimeric pair of 1′-(4-hydroxyphenyl)-2′-propanol 4-*O*-β-D-glucopyranosides at C-2′.

Glycoside **13** ($C_{14}H_{20}O_7$, mp 137—138 °C, $[\alpha]_D^{21}$ −51.1°) showed the presence of one 1,4-substituted benzene ring, one methoxyl and one hydroxymethylene group. By comparison of the spectral data with those of **5**, **13** was characterized as *p*-anisyl β-D-glucopyranoside.[7]

Glycoside **14** ($C_{14}H_{19}O_{10}SNa$, mp 149—151 °C, $[\alpha]_D^{21}$ −34.6°) showed $[M+Na]^+$, $[M+H]^+$ and $[M-(SO_3Na)]^+$ ion peaks at *m/z* 425, 403 and 299 in the positive FAB-MS, and $[M-H]^-$ and $[M-Na]^-$ ion peaks at *m/z* 401 and 379 in the negative FAB-MS. The presence of a sodium sulfate group in **14** was suggested by a positive result in the potassium rhodizonate test.[8] From comparison of its ^{1}H- and ^{13}C-NMR data with those of **13**, **14** was concluded to be sodium sulfate of **13**. The position of the sodium sulfate group was revealed to be C-2 of the glucose moiety by the downfield shift of H-2 (by 1.1 ppm) and C-2 (by 4.9 ppm) signals and the upfield shift of C-1 (by 2.9 ppm) and C-3 (by 1.0 ppm) signals of the glucosyl moiety. From these results, **14** was determined to be *p*-anisyl 2-*O*-sodium sulfo-β-D-glucopyra-

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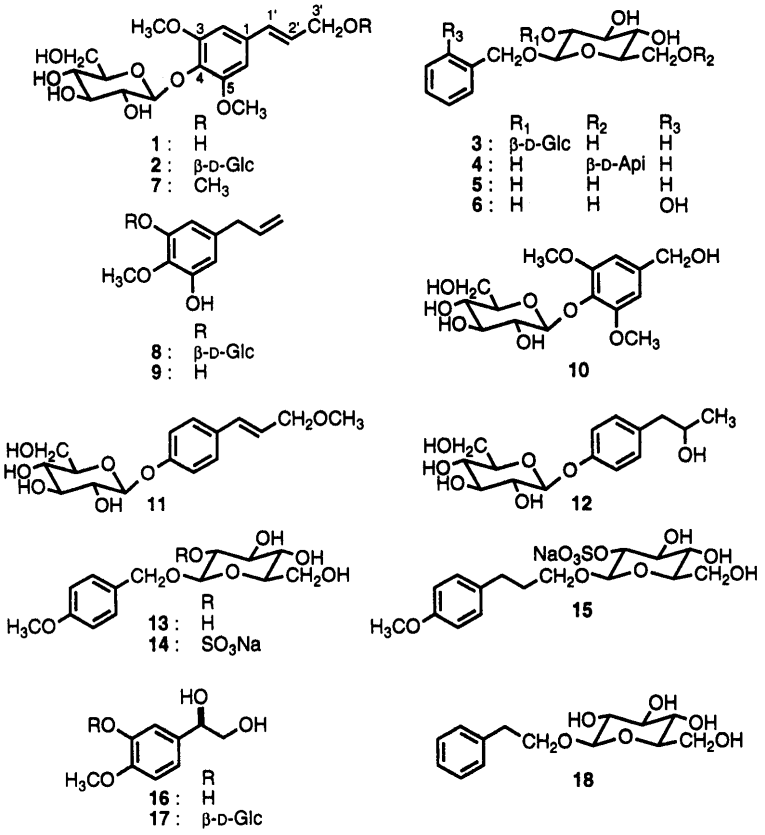

Chart 1. Structures of **1**—**18**

noside.

Glycoside **15** ($C_{16}H_{23}O_{10}SNa$, an amorphous powder, $[\alpha]_D^{23}$ −25.5°) obtained from the same fraction as **14**, was also sodium sulfate, as suggested from a positive potassium rhodizonate test. The ^1H- and ^{13}C-NMR spectral data showed the presence of one 2-*O*-sodium sulfo-β-glucopyranose, one 1,4-substituted benzene ring, one methoxyl and one propanoyl group. **15** was thus considered to be a sodium sulfo-β-glucopyranoside of *p*-methoxyphenylpropanol. The position of the glucosyl and methoxyl units were verified to be at C-3′ and C-4, respectively, from the observed NOE interactions between the anomeric proton and H_2-3′, and between the methoxyl proton and H-3 in its NOESY spectrum. From these facts, **15** was concluded to be *p*-methoxyphenylpropyl 2-*O*-sodium sulfo-β-D-glucopyranoside.

Triol **16** ($C_9H_{12}O_4$, an amorphous powder, $[\alpha]_D^{23}$ −22.5°) showed the presence of one 1,3,4-trisubstituted benzene ring, one dihydroxyethyl and one methoxyl group. As the NOESY spectrum showed the NOE interactions between the methoxyl proton and H-5, between the hydroxymethine proton and H-2, and between the hydroxymethine proton and H-6, **16** was suggested to have a 1′-(3-hydroxy-4-methoxyphenyl)ethane-1′,2′-diol structure. Since the (1′*R*)-1′-phenylethane-1′,2′-diol showed negative optical rotation ($[\alpha]_D$ −47.1°),[9] the configuration of **16** at C-1′ was suggested to be *R*.

Glycoside **17** ($C_{15}H_{22}O_9$, an amorphous powder, $[\alpha]_D^{23}$ −52.0°) was suggested to be a β-glucopyranoside of **16** by the ^1H- and ^{13}C-NMR spectral data. The position of the glucosyl unit was indicated to be C-3 from the observed NOE interactions between the anomeric proton and H-2. Thus, **17** was characterized as (1′*R*)-1′-(3-hydroxy-4-methoxyphenyl)-ethane-1′,2′-diol 3-*O*-β-D-glucopyranoside.

Glycoside **18** ($C_{14}H_{20}O_6$, an amorphous powder, $[\alpha]_D^{23}$ −36.5°) was identified as phenethyl β-D-glucopyranoside[10] by comparison of physical and NMR data with those reported.

Experimental

The instruments used and the experimental conditions for obtaining spectral data and for chromatography were the same as in the preceding paper.[2a]

Extraction and Separation of 1—8 and 10—18 The methanol extract of fennel (2.0 kg) was treated as described in Part I, and frs. A to G were obtained from the aqueous portion by Amberlite XAD-II and Sephadex LH-20 chromatographies.[2a] Fraction C (16.9 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)→MeOH] to give fifteen fractions (frs. C_1—C_{15}). Fraction C_3 (1.3 g) was subjected to a Lobar RP-8 column [CH_3CN–H_2O (3 : 17)] to give ten fractions (frs. $C_{3\text{-}1}$—$C_{3\text{-}10}$). Fraction $C_{3\text{-}9}$ was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (9 : 1 : 0.1)] to afford **7** (61 mg). Fraction C_4 (0.9 g) was chromatographed over silica gel [$CHCl_3$–MeOH (9 : 1)], then subjected to HPLC [ODS, CH_3CN–H_2O (3 : 17)], and finally Sephadex LH-20 (MeOH) to give **16** (3 mg). Fraction C_5 (1.7 g) was subjected to a Lobar RP-8 column [CH_3CN–H_2O (3 : 17)] to give twelve fractions (frs. $C_{5\text{-}1}$—$C_{5\text{-}12}$). Fraction $C_{5\text{-}6}$ was subjected to HPLC [ODS, CH_3CN–H_2O (1 : 9)] to give **5** (150 mg). Fraction $C_{5\text{-}7}$ was acetylated with Ac_2O and pyridine, and the acetylated compounds were subjected to HPLC [ODS, CH_3CN–H_2O (1 : 1)] to give four fractions (frs. $C_{5\text{-}7\text{-}1}$—$C_{5\text{-}7\text{-}4}$). Fraction $C_{5\text{-}7\text{-}2}$ was deacetylated by heating in a water bath with 5% NH_4OH–MeOH for 2 h to give **13** (88 mg). Fraction $C_{5\text{-}9}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (24 : 1)] to give four fractions (frs. $C_{5\text{-}9\text{-}1}$—$C_{5\text{-}9\text{-}4}$). Fraction $C_{5\text{-}9\text{-}2}$ was chromatographed over Sephadex LH-20 (MeOH) to give **18** (4 mg). Fraction $C_{5\text{-}11}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (24 : 1)] to afford **11** (5 mg). Fraction C_6 (1.9 g) was subjected to a Lobar RP-8 column [CH_3CN–H_2O (3 : 17)] to give **1** (940 mg) and thirteen other fractions (frs. $C_{6\text{-}1}$—$C_{6\text{-}13}$). Fraction $C_{6\text{-}11}$ was subjected to HPLC [ODS, CH_3CN–H_2O (3 : 17)] to give **8** (83 mg). Fraction C_7 (0.7 g) was subjected to a Lobar RP-8 column [CH_3CN–H_2O (1 : 9→3 : 17)] to give nine fractions (frs. $C_{7\text{-}1}$—$C_{7\text{-}9}$). Fraction $C_{7\text{-}3}$ was subjected to HPLC [ODS, CH_3CN–H_2O (1 : 9)] to give **10** (100 mg). Fraction $C_{7\text{-}5}$ was

Table 1. ^{13}C-NMR Chemical Shifts of **1**, **5**—**18** (in Pyridine-d_5, 125 MHz)

	1	**5**	**6**	**7**	**8**	**9**[a]	**10**	**11**
C-1	133.97	138.94	125.80	133.31	136.41	135.92	134.76	131.25
C-2	105.21	128.25	156.42	105.34	108.27	108.83	105.12	128.10
C-3	153.90	128.62	129.66	153.89	152.28	152.39	153.75	117.11
C-4	135.64	127.79	128.91	135.81	136.86	136.51	139.63	158.29
C-5	153.90	128.62	119.44	153.89	152.39	152.39	153.75	117.11
C-6	105.21	128.25	115.78	105.34	111.42	108.83	105.12	128.10
C-1′	131.17	70.87	67.19	132.17	40.42	40.37	64.32	131.78
C-2′	129.40	—	—	126.44	138.06	138.43	—	125.15
C-3′	62.81	—	—	73.09	115.68	115.45	—	73.22
OCH_3	56.57	—	—	56.59	60.86	60.26	56.48	—
3′-OCH_3	—	—	—	57.78	—	—	—	57.67
Glc-1	104.93	104.03	104.35	104.81	102.56		105.07	102.10
Glc-2	76.08	75.26	75.27	76.06	75.07		76.08	74.99
Glc-3	78.42	78.57	78.53	78.41	78.88		78.39	78.56
Glc-4	71.61	71.68	71.59	71.57	71.28		71.57	71.28
Glc-5	78.78	78.65	78.59	78.82	78.76		78.72	79.00
Glc-6	62.62	62.80	62.64	62.58	62.30		62.59	62.37

	12a	**12b**[b]	**13**	**14**	**15**	**16**	**17**	**18**
C-1	133.82		130.78	130.38	134.61	137.73	137.18	139.33
C-2	131.00		130.03	129.72	130.07	115.18	114.95	128.72
C-3	116.73		114.11	114.11	114.09	147.85	149.17	129.42
C-4	157.13		159.66	159.48	158.12	148.14	147.71	126.53
C-5	116.73		114.11	114.11	114.09	112.37	112.81	129.42
C-6	131.00		130.03	129.72	130.07	117.73	120.54	128.72
C-1′	45.92		70.63	70.20	32.06	75.28	75.23	36.68
C-2′	68.54		—	—	31.23	69.46	69.19	70.59
C-3′	23.70	[23.67]	—	—	68.59	—	—	—
OCH_3	—	—	55.17	55.05	55.01	56.06	56.04	—
Glc-1	102.41		103.72	100.80	102.03		102.10	104.78
Glc-2	75.03		75.24	80.16	80.42		74.87	75.20
Glc-3	78.58		78.58	77.63	78.00		78.45	78.64
Glc-4	71.30		71.71	71.28	71.59		71.14	71.71
Glc-5	78.88		78.61	78.12	78.19		78.58	78.64
Glc-6	62.38		62.82	62.15	62.52		62.24	62.84

δ in ppm from TMS. *a*) Measured at 67.5 MHz. *b*) Minor epimeric component is given in brackets.

subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (19 : 1)] to give three fractions (frs. $C_{7\text{-}5\text{-}1}$—$C_{7\text{-}5\text{-}3}$). Fraction $C_{7\text{-}5\text{-}2}$ was chromatographed over silica gel [$CHCl_3$–MeOH (17 : 3)] to afford **6** (4 mg). Fraction C_8 (0.4 g) was chromatographed over Sephadex LH-20 (MeOH) and then subjected to HPLC [ODS, CH_3CN–H_2O (3 : 17)] to give **4** (62 mg). Fraction C_9 (1.3 g) was subjected to a Lobar RP-8 column [MeOH–H_2O (3 : 17 → 1 : 4)] to give eleven fractions (frs. $C_{9\text{-}1}$—$C_{9\text{-}11}$). Fraction $C_{9\text{-}9}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (9 : 1)] to give **12** (6 mg). Fraction C_{10} (0.4 g) was subjected to a Lobar RP-8 column [MeOH–H_2O (1 : 4)] to give seven fractions (frs. $C_{10\text{-}1}$—$C_{10\text{-}7}$). Fraction $C_{10\text{-}2}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (19 : 1)] to give four fractions (frs. $C_{10\text{-}2\text{-}1}$—$C_{10\text{-}2\text{-}4}$). Fraction $C_{10\text{-}2\text{-}3}$ was subjected to HPLC [ODS, MeOH–H_2O (3 : 37)] to give **17** (5 mg). Fraction $C_{10\text{-}6}$ was recrystallized from MeOH to give **3** (60 mg). Fraction C_{12} (1.1 g) was subjected to a Lobar RP-8 column [MeOH–H_2O (1 : 4)] to give **2** (120 mg). Fraction E (1.8 g) was subjected to a Lobar RP-8 column [CH_3CN–H_2O (1 : 19 → 1 : 9)] to give six fractions (frs. E_1—E_6). Fraction E_2 was subjected to HPLC [ODS, MeOH–H_2O (1 : 4)] to give **14** (41 mg). Fraction E_5 was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to give two fractions (frs. $E_{5\text{-}1}$ and $E_{5\text{-}2}$). Fraction $E_{5\text{-}2}$ was subjected to HPLC [ODS, MeOH–H_2O (1 : 4)] to give **15** (4 mg).

Benzyl β-D-Glucopyranoside (5) Colorless needles (EtOAc), mp 120—121 °C, $[\alpha]_D^{21}$ −53.0° (*c*=1.8, MeOH), [lit.[3]; $[\alpha]_D$ −59.2° (MeOH)]. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 4.83 (1H, d, *J*=12.0 Hz, H-1′a), 4.99 (1H, d, *J*=7.5 Hz, Glc H-1), 5.18 (1H, d, *J*=12.0 Hz, H-1′b), 7.26—7.35 (3H, m, H-3, 4, 5), 7.53 (2H, dd, *J*=2.0, 7.0 Hz, H-2, 6).

Isosalicin (6) An amorphous powder, $[\alpha]_D^{23}$ −41.0° (*c*=0.2, MeOH), [lit.[4]; mp 66—68 °C, $[\alpha]_D$ −45.2° (MeOH)].

Methylsyringin (7) Colorless needles (MeOH), mp 193—195 °C, $[\alpha]_D^{21}$ −33.4° (*c*=1.5, pyridine). Positive FAB-MS *m/z*: 387.1650 $[M+H]^+$ (Calcd for $C_{18}H_{27}O_4$: 387.1655), 225 $[M-C_6H_{10}O_5+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.35 (3H, s, OCH_3), 3.79 (6H, s, OCH_3×2), 4.10 (2H, dd, *J*=1.5, 6.0 Hz, H_2-3′), 5.85 (1H, d, *J*=7.0 Hz, Glc H-1), 6.39 (1H, td, *J*=6.0, 16.0 Hz, H-2′), 6.68 (1H, d, *J*=16.0 Hz, H-1′), 6.89 (2H, s, H-2, 6).

3,5-Dihydroxyestragole 3-*O*-β-D-Glucopyranoside (8) Colorless needles (EtOAc), mp 145—147 °C, $[\alpha]_D^{21}$ −48.0° (*c*=0.8, MeOH). Positive FAB-MS *m/z*: 343.1411 $[M+H]^+$ (Calcd for $C_{16}H_{23}O_8$: 343.1393), 181 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.29 (2H, d, *J*=6.5 Hz, H-1′), 4.01 (3H, s, OCH_3), 5.00 (1H, dd, *J*=2.0, 10.0 Hz, H-3′a), 5.08 (1H, dd, *J*=2.0, 17.0 Hz, H-3′b), 5.73 (1H, d, *J*=7.0 Hz, Glc H-1), 5.97 (1H, tdd, *J*=6.5, 10.0, 17.0 Hz, 2′-H), 6.89 (1H, d, *J*=2.0 Hz, H-6), 7.13 (1H, d, *J*=2.0 Hz, H-2).

Enzymatic Hydrolysis of 8 A mixture of **8** (10 mg) and hesperidinase (3 mg) in water (5 ml) was shaken in a water bath at 37 °C for 48 h. The mixture was evaporated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH (19 : 1) and $CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to afford **9** (4 mg) and the sugar fraction. The sugar fraction was passed through Sephadex LH-20 (MeOH) to give a syrup, and HPLC [column: carbohydrate analysis, detector; JASCO RI-930 detector and JASCO OR-990 chiral detecter: CH_3CN–H_2O (17 : 3), 2 ml/min; t_R 4.53 min, positive polarity] showed the presence of D-glucose.

3,5-Dihydroxyestragole (9) An amorphous powder, $[\alpha]_D^{21}$ ±0° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 181 $[M(C_{10}H_{22}O_3)+H]^+$. ^{1}H-NMR (pyridine-d_5, 270 MHz) δ: 3.32 (2H, d, *J*=6.5 Hz, H-1′), 3.98 (3H, s, OCH_3), 5.01 (1H, dd, *J*=2.0, 10.0 Hz, H-3′a), 5.11 (1H, dd, *J*=2.0, 17.0 Hz, H-3′b), 6.04 (1H, tdd, *J*=6.5, 10.0, 17.0 Hz, H-2′), 6.78 (2H, br s, H-2, 6).

3,5-Dimethoxy-4-hydroxybenzyl Alcohol 4-*O*-β-D-Glucopyranoside (10) Colorless needles (MeOH), mp 175—177°C, $[\alpha]_D^{21}$ −20.7° (*c*=2.0,

MeOH). Positive FAB-MS *m/z*: 369 $[M+Na]^+$, 347.1337 $[M+H]^+$ (Calcd for $C_{15}H_{23}O_9$: 347.1342), 167 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.84 (6H, s, $OCH_3\times2$), 4.55 (2H, br s, H-1′), 4.84 (1H, d, J=7.0 Hz, Glc H-1), 6.70 (2H, br s, H-2, 6).

3′-*O*-Methyl-*p*-hydroxycinnamyl Alcohol 4-*O*-β-D-Glucopyranoside (11) An amorphous powder, $[\alpha]_D^{23}$ −60.0° (c=0.2, MeOH). Positive FAB-MS *m/z*: 349 $[M+Na]^+$, 327.1414 $[M+H]^+$ (Calcd for $C_{16}H_{23}O_7$: 327.1444), 295 $[M-CH_3OH+H]^+$, 133 $[M-C_6H_{10}O_5-CH_3OH+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.30 (3H, s, OCH_3), 4.04 (2H, dd, J=1.5, 6.0 Hz, H_2-3′), 5.67 (1H, d, J=7.5 Hz, Glc H-1), 6.28 (1H, dt, J=6.0, 16.0 Hz, H-2′), 6.65(1H, d, J=16.0 Hz, H-1′), 7.35 (2H, d, J=9.0 Hz, H-3, 5), 7.42 (1H, d, J=9.0 Hz, H-2, 6).

1′-(4-Hydroxyphenyl)-2′-propanol 4-*O*-β-D-Glucopyranoside (12) An amorphous powder, $[\alpha]_D^{21}$ −52.0° (c=0.4, MeOH). Positive FAB-MS *m/z*: 337 $[M+Na]^+$, 315.1432 $[M+H]^+$ (Calcd for $C_{15}H_{23}O_7$: 315.1444), 135 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 1.33 (3H, d, J=6.0 Hz, H_3-3′), 2.88, 2.96 (2H, each dd, J=6.0, 13.0 Hz, H_2-1′), 4.23 (1H, ddd, J=6.0, 13.0, 13.0 Hz, H-2′), 5.63 (1H, d, J=7.5 Hz, Glc H-1), 7.30 (2H, d, J=8.5 Hz, H-3, 5), 7.36 (2H, d, J=8.5 Hz, H-2, 6); epimeric isomer: 1.34 (3H, d, J=6,0 Hz, H_3-3′), 2.79, 3.00 (2H, each dd, J=6.0, 13.0 Hz, H_2-1′), 7.29 (2H, d, J=8.5 Hz, H-3, 5), 7.35 (2H, d, J=8.5 Hz, H-2, 6).

***p*-Anisyl β-D-Glucopyranoside (13)** Colorless needles (EtOAc), mp 137—138 °C, $[\alpha]_D^{21}$ −51.1° (c=1.2, MeOH). Positive FAB-MS *m/z*: 301.1292 $[M+H]^+$ (Calcd for $C_{14}H_{21}O_7$: 301.1287), 121 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.66 (3H, s, OCH_3), 4.12 (1H, dd, J=7.5, 9.0 Hz, Glc H-2), 4.81, 5.13 (each 1H, d, J=11.5 Hz, H_2-1′), 4.99 (1H, d, J=7.5 Hz, Glc H-1), 6.95 (2H, d, J=8.5 Hz, H-2, 6), 7.48 (2H, d, J=8.5 Hz, H-3, 5).

***p*-Anisyl 2-*O*-Sodium Sulfo-β-D-glucopyranoside (14)** Colorless needles (MeOH), mp 149—151 °C, $[\alpha]_D^{21}$ −34.6° (c=0.8, MeOH). Positive FAB-MS *m/z*: 425 $[M+Na]^+$, 403.0658 $[M+H]^+$ (Calcd for $C_{14}H_{19}O_{10}SNa$: 403.0675), 381 $[M-Na+2H]^+$, 299 $[M-SO_3Na]^+$ (base); Negative FAB-MS *m/z*: 401 $[M-H]^-$, 379 $[M-Na]^-$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.57 (3H, s, OCH_3), 4.89, 5.12 (each 1H, d, J=12.0 Hz, H_2-1′), 5.00 (1H, d, J=8.0 Hz, Glc H-1), 5.22 (1H, t, J=9.0 Hz, Glc H-2), 6.86 (2H, d, J=9.0 Hz, H-2, 6), 7.60 (2H, d, J=9.0 Hz, H-3, 5).

***p*-Methoxyphenylpropyl 2-*O*-Sodium Sulfo-β-D-glucopyranoside (15)** An amorphous powder, $[\alpha]_D^{23}$ −25.5° (c=0.3, MeOH). Positive FAB-MS *m/z*: 453 $[M+Na]^+$, 431.0998 $[M+H]^+$ (Calcd for $C_{16}H_{24}O_{10}SNa$: 431.0988; base), 327 $[M-SO_3Na]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 1.92 (2H, m, H-1′), 2.71, 2.80 (each 1H, ddd, J=6.5, 8.0, 14.0 Hz, H_2-2′), 3.67, 4.04 (each 1H, dd, J=6.5, 16.0 Hz, H_2-3′), 4.90 (1H, d, J=7.5 Hz, Glc H-1), 5.10 (1H, dd, J=7.5, 8.0 Hz, Glc H-2), 6.87 (2H, d, J=8.5 Hz, H-3, 5), 7.24 (2H, d, J=8.5 Hz, H-2, 6).

Detection of Sulfate Group in 14 and 15 A solution of **15** and **16** (2 mg of each) in aq. 2 N HCl (1 ml) was heated for 2 h, neutralized with dil. NaOH and evaporated to dryness under reduced pressure. The residue was subjected to paper partition chromatography, and developed with a MeOH–H_2O (9 : 1) mixture. After drying in air, the paper was sprayed with a solution of $BaCl_2$ (20 mg) in 70% methanol (10 ml) and dried again in air. The paper was then sprayed with a solution of potassium rhodizonate (5 mg) in 50% methanol (25 mg) to develop the positive coloration (yellow).

(1′*R*)-1′-(3-Hydroxy-4-methoxyphenyl)ethane-1′,2′-diol (16) An amorphous powder, $[\alpha]_D^{23}$ −22.5° (c=0.2, MeOH). Positive FAB-MS *m/z*: 185.0825 $[M+H]^+$ (Calcd for $C_9H_{13}O_4$: 185.0814; base), 131 $[M-3H_2O+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.75 (3H, s, OCH_3), 4.21 (2H, br d, J=6.0 Hz, H_2-2′), 5.28 (1H, dd, J=6.0, 6.0 Hz, H-1′), 7.01 (1H, d, J=8.0 Hz, H-5), 7.25 (1H, dd, J=2.0, 8.0 Hz, H-6), 7.68 (1H, d, J=2.0 Hz, H-2).

(1′*R*)-1′-(3-Hydroxy-4-methoxyphenyl)ethane-1′,2′-diol 3-*O*-β-D-Glucopyranoside (17) An amorphous powder, $[\alpha]_D^{23}$ −52.0° (c=0.3, MeOH). Positive FAB-MS *m/z*: 385 $[M+K]^+$, 369.1143 $[M+Na]^+$ (Calcd for $C_{15}H_{22}O_9Na$: 369.1161; base), 329 $[M-H_2O+H]^+$, 167 $[M-C_6H_{12}O_6+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.72 (3H, s, OCH_3), 4.14 (1H, dd, J=4.5, 11.5 Hz, H-2′a), 4.19 (1H, dd, J=7.5, 11.5 Hz, H-2′b), 5.26 (1H, dd, J=4.5, 7.5 Hz, H-1′), 5.72 (1H, d, J=7.5 Hz, Glc H-1), 6.99 (1H, d, J=8.0 Hz, H-5), 7.35 (1H, dd, J=2.0, 8.0 Hz, H-6), 7.98 (1H, d, J=2.0 Hz, H-2).

Phenethyl β-D-Glucopyranoside (18) An amorphous powder, $[\alpha]_D^{23}$ −36.5° (c=0.2, MeOH), [lit.[10]; $[\alpha]_D$ −36.6° (MeOH)].

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References and Notes

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2) *a*) Kitajima J., Ishikawa T., Tanaka Y., *Chem. Pharm. Bull.*, accepted; *b*) *Idem*, *ibid.*, accepted; *c*) Ishikawa T., Kitajima J., Tanaka Y., *ibid.*, accepted; *d*) Ono M., Ito Y., Ishikawa T., Kitajima J., Tanaka Y., Niiho Y., Nohara T., *ibid.*, **44**, 337—342 (1996).
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