Water-Soluble Constituents of Fennel. III.¹⁾ Fenchane-Type Monoterpenoid Glycosides

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Received March 27, 1998; accepted July 6, 1998

From the water-soluble portion of the methanolic extract of fennel, the fruit of *Foeniculum vulgare* MILLER (Umbelliferae), nine fenchane-type monoterpenoid glycosides were isolated.

Based on the spectral evidence, they were characterized as (1*R*,4*R*,5*S*)-5-hydroxyfenchone β -D-glucopyranoside, (1*R*,4*S*,6*R*)-6-hydroxyfenchone β -D-glucopyranoside, (1*R*,3*S*,4*S*,6*R*)-6,9-dihydroxyfenchone 6-*O*- β -D-glucopyranoside, (1*S*,4*R*)-10-hydroxyfenchone β -D-glucopyranoside, (1*S*,3*S*,4*R*)-9,10-dihydroxyfenchone 10-*O*- β -D-glucopyranoside, (1*S*,3*R*,4*R*)-8,10-dihydroxyfenchone 10-*O*- β -D-glucopyranoside, (1*R*,2*R*,4*S*,6*R*)-2,6-dihydroxyfenchane 2-*O*- β -D-glucopyranoside, (1*R*,2*S*,4*R*,5*S*)-2,5-dihydroxyfenchane 2-*O*- β -D-glucopyranoside and (1*S*,2*S*,4*S*,6*R*,7*S*)-2,6,7-trihydroxyfenchane 2-*O*- β -D-glucopyranoside. The latter seven glycosides were new, and this is the first report of the isolation of fenchane-type glycosides from plant sources.

Key words fennel; *Foeniculum vulgare* fruit; Umbelliferae; fenchane-type glycoside; hydroxyfenchane

In previous papers, we reported the isolation and characterization of *erythro*-anethole glycosides,¹⁾ alkyl glycosides²⁾ and 1,8-cineole derived monoterpenoid glycosides³⁾ from fennel. In this paper, we describe the isolation and structure elucidation of nine fenchane-type monoterpenoid glycosides.

The methanolic extract of commercial fennel [prepared from the fruit of *Foeniculum vulgare* MILLER (Umbelliferae)] was worked up as described in the Experimental section, and from the water-soluble portion of this extract, fenchane-type monoterpenoid glycosides 1 to 9 were isolated.

Glycoside 1 ($C_{16}H_{26}O_7$, an amorphous powder, $[\alpha]_D^{26} -6.2^\circ$) and glycoside 2 ($C_{16}H_{26}O_7$, an amorphous powder, $[\alpha]_D^{21} -44.0^\circ$) showed $[M+H]^+$ and $[M-C_6H_{10}O_5+H]^+$ ion peaks at m/z 331 and 169 in the positive FAB-MS, and acid hydrolysis of 2 gave D-glucose as a sugar component. The 1H -, ^{13}C - and ^{13}C - 1H correlation spectroscopy (COSY) NMR spectral data for 1 and 2 (Tables 1 and 2) revealed the presence of one β -glucopyranosyl, three *tert*-methyls, two methylenes, two methines (one of them oxygenated), one carbonyl group and two quaternary carbons. The planar structures of 1 and 2 were confirmed from a heteronuclear multiple-bond correlation (HMBC) experiment, and they were concluded to be glucosides of 5-hydroxy and 6-hydroxyfenchone, respectively. As nuclear Overhauser effect (NOE) interactions between H-5 and H₃-9 were observed in the nuclear Overhauser enhancement and exchange spectroscopy (NOESY) spectrum of 1 (Fig. 2), the configuration of H-5 of 1 should be *endo*. In contrast, from the cross peak between H-6 and H₃-9 observed in the NOESY spectrum of 2 (Fig. 2), the configuration of H-6 of 2 should be *endo*. From these results, 1 and 2 were confirmed as 5 β -hydroxyfenchone β -D-glucopyranoside and 6 β -hydroxyfenchone β -D-glucopyranoside, respectively. Orihara *et al.*⁴⁾ obtained biotransformation products from a cell suspension culture of *Eucalyptus perriniana* following administration of (+)-fenchone. Both 1 and 2 were identified as its main biotransformation products, (1*R*,4*R*,5*S*)-5-hydroxyfenchone β -D-glucopyranoside and (1*R*,4*S*,6*R*)-6-hydroxyfenchone β -D-glucopyranoside, by comparison of ^{13}C -NMR data and the $[\alpha]_D$ value (all reported 1H -chemical shifts for 1 and 2 were about 0.13 ppm

downfield from our data). Although 1 and 2 are not new, this is the first report of their isolation from plant sources.

Glycoside 3 ($C_{16}H_{26}O_8$, an amorphous powder, $[\alpha]_D^{23} -64.5^\circ$) showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at m/z 347 and 167 in the positive FAB-MS. Acid hydrolysis of 3 gave D-glucose as a sugar component. The 1H -, ^{13}C - and ^{13}C - 1H COSY NMR spectral data (Tables 1 and 2) for 3 showed the presence of one β -glucopyranosyl, two *tert*-methyls, two methylenes, one hydroxymethyl, two methines (one of them oxygenated), one carbonyl group, and two quaternary carbons. By comparison of its 1H - and ^{13}C -NMR data with those of 2, and analysis of the HMBC spectral data, 3 was concluded to be a monohydroxy derivative of 2, one *gem*-dimethyl of which was oxygenated. Further, similarity in the ^{13}C -chemical shifts of C-6 [(2; δ 76.37), (3; δ 76.70)] and glucosyl C-1 [(2; δ 101.78), (3; δ 101.92)] showed that the aglycone of 3 was also a derivative of (+)-fenchone. As NOE interactions between the signals of H₃-8 and H-7a, H₃-8 and H₂-9 were observed in its NOESY spectrum, the position of the other hydroxy group should be C-9. From these results, 3 was characterized as (1*R*,3*S*,4*S*,6*R*)-6,9-dihydroxyfenchone 6-*O*- β -D-glucopyranoside.

Glycoside 4 ($C_{16}H_{26}O_7$, mp 91–92 °C, $[\alpha]_D^{21} -1.8^\circ$) showed $[M+K]^+$, $[M+Na]^+$, $[M+H]^+$ and $[M-C_6H_{10}O_5+H]^+$ ion peaks at m/z 369, 353, 331 and 169 in the positive FAB-MS. Acid hydrolysis of 4 gave D-glucose as a sugar component. From the analysis of 1H -, ^{13}C - and ^{13}C - 1H COSY NMR spectral data (Tables 1 and 2), and an HMBC experiment which showed correlations from the two *tert*-methyl protons to the C-2, C-3 and C-4 carbons, one hydroxymethyl proton to the C-1, C-2, C-6, C-7 and glucosyl C-1 carbons, one methine proton to the C-2, C-6 and C-7 carbons, and glucosyl H-1 to the C-10 carbon, the planar structure of 4 (Fig. 1, shown in heavy lines) was obtained. Therefore, the aglycone of 4 was concluded to be 10-hydroxyfenchone and the location of the glucosyl group was C-10. As (+)-fenchone⁵⁾ and glycosides 1, 2, and 3 were obtained from fennel, the absolute configuration of 4 was deduced to be the same as that of (+)-fenchone. This was also supported by the $[M]_D$ values (-6°) of 4, which showed a plus value when calculated using

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the value of methyl β -D-glucopyranoside (-62° ; 4-methyl β -D-glucopyranoside $= +56^\circ$).⁶⁾ From these results, **4** was characterized as (1*S*,4*R*)-10-hydroxyfenchone β -D-glucopyranoside.

Glycoside **5** ($C_{16}H_{26}O_8$, mp 167–169 °C, $[\alpha]_D^{26} -13.8^\circ$) showed $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at m/z 347 and 167 in the positive FAB-MS. The 1H -, ^{13}C - and ^{13}C - 1H COSY NMR spectral data (Tables 1 and 2) showed the presence of one β -glucopyranosyl, one *tert*-methyl, two hydroxymethyls, three methylenes, one methine, one carbonyl group, and two quaternary carbons. From an HMBC experiment (Fig. 1, shown in heavy lines) and comparison of NMR data with those of **4**, **5** was concluded to be a monohydroxy derivative of **4**. The other hydroxyl group was located at C-9 from the observed cross peaks between H-5*endo* and H₂-9, H-7a and H₃-8 in its NOESY spectrum (Fig. 2). Therefore, **5** was characterized as (1*S*,3*S*,4*R*)-9,10-dihydroxyfenchone 10-*O*- β -D-glucopyranoside.

Fig. 1. Planar Structures of 1–9 Solved by HMBC Spectra (Heavy Lines)

chone 10-*O*- β -D-glucopyranoside.

Glycoside **6** ($C_{16}H_{26}O_8$, mp 86–88 °C, $[\alpha]_D^{23} +12.7^\circ$) showed $[M+K]^+$, $[M+H]^+$ and $[M-C_6H_{10}O_5+K]^+$ ion peaks at m/z 385, 347 and 223 in the positive FAB-MS. From the 1H -, ^{13}C - and ^{13}C - 1H COSY NMR spectral data (Tables 1 and 2) and analysis of the HMBC spectral data (Fig. 1, shown in heavy lines), **6** was also concluded to be a monohydroxy derivative of **4**. The other hydroxyl group was located at C-8 from the observed cross peaks between H-5*endo* and H₃-9, H-7a and H₂-8 in its NOESY spectrum (Fig. 2). So, **6** was characterized as (1*S*,3*R*,4*R*)-8,10-dihydroxyfenchone 10-*O*- β -D-glucopyranoside.

Glycoside **7** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{23} -34.8^\circ$) showed $[2M+H]^+$, $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at m/z 665, 333 and 153 in the positive FAB-MS. Acid hydrolysis of **7** gave D-glucose as a sugar component. The 1H -, ^{13}C - and ^{13}C - 1H COSY NMR spectral data (Tables 1 and 2) for **7** showed the presence of one β -glucopyranosyl, three *tert*-methyls, two methylenes and three methines (two of them oxygenated) and two quaternary carbons. From an HMBC experiment, **7** was concluded to be a glucoside of fenchane-2,6-diol and the position of the glucosyl unit was ascertained to be C-2. Furthermore, from NOE interactions between the signals of H-2 and H₃-10, H-2 and H-7a, H-2 and H₃-8, H-6 and H₃-9 observed in its NOESY spectrum (Fig. 2), the configuration of H-2 and H-6 was confirmed as *exo* and *endo*, respectively. Thus, **7** was concluded to be fenchane-2 α ,6 β -diol 2-*O*- β -D-glucopyranoside.

Glycoside **8** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{23} -3.5^\circ$) showed $[M+K]^+$, $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at m/z 371, 333 and 153 in the positive FAB-MS. The analysis of 1H -, ^{13}C - and ^{13}C - 1H COSY NMR spectral data (Tables 1 and 2) and the results of an HMBC experiment

Fig. 2. Structures and NOE Interactions Observed in the NOESY Spectra of 1–9

(Fig. 1, shown in heavy lines) suggested that **8** was a β -glucopyranoside of fenchane-2,5-diol and the position of the glucosyl unit was C-2. From the observed NOE interactions between the signals of H-2 and H₃-9, H-2 and H-6, H-7a and H₃-8, H-5 and H₃-9 (Fig 2), the configuration of H-2 and H-5 should be *endo*. Therefore, **8** was concluded to be fenchane-

2 α ,5 α -diol 2-*O*- β -D-glucopyranoside.

Glycoside **9** (C₁₆H₂₈O₈, mp 211–213 °C, [α]_D²³ –6.5°) showed [M+H]⁺ and [M–C₆H₁₀O₅+H]⁺ ion peaks at *m/z* 349 and 187 in the positive FAB-MS. The ¹H-, ¹³C- and ¹³C–¹H COSY NMR spectral data (Tables 1 and 2) showed the presence of one β -glucopyranosyl, three *tert*-methyls,

Table 1. ¹H-NMR Chemical Shifts of **1–9** (in Pyridine-*d*₅, 500 MHz)

	1	2	3	4	5
H-4	2.55 br s	2.06 br d (3.0)	2.56 br d (4.5)	1.96 br d (3.0)	2.46 br d (3.0)
H-5 <i>endo</i>	4.69 m	2.39 ddd (3.0, 6.0, 12.5)	2.94 ddd (3.0, 6.5, 13.0)	1.62 br ddd (3.0, 12.5, 12.5)	2.13 dddd (3.0, 3.0, 9.0, 12.0)
<i>exo</i>	—	2.05 m	2.22 ddd (4.5, 4.5, 13.0)	1.48 m	1.61 m
H-6 <i>endo</i>	1.92 m	4.19 br d (6.0)	4.38 dd (4.5, 6.5)	1.23 m	1.41 m
<i>exo</i>	1.91 dd (2.0, 12.5)	—	—	1.90 ddd (3.0, 12.5, 12.5)	1.98 ddd (3.0, 12.0, 12.0)
H-7a	1.64 br d (10.5)	1.69 br d (11.0)	1.73 br d (10.5)	2.13 dd (1.5, 10.5)	2.17 br d (10.5)
b	2.23 dd (1.5, 10.5)	2.04 br d (11.0)	2.12 dd (2.0, 10.5)	1.65 dd (1.5, 10.5)	1.75 dd (1.5, 10.5)
H ₃ -8	0.99 s	0.98 s	1.31 s	0.94 s	1.29 s
H ₃ -9	0.95 s	0.88 s	—	0.97 s	—
H ₂ -9	—	—	3.79 d (11.0)	—	3.88 d (11.0)
—	—	—	3.84 d (11.0)	—	3.91 d (11.0)
H ₃ -10	1.07 s	1.40 s	1.45 s	—	—
H ₂ -10	—	—	—	3.88 d (11.0)	3.92 d (10.5)
—	—	—	—	4.53 d (11.0)	4.58 d (10.5)
Glc-1	5.03 d (7.5)	4.89 d (8.0)	4.91 d (8.0)	4.85 d (8.0)	4.88 d (8.0)

	6	7	8	9
H-2 <i>endo</i>	—	—	3.21 s	3.20 s
<i>exo</i>	—	3.88 s	—	—
H-4	2.67 br d (3.0)	1.68 br d (4.0)	1.94 br s	1.96 br d (4.0)
H-5 <i>endo</i>	1.70 dddd (3.0, 3.0, 9.0, 12.5)	2.49 ddd (2.5, 7.5, 13.0)	4.49 br d (6.5)	2.45 br dd (7.5, 13.5)
<i>exo</i>	1.58 m	1.60 ddd (4.0, 4.0, 13.0)	—	2.17 ddd (4.0, 4.0, 13.5)
H-6 <i>endo</i>	1.34 m	4.60 dd (4.0, 7.5)	1.63 br d (13.5)	3.77 dd (4.0, 7.5)
<i>exo</i>	2.00 ddd (3.0, 12.5, 12.5)	—	1.77 ddd (2.0, 6.5, 13.5)	—
H-7a	2.46 dd (1.5, 10.5)	1.44 br d (10.0)	1.87 br d (10.0)	4.55 d (4.0)
b	1.75 dd (1.5, 10.5)	1.72 br d (10.0)	1.95 br d (10.0)	—
H ₃ -8	—	1.14 s	1.24 s	1.25 s
H ₂ -8	3.70 d (11.0)	—	—	—
—	3.96 d (11.0)	—	—	—
H ₃ -9	1.29 s	1.28 s	1.22 s	1.17 s
H ₃ -10	—	1.64 s	1.50 s	1.81 s
H ₂ -10	3.93 d (11.0)	—	—	—
—	4.57 d (11.0)	—	—	—
Glc-1	4.86 d (7.5)	4.83 d (8.0)	4.77 d (7.5)	4.79 d (7.5)

δ in ppm from TMS [coupling constants (*J*) in Hz are given in parentheses].

Table 2. ¹³C-NMR Chemical Shifts of **1–9** (in Pyridine-*d*₅, 125 MHz)

	1	2	3	4	5	6	7	8	9
C-1	53.29	60.31	60.84	59.51	59.73	59.44	54.09	49.19	55.60
C-2	221.29	221.57	220.41	220.49	219.34	219.37	91.07	93.32	90.24
C-3	45.16	46.98	53.69	47.84	54.62	54.68	40.07	42.12	39.60
C-4	50.09	44.49	42.54	45.33	43.18	41.28	47.84	56.75	52.37
C-5	77.63	35.86	36.16	24.47	24.74	24.68	39.40	70.39	35.78
C-6	41.62	76.38	76.70	27.08	27.15	27.75	67.99	46.80	76.36
C-7	37.88	38.33	38.45	37.91	37.94	37.98	37.75	37.90	80.38
C-8	23.63	23.70	19.62	23.11	18.91	65.20	31.77	25.90	25.36
C-9	21.35	21.44	64.54	21.59	64.89	17.87	21.77	25.16	26.00
C-10	14.40	11.71	11.68	68.49	68.45	68.55	15.78	17.67	10.62
Glc-1	103.54	101.78	101.92	105.58	105.62	105.65	105.13	105.75	105.98
Glc-2	75.28	75.06	75.12	75.13	75.14	75.17	75.73	75.56	75.54
Glc-3	78.65	78.61	78.60	78.55	78.55	78.58	78.70	78.63	78.62
Glc-4	71.65	71.56	71.51	71.62	71.63	71.62	72.09	72.29	72.18
Glc-5	78.66	78.69	78.63	78.62	78.63	78.63	78.26	77.97	78.03
Glc-6	62.77	62.56	62.54	62.74	62.75	62.73	63.21	63.28	63.09

δ in ppm from TMS.

one methylene, four methines (three of them oxygenated), and two quaternary carbons. From analysis of the HMBC spectral data (Fig. 1, shown in heavy lines), **9** was concluded to be a 2-*O*- β -D-glucopyranoside of fenchane-2,6,7-triol. Further, from NOE interactions between the signals of H-2 and H₃-9, H-2 and H-6, H-7a and H₃-8 observed in its NOESY spectrum (Fig. 2), the configuration of H-2 and H-6 should be *endo* and the position of the third hydroxyl group was C-7b. Thus, the structure of this glycoside was assigned as **9** in Fig. 2.

As these nine fenchane-type monoterpenoid glycosides are believed to be closely related to each other due to their biosynthesis, the absolute configurations of **7**, **8** and **9** were considered to be the same as (+)-fenchone. Accordingly, **7**, **8** and **9** were characterized as (1*R*,2*R*,4*S*,6*R*)-2,6-dihydroxyfenchane 2-*O*- β -D-glucopyranoside, (1*R*,2*S*,4*R*,5*S*)-2,5-dihydroxyfenchane 2-*O*- β -D-glucopyranoside and (1*S*,2*S*,4*S*,6*R*,7*S*)-2,6,7-trihydroxyfenchane 2-*O*- β -D-glucopyranoside, respectively.

3 to **9** are new compounds and have not been described previously. As far as we know, this is the first report of the isolation of fenchane-type monoterpenoid glycosides from plant sources.

Fennel contains an essential oil accounting for about 3–8% of its total weight, and (+)-fenchone is the most abundant monoterpenoid component (yield; 6–27%).⁷⁾ Since we have isolated nine kinds of fenchane-derived glycosides from fennel, a biogenetic relationship between the essential oil and its glycoside constituents is suggested.

Experimental

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

Extraction and Isolation of Fenchane-Type Glycosides Commercial fennel (purchased from Kinokuniya Chinese Medicine Pharmacy, Ltd., lot. No. AOCJ0D28J; 2.0 kg) was extracted with methanol (10 l) at room temperature. The methanol extract (329.4 g) was partitioned between ether–water and then ethyl acetate–water, and the aqueous portion obtained was subjected to Amberlite XAD-II (H₂O→MeOH) chromatography. The methanol eluate (29.5 g) was chromatographed over Sephadex LH-20 (MeOH) to give seven fractions (frs. A–G). Fraction C (16.9 g) was chromatographed over silica gel [CHCl₃–MeOH–H₂O (4 : 1 : 0.1)→MeOH] to give fifteen fractions (frs. C₁–C₁₅). Fraction C₅ (1.7 g) was passed through a Lobar RP-8 column [CH₃CN–H₂O (3 : 17)] to give twelve fractions (frs. C₅₋₁–C₅₋₁₂). Fraction C₅₋₆ was subjected to HPLC [octadecyl silica (ODS), CH₃CN–H₂O (1 : 9)] to give **1** (25 mg). Fraction C₅₋₉ was subjected to HPLC [carbohydrate analysis, CH₃CN–H₂O (24 : 1)] to give **2** (26 mg). Fraction C₅₋₁₀ was subjected to HPLC [ODS, CH₃CN–H₂O (3 : 17)] to give **4** (25 mg). Fraction C₆ (1.9 g) was passed through a Lobar RP-8 column [CH₃CN–H₂O (3 : 17)] to give thirteen fractions (frs. C₆₋₁–C₆₋₁₃). Fraction C₆₋₁₀ was subjected to HPLC [carbohydrate analysis, CH₃CN–H₂O (19 : 1)] to give **7** (8 mg). Fraction C₇ (0.7 g) was passed through a Lobar RP-8 column [CH₃CN–H₂O (1 : 9→3 : 17)] to give nine fractions (frs. C₇₋₁–C₇₋₉). Fraction C₇₋₅ was subjected to HPLC [carbohydrate analysis, CH₃CN–H₂O (19 : 1)] to give three fractions (frs. C₇₋₅₋₁–C₇₋₅₋₃). Fraction C₇₋₅₋₁ was chromatographed over silica gel [CHCl₃–MeOH (17 : 3)] to give **8** (6 mg). Fraction C₉ (1.3 g) was passed through a Lobar RP-8 column [MeOH–H₂O (3 : 17→1 : 4)] to give eleven fractions (frs. C₉₋₁–C₉₋₁₁). Fraction C₉₋₅ was acetylated with Ac₂O and pyridine at room temperature, and the acetylated fraction was subjected to HPLC [ODS, CH₃CN–H₂O (1 : 1)] to give seven fractions (frs. C₉₋₅₋₁–C₉₋₅₋₇). Fraction C₉₋₅₋₆ was deacetylated by heating in a water bath with 15%

NH₄OH–MeOH for 4 h, and finally subjected to HPLC [carbohydrate analysis, CH₃CN–H₂O (14 : 1)] to give **5** (45 mg). Fraction C₉₋₆ was subjected to HPLC [carbohydrate analysis, CH₃CN–H₂O (14 : 1)] to give **3** (12 mg) and **9** (6 mg). Fraction C₉₋₁₀ was subjected to HPLC [carbohydrate analysis, CH₃CN–H₂O (14 : 1)] to give **6** (7 mg).

(1*R*,4*R*,5*S*)-5-Hydroxyfenchone β -D-Glucopyranoside (1) An amorphous powder, $[\alpha]_D^{26}$ –6.2° (*c*=0.8, MeOH), [lit.⁴⁾ $[\alpha]_D$ –9° (*c*=5.4, MeOH)]. Positive FAB-MS *m/z*: 331.1739 [M+H]⁺ (Calcd for C₁₆H₂₇O₇: 331.1757), 169 [M–C₆H₁₀O₅+H]⁺ (base).

(1*R*,4*S*,6*R*)-6-Hydroxyfenchone β -D-Glucopyranoside (2) An amorphous powder, $[\alpha]_D^{26}$ –44.0° (*c*=1.1, MeOH), [lit.⁴⁾ $[\alpha]_D$ –48° (*c*=4.4, MeOH)]. Positive FAB-MS *m/z*: 661 [2M+H]⁺, 331.1733 [M+H]⁺ (Calcd for C₁₆H₂₇O₇: 331.1757), 169 [M–C₆H₁₀O₅+H]⁺ (base).

(1*R*,3*S*,4*S*,6*R*)-6,9-Dihydroxyfenchone 6-*O*- β -D-Glucopyranoside (3) An amorphous powder, $[\alpha]_D^{23}$ –64.5° (*c*=0.7, MeOH). Positive FAB-MS *m/z*: 439 [M+H+glycerol]⁺, 347.1692 [M+H]⁺ (Calcd for C₁₆H₂₇O₈: 347.1706), 329 [M–H₂O+H]⁺, 167 [M–C₆H₁₂O₆+H]⁺ (base).

(1*S*,4*R*)-10-Hydroxyfenchone β -D-Glucopyranoside (4) Colorless needles (MeOH), mp 91–92°C, $[\alpha]_D^{21}$ –1.8° (*c*=1.1, MeOH). Positive FAB-MS *m/z*: 661 [2M+H]⁺, 369 [M+K]⁺, 353 [M+Na]⁺, 331.1759 [M+H]⁺ (Calcd for C₁₆H₂₇O₇: 331.1757), 169 [M–C₆H₁₀O₅+H]⁺ (base).

(1*S*,3*S*,4*R*)-9,10-Dihydroxyfenchone 10-*O*- β -D-Glucopyranoside (5) Colorless needles (MeOH), mp 167–169°C, $[\alpha]_D^{26}$ –13.8° (*c*=1.4, MeOH). Positive FAB-MS *m/z*: 385 [M+K]⁺, 369 [M+Na]⁺ (base), 347.1708 [M+H]⁺ (Calcd for C₁₆H₂₇O₈: 347.1706), 167 [M–C₆H₁₂O₆+H]⁺.

(1*S*,3*R*,4*R*)-8,10-Dihydroxyfenchone 10-*O*- β -D-Glucopyranoside (6) Colorless needles (MeOH), mp 86–88°C, $[\alpha]_D^{23}$ +12.7° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 385.1281 [M+K]⁺ (Calcd for C₁₆H₂₇O₈: 385.1265), 347.1699 [M+H]⁺ (Calcd for C₁₆H₂₇O₈: 347.1706), 223 [M–C₆H₁₀O₅+K]⁺ (base).

(1*R*,2*R*,4*S*,6*R*)-2,6-Dihydroxyfenchane 2-*O*- β -D-Glucopyranoside (7) An amorphous powder, $[\alpha]_D^{23}$ –34.8° (*c*=0.6, MeOH). Positive FAB-MS *m/z*: 665 [2M+H]⁺, 425 [M+H+glycerol]⁺, 333.1923 [M+H]⁺ (Calcd for C₁₆H₂₉O₇: 333.1913), 315 [M–H₂O+H]⁺, 153 [M–C₆H₁₂O₆+H]⁺ (base).

(1*R*,2*S*,4*R*,5*S*)-2,5-Dihydroxyfenchane 2-*O*- β -D-Glucopyranoside (8) An amorphous powder, $[\alpha]_D^{23}$ –3.5° (*c*=0.4, MeOH). Positive FAB-MS *m/z*: 425 [M+H+glycerol]⁺ (base), 371 [M+K]⁺, 333.1921 [M+H]⁺ (Calcd for C₁₆H₂₉O₇: 333.1913), 153 [M–C₆H₁₂O₆+H]⁺.

(1*S*,2*S*,4*S*,6*R*,7*S*)-2,6,7-Trihydroxyfenchane 2-*O*- β -D-Glucopyranoside (9) Colorless needles (MeOH), mp 211–213°C, $[\alpha]_D^{23}$ –6.5° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 441 [M+H+glycerol]⁺, 349.1883 [M+H]⁺ (Calcd for C₁₆H₂₉O₈: 349.1863), 187 [M–C₆H₁₀O₅+H]⁺ (base).

Acid Hydrolysis of 2, 3, 4 and 7 Glycosides **2**, **3**, **4** and **7** (3 mg) were each dissolved in aq. 2*N* H₂SO₄ and heated on a water bath for 3 h. The hydrolysate was then neutralized with NaHCO₃, the salt was filtered off, and the filtrate was chromatographed over silica gel [CHCl₃–MeOH–H₂O (7 : 3 : 0.5)]. The sugar fraction subjected to HPLC [column; carbohydrate analysis, detector; JASCO RI-930 detector and OR-990 chiral detector, solv.; CH₃CN–H₂O (17 : 3), 2 ml/min, *t*_R 4.53 min] showed the presence of D-glucose.

Acknowledgments The authors thank Messrs. Y. Takase and H. Suzuki of the Analytical Center of this college for NMR and MS measurements.

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