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

Toru ISHIKAWA, Junichi KITAJIMA,* and Yasuko TANAKA

Showa College of Pharmaceutical Sciences, Higashi-Tamagawagakuen 3, Machida, Tokyo 194–8543, Japan.
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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 glucosides 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 glycosides[2] and 1,8-cineole derived monoterpenoid glycosides[3] 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, $[\alpha]_D^{26}$ $-6.2°$) and glycoside **2** ($C_{16}H_{26}O_7$, an amorphous powder, $[\alpha]_D^{21}$ $-44.0°$) 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 ^{1}H-, ^{13}C- and ^{13}C–^{1}H 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 H_3-9 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 H_3-9 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 5β-hydroxyfenchone β-D-glucopyranoside and 6β-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 ^{1}H-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, $[\alpha]_D^{23}$ $-64.5°$) 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 ^{1}H-, ^{13}C- and ^{13}C–^{1}H 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 ^{1}H- 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 H_3-8 and H-7a, H_3-8 and H_2-9 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, $[\alpha]_D^{21}$ $-1.8°$) 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 ^{1}H-, ^{13}C- and ^{13}C–^{1}H 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 (+)-fenchone[5] 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

* To whom correspondence should be addressed.

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the value of methyl β-D-glucopyranoside ($-62°$; 4−methyl β-D-glucopyranoside$=+56°$).[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, $[\alpha]_D^{26}$ $-13.8°$) 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 ^{1}H-, ^{13}C- and ^{13}C–^{1}H 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 H_2-9, H-7a and H_3-8 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.

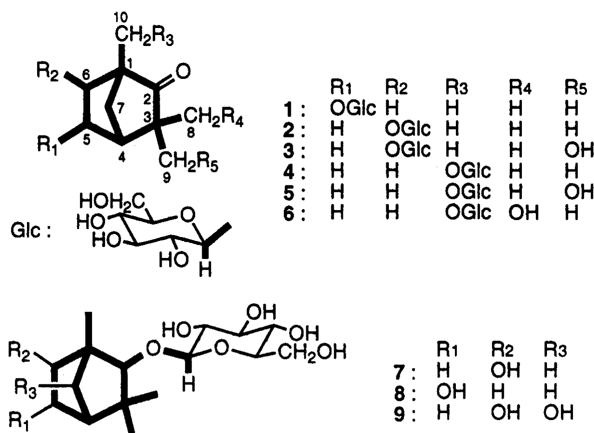

Fig. 1. Planar Structures of **1**—**9** Solved by HMBC Spectra (Heavy Lines)

Glycoside **6** ($C_{16}H_{26}O_8$, mp 86—88 °C, $[\alpha]_D^{23}$ $+12.7°$) 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 ^{1}H-, ^{13}C- and ^{13}C–^{1}H 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 H_3-9, H-7a and H_2-8 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, $[\alpha]_D^{23}$ $-34.8°$) 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 ^{1}H-, ^{13}C- and ^{13}C–^{1}H 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 H_3-10, H-2 and H-7a, H-2 and H_3-8, H-6 and H_3-9 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-2α,6β-diol 2-*O*-β-D-glucopyranoside.

Glycoside **8** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{23}$ $-3.5°$) 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 ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data (Tables 1 and 2) and the results of an HMBC experiment

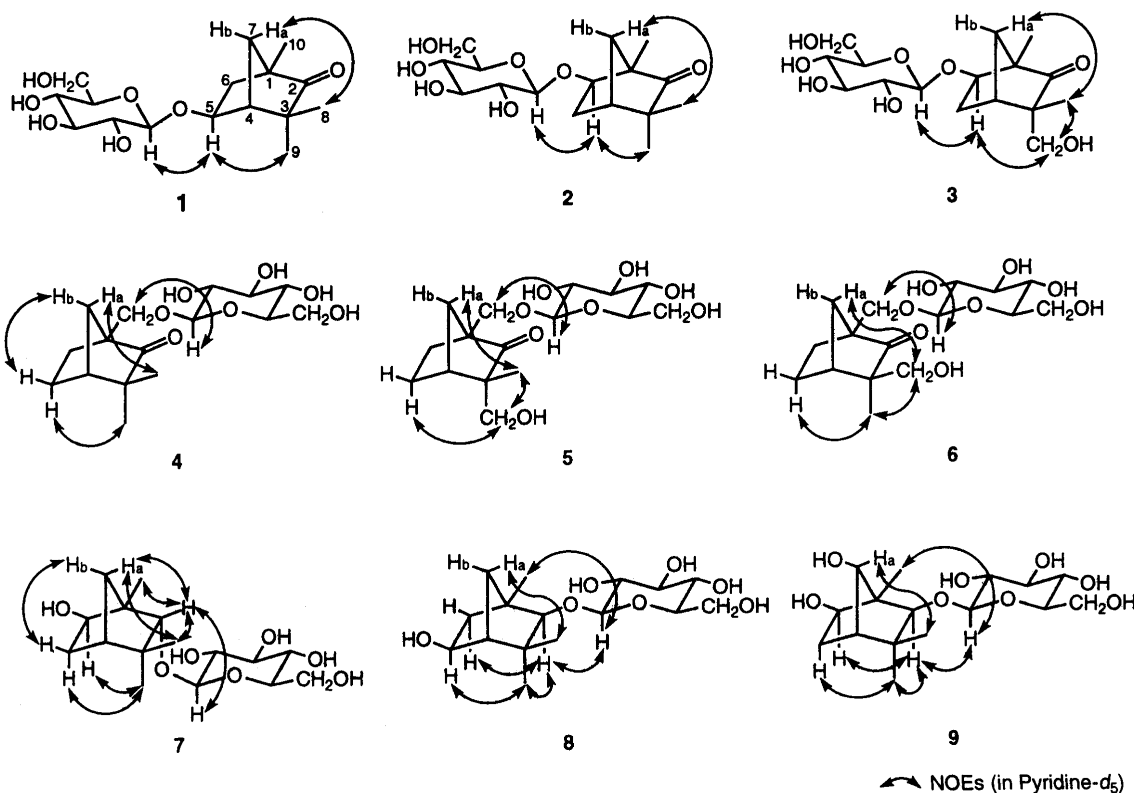

Fig. 2. Structures and NOE Interactions Observed in the NOESY Spectra of **1**—**9**

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(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 H_3-9, H-2 and H-6, H-7a and H_3-8, H-5 and H_3-9 (Fig 2), the configuration of H-2 and H-5 should be *endo*. Therefore, **8** was concluded to be fenchane-$2\alpha,5\alpha$-diol 2-*O*-β-D-glucopyranoside.

Glycoside **9** ($C_{16}H_{28}O_8$, mp 211—213 °C, $[\alpha]_D^{23}$ −6.5°) showed $[M+H]^+$ and $[M-C_6H_{10}O_5+H]^+$ ion peaks at *m/z* 349 and 187 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, 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 *endo*	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)
exo	—	2.05 m	2.22 ddd (4.5, 4.5, 13.0)	1.48 m	1.61 m
H-6 *endo*	1.92 m	4.19 br d (6.0)	4.38 dd (4.5, 6.5)	1.23 m	1.41 m
exo	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 *endo*	—	—	3.21 s	3.20 s
exo	—	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 *endo*	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)
exo	1.58 m	1.60 ddd (4.0, 4.0, 13.0)	—	2.17 ddd (4.0, 4.0, 13.5)
H-6 *endo*	1.34 m	4.60 dd (4.0, 7.5)	1.63 br d (13.5)	3.77 dd (4.0, 7.5)
exo	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. ^{13}C-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.

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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 H_3-9, H-2 and H-6, H-7a and H_3-8 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. A0CJ0D28J; 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 ($H_2O \rightarrow$ 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 [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)$\rightarrow$MeOH] to give fifteen fractions (frs. C_1—C_{15}). Fraction C_5 (1.7 g) was passed through 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 [octadecyl silica (ODS), CH_3CN–H_2O (1 : 9)] to give **1** (25 mg). Fraction $C_{5\text{-}9}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (24 : 1)] to give **2** (26 mg). Fraction $C_{5\text{-}10}$ was subjected to HPLC [ODS, CH_3CN–H_2O (3 : 17)] to give **4** (25 mg). Fraction C_6 (1.9 g) was passed through a Lobar RP-8 column [CH_3CN–H_2O (3 : 17)] to give thirteen fractions (frs. $C_{6\text{-}1}$—$C_{6\text{-}13}$). Fraction $C_{6\text{-}10}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (19 : 1)] to give **7** (8 mg). Fraction C_7 (0.7 g) was passed through a Lobar RP-8 column [CH_3CN–H_2O (1 : 9$\rightarrow$3 : 17)] to give nine fractions (frs. $C_{7\text{-}1}$—$C_{7\text{-}9}$). Fraction $C_{7\text{-}5}$ was 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 $C_{7\text{-}5\text{-}1}$ was chromatographed over silica gel [$CHCl_3$–MeOH (17 : 3)] to give **8** (6 mg). Fraction C_9 (1.3 g) was passed through a Lobar RP-8 column [MeOH–H_2O (3 : 17$\rightarrow$1 : 4)] to give eleven fractions (frs. $C_{9\text{-}1}$—$C_{9\text{-}11}$). Fraction $C_{9\text{-}5}$ was acetylated with Ac_2O and pyridine at room temperature, and the acetylated fraction was subjected to HPLC [ODS, CH_3CN–H_2O (1 : 1)] to give seven fractions (frs. $C_{9\text{-}5\text{-}1}$—$C_{9\text{-}5\text{-}7}$). Fraction $C_{9\text{-}5\text{-}6}$ was deacetylated by heating in a water bath with 15% NH_4OH–MeOH for 4 h, and finally subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (14 : 1)] to give **5** (45 mg). Fraction $C_{9\text{-}6}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (14 : 1)] to give **3** (12 mg) and **9** (6 mg). Fraction $C_{9\text{-}10}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (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 $C_{16}H_{27}O_7$: 331.1757), 169 $[M-C_6H_{10}O_5+H]^+$ (base).

(1*R*,4*S*,6*R*)-6-Hydroxyfenchone β-D-Glucopyranoside (2) An amorphous powder, $[\alpha]_D^{21}$ −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 $C_{16}H_{27}O_7$: 331.1757), 169 $[M-C_6H_{10}O_5+H]^+$ (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 $[M+H+\text{glycerol}]^+$, 347.1692 $[M+H]^+$ (Calcd for $C_{16}H_{27}O_8$: 347.1706), 329 $[M-H_2O+H]^+$, 167 $[M-C_6H_{12}O_6+H]^+$ (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 $C_{16}H_{27}O_7$: 331.1757), 169 $[M-C_6H_{10}O_5+H]^+$ (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 $C_{16}H_{27}O_8$: 347.1706), 167 $[M-C_6H_{12}O_6+H]^+$.

(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 $C_{16}H_{27}O_8$: 385.1265), 347.1699 $[M+H]^+$ (Calcd for $C_{16}H_{27}O_8$: 347.1706), 223 $[M-C_6H_{10}O_5+K]^+$ (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 $[M+H+\text{glycerol}]^+$, 333.1923 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$: 333.1913), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (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 $[M+H+\text{glycerol}]^+$ (base), 371 $[M+K]^+$, 333.1921 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$: 333.1913), 153 $[M-C_6H_{12}O_6+H]^+$.

(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 $[M+H+\text{glycerol}]^+$, 349.1883 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_8$: 349.1863), 187 $[M-C_6H_{10}O_5+H]^+$ (base).

Acid Hydrolysis of 2, 3, 4 and 7 Glycosides **2**, **3**, **4** and **7** (3 mg) were each dissolved in aq. 2 N H_2SO_4 and heated on a water bath for 3 h. The hydrolysate was then neutralized with $NaHCO_3$, the salt was filtered off, and the filtrate was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)]. The sugar fraction subjected to HPLC [column; carbohydrate analysis, detector; JASCO RI-930 detector and OR-990 chiral detector, solv.; CH_3CN–H_2O (17 : 3), 2 ml/min, t_R 4.53 min] showed the presence of D-glucose.

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