Water-Soluble Constituents of Fennel. VIII. Monoterpenoid Alcohols and Thujane-, Camphane-, Norfenchane-Type Monoterpenoid Glycosides

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Received January 5, 1999; accepted March 2, 1999

Three monoterpenoid alcohols (one new fenchane-type and two new acyclic) and four monoterpenoid glycosides (two new thujane-type, one camphane-type and one new norfenchane-type) were isolated from the water-soluble portion of the methanolic extract of fennel. Their structures were clarified by spectral investigation.

Key words fennel; *Foeniculum vulgare* fruit; thujane-type glycoside; norfenchane-type glycoside; camphane-type glycoside; monoterpenoid

In our previous papers, we reported the isolation and characterization of new alkyl glycosides,[1)] aromatic compound glycosides,[2)] and 1,8-cineole-type,[3)] fenchane-type,[4)] menthane-type[5)] and acyclic[6)] monoterpenoid glycosides from the herbal medicine fennel. In this paper we describe the isolation and structure elucidation of monoterpenoid-diol, triol and tetrol, and thujane-, camphane- and norfenchane-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 by detailed examination of the water-soluble portion, three free-form (**1**—**3**) and four glycosyl-form (**4**—**7**) monoterpenoids were newly isolated. Their molecular formulae were established from the accurate mass number of $[M+H]^+$ or $[M+Na]^+$ ion peaks in the high-resolution positive FAB-MS. All glycosides obtained in this paper were determined to be β-D-glucopyranosides like the other glucosides in this plant by their ^{13}C-NMR data (Table 2), and this was confirmed by acid hydrolysis of **5** to yield D-glucose.

Diol **1** ($C_{10}H_{16}O_3$, an amorphous powder, $[\alpha]_D^{23}$ +4.6°) was identified as (1*S*,3*S*,4*R*)-9,10-dihydroxyfenchone by comparison with a sample which was obtained by the acid hydrolysis of its 10-*O*-β-D-glucopyranoside.[4)] It was also supported by the observed nuclear Overhauser effect (NOE) interaction between the signals of H-5*endo* and H_2-9, H-7a and H_3-8 in its nuclear Overhauser and exchange spectroscopy (NOESY) spectrum (Fig. 1), and the result of a circular dichroism (CD) spectrum which showed a positive Cotton effect at 288 nm ($\Delta\varepsilon$+0.41) as (+)-fenchone [292 nm ($\Delta\varepsilon$+0.14)].[7)]

Triol **2** ($C_{10}H_{20}O_3$, an amorphous powder, $[\alpha]_D^{25}$ −23.0°) showed an $[M+H]^+$ ion peak at *m*/*z* 189 in the positive FAB-MS. The ^1H-, ^{13}C- and ^{13}C–^1H correlation spectroscopy (COSY) NMR spectral data for **2** revealed that **2** was an acyclic monoterpenoid with one terminal-methylene, one *prim*-, one *sec*- and one *tert*-alcohol. On comparison of the ^1H- and ^{13}C-NMR data of **2** with those of 3,7-dimethyloct-3(10)-ene-1,2,6,7-tetrol (**8**, a mixture of two stereoisomers), which was also obtained from fennel,[6)] the H-5, H-6, H_3-8 and H_3-9, and C-5 to C-10 signals appeared at nearly identical chemical shifts with those of **8** (Tables 1 and 2). So, **2** was concluded to be 3,7-dimethyloct-3(10)-ene-1,6,7-triol.

Tetrol **3** ($C_{10}H_{20}O_4$, a colorless syrup, $[\alpha]_D^{23}$ −41.8°) was revealed to be an acyclic monoterpenoid with one tri-substituted double bond, two *prim*-, one *sec*- and one *tert*-alcohols by the analysis of its ^1H-, ^{13}C- and ^{13}C–^1H COSY NMR spectral data (Tables 1 and 2). From the results of a heteronuclear multiple-bond correlation (HMBC) experiment, **3** was concluded to be a 3,7-dimethyloct-6-ene-1,2,3,8-tetrol. As an NOE interaction between H-6 and H_2-8 was observed in its NOESY spectrum (Fig. 1), the double bond must be *E* configuration. Thus, **3** was characterized as (6*E*)-3,7-dimethyloct-6-ene-1,2,3,8-tetrol.

Glycoside **4** ($C_{16}H_{28}O_8$, an amorphous powder, $[\alpha]_D^{25}$ −30.0°) showed the $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 349 and 169 in the positive FAB-MS, and $[M+H]^-$ ion peak at *m*/*z* 347 in the negative FAB-MS. It had three *tert*-methyls, two methylenes (one of them was considered to be a methylene of a cyclopropane ring), two methines (one of them was oxygenated) and three quaternary carbons (two of them were oxygenated) in addition to the glucopyranosyl moiety. From an analysis of the HMBC spectrum, the planar structure shown in heavy lines (Fig. 2) was obtained from the two or three bond correlation data from the signals of the three methyl protons, the H_2-3 and H_2-6 protons, and the anomeric proton of glucose. Not only from the unsaturation degree, but also from the fact that C-1 and C-5 were quaternary and tertiary carbons respectively, the aglycone of **4** should be bonded between C-1 and C-5. So, **4** was concluded to be a glucoside of thujane-2,4,7-triol and the location of the glucosyl group was C-4. As cross peaks between H_3-9 and H-6α, H_3-9 and H-5, H_3-10 and H-6β, H_3-8 and H-2 were observed in its NOESY spectrum (Fig. 1), the aglycone of **4** should have a 7,10-*trans*-thujane form and the configuration of the 2- and 4-hydroxyl groups should be β and α, respectively. From these results, **4** was characterized as *trans*-thujane-2β,4α,7-triol 4-*O*-β-D-glucopyranoside.

Acid hydrolysis of glycoside **5** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{23}$ −10.0°) gave D-glucose as the sugar component, and its ^1H-, ^{13}C- and ^{13}C–^1H COSY NMR spectral data (Tables 1 and 2) revealed the presence of one *tert*-methyl, two *sec*-methyls, two methylenes (one of them was considered to be a methylene of a cyclopropane ring), three methines (one of them was oxygenated) and two quaternary carbons (one of them was oxygenated) in the aglycone moiety. By comparison of its ^1H- and ^{13}C-NMR data (Tables 1 and 2)

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Table 1. ^{1}H-NMR Chemical Shifts of **1**—**8** (in Pyridine-d_5, 500 MHz)

	2	**8**		**3**
H_2-1	4.05 t (7.0)	4.08 dd (7.5, 11.0)	4.08 dd (7.5, 11.0)	4.02 dd (7.5, 10.5)
	—	4.18 dd (4.0, 11.0)	4.18 dd (4.0, 11.0)	4.34 dd (3.5, 10.5)
H-2	—	4.76 dd (4.0, 7.5)	4.76 dd (4.0, 7.5)	4.16 dd (3.5, 7.5)
H_2-2	2.61 t (7.0)	—	—	—
H_2-4	2.45 ddd (6.0, 9.5, 15.0)	2.67 ddd (7.0, 10.0, 15.5)	2.51 ddd (6.0, 10.5, 15.5)	1.98 ddd (5.5, 12.0, 13.5)
	2.81 ddd (4.5, 9.5, 15.0)	2.90 ddd (4.5, 10.0, 15.5)	3.05 ddd (4.0, 10.5, 15.5)	2.07 ddd (5.5, 12.0, 13.5)
H_2-5	1.87 m	1.96 m	1.96 m	2.55 m
	2.15 m	2.24 m	2.24 m	—
H-6	3.79 dd (1.0, 10.5)	3.84 br d (9.0)	3.82 br d (9.0)	5.79 tq (1.5, 7.5)
H_2-8	—	—	—	4.30 br s
	—	—	—	—
H_3-8	1.48[a] s	1.46[a] s	1.47[a] s	—
H_3-9	1.51[a] s	1.49[a] s	1.50[a] s	1.54 s
H_2-10	*ca*. 5.02 (overlapped with H_2O)	5.21 br s	5.20 br s	—
	—	5.57 br s	5.55 br s	—
H_3-10	—	—	—	1.82 s

	1	**6**	**7**		**4**	**5**
H-3*endo*	—	2.08 br d (18.0)	—	H-2α	5.75 t (8.0)	5.24 t (8.0)
exo	—	2.31 ddd (3.5, 4.5, 18.0)	2.08 dd (5.0, 7.0)	H_2-3	1.69 dd (8.5, 13.5)	1.59 dd (8.0, 14.0)
H-4	2.55 br d (3.0)	1.96 dd (4.5, 4.5)	2.21 m		2.67 dd (8.5, 13.5)	2.80 dd (8.0, 14.0)
H-5*endo*	2.21 dddd (3.0, 3.0, 12.5, 12.5)	1.82 br dd (3.0, 13.5)	1.46 m	H-5α	2.08 dd (4.0, 8.0)	1.69 dd (4.0, 8.0)
exo	1.74 m	2.45 dddd (3.5, 4.5, 10.0, 13.5)	1.43 m	H-6α	0.99 dd (5.0, 8.0)	0.59 dd (5.0, 8.0)
H-6*endo*	1.46 m	—	1.14 m	β	1.04 dd (4.0, 5.0)	0.85 dd (4.0, 5.0)
exo	1.93 ddd (3.0, 12.5, 12.5)	4.59 br d (10.0)	1.79 ddd (5.0, 12.0, 12.0)	H-7	—	1.96 septet (6.5)
H-7a	2.23 dd (1.5, 10.5)	—	1.90 dd (2.0, 10.0)	H_3-8	1.86 s	1.26 d (6.5)
b	1.75 dd (1.5, 10.5)	—	1.69 dd (2.0, 10.0)	H_3-9	1.41 s	1.12 d (6.5)
H_3-8	1.38 s	0.70 s	—	H_3-10	1.58 s	1.56 s
H_3-9	—	0.80 s	0.96 d (7.0)	Glc-1	5.19 d (7.5)	5.06 d (7.5)
H_2-9	3.94 d (11.0)	—	—			
	3.98 d (11.0)	—	—			
H_3-10	—	1.14 s	—			
H_2-10	4.01 d (11.5)	—	3.86 d (10.5)			
	4.34 d (11.5)	—	4.58 d (10.5)			
Glc-1	—	4.83 d (7.5)	4.86 d (8.0)			

δ in ppm from TMS [coupling constants (J) in Hz are given in parentheses]. *a*) Assignments may be interchanged.

with those of **4**, and by the analysis of HMBC (Fig. 2) and ^{1}H–^{1}H COSY correlation data, the planar structure of **5** was obtained. So, **5** was considered to be a 7-deoxy derivative of **4**. As cross peaks between H_3-9 and H-6α, H_3-9 and H-5, H_3-10 and H-6β, H_3-8 and H-2 were observed in its NOESY spectrum (Fig. 2), the aglycone of **5** should be the 2β,4α-hydroxyl form of *trans*-thujane. From these results, **5** was characterized as *trans*-thujane-2β,4α-diol 4-*O*-β-D-glucopyranoside.

Glycoside **6** ($C_{16}H_{26}O_7$, an amorphous powder, $[\alpha]_D^{23}$ −8.0°) revealed the presence of three *tert*-methyls, two methylenes, two methines (one of them was oxygenated), two quaternary carbons and one carbonyl group in its ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data (Tables 1 and 2). The planar structure of **6** which is indicated in heavy lines (Fig. 2) was obtained from the results of HMBC experiments, and the NOE interactions observed in its NOESY spectrum (Fig. 1) suggested the configuration at H-6 should be *exo*. So, **6** must be 6-*O*-β-D-glucopyranoside of 6-*endo*-hydroxycamphor. The absolute configuration at C-6 was assigned as *R* since the anomeric carbon of **6** appeared at δ 103.55, in comparison with those of (2*R*,5*S*)- and (2*S*,5*R*)-forms of bornane-2,5-diol 2-*O*-β-D-glucopyranoside which appeared at δ 103.54 and δ 106.25, respectively.[8] From these facts, **6** was characterized as (1*S*,4*R*,6*R*)-6-hydroxycamphor β-D-glucopyranoside. Orihara *et al*.[9] obtained (1*S*,4*R*,6*R*)-6-hydroxycamphor β-D-glucopyranoside as a biotransformation product from a cell culture of *Eucalyptus perriniana* with (+)-camphor, and the ^{13}C-NMR data and $[\alpha]_D$ value are identical with that of **6**.[10] This is the first report of the isolation of **6** from plant sources.

Glycoside **7** ($C_{15}H_{24}O_7$, an amorphous powder, $[\alpha]_D^{23}$ −7.7°) showed the $[M+H]^+$ and $[M-C_6H_{10}O_5+H]^+$ ion peaks at *m/z* 317 and 155 in the positive FAB-MS. The ^{1}H-, ^{13}C- and ^{13}C–^{1}H COSY NMR spectral data of **7** showed the presence of one β-glucopyranosyl, one *sec*-methyl, four methylenes (one of them was oxygenated), two methines, one quaternary carbon and one carbonyl group. These data suggested that **7** was a glucoside of a normonoterpenoid. From the analysis of HMBC and ^{1}H–^{1}H COSY spectral data, the planar structure of **7** (Fig. 2) was obtained. So, **7** was concluded to be a derivative of 10-hydroxyfenchone β-D-glucopyranoside with one of the *gem*-dimethyls eliminated. The eliminated methyl group should be C-8 as cross peaks between the remaining methyl and H-5*endo*, H-3 and H-7a were observed in its NOESY spectrum (Fig. 1). So, **7** was characterized as 10-hydroxy-8-norfenchone β-D-glucopyranoside.

Table 2. ^{13}C-NMR Chemical Shifts of **1**—**8** (in Pyridine-d_5, 125 MHz)

	1	**2**	**8**		**3**
C-1	61.73	61.12	66.79	66.75	64.01
C-2	220.33	40.66	76.30	76.56	78.42
C-3	54.88	148.38	151.72	151.88	73.91
C-4	43.14	34.35	30.49	30.54	39.16
C-5	24.97	30.59	30.83	30.97	22.53
C-6	27.16	78.42	78.38	78.66	125.60
C-7	37.81	72.61	72.68	72.71	136.15
C-8	18.86	25.99	25.94	25.94	68.21
C-9	65.00	25.99	25.94	25.94	13.91
C-10	60.52	110.62	110.07	109.85	23.59

	4	**5**	**6**	**7**
C-1	42.16	38.88	62.61	59.65
C-2	72.07	74.48	214.62	218.37
C-3	46.83	45.78	43.18	49.19
C-4	84.89	85.28	41.94	39.69
C-5	30.81	32.07	35.77	22.24
C-6	9.91	9.40	82.14	28.22
C-7	70.36	31.35	48.39	39.94
C-8	28.84	20.92	20.18	—
C-9	28.25	20.67	19.98	10.96
C-10	22.89	24.09	8.14	68.71
Glc-1	99.09	99.64	103.55	105.77
Glc-2	75.43	75.26	74.61	75.21
Glc-3	78.94	78.84	78.66	78.56
Glc-4	71.77	71.93	71.57	71.63
Glc-5	78.23	78.18	78.54	78.60
Glc-6	62.91	63.03	62.95	62.74

δ in ppm from TMS.

The compounds **1**—**5** and **7** are new, and this is the first report of the isolation of thujane-type monoterpenoid glycosides.

Experimental

The CD spectrum was recorded with a JASCO J-600 spectropolarimeter at 22 °C. The other instruments used and the experimental conditions for the spectral data and for chromatography were the same as in the preceding paper.[1)]

Extraction and Isolation of 1—7 As reported in the previous paper, commercial fennel (2.0 kg) was extracted with methanol. The methanol extract (329.4 g) was suspended in water and extracted with ether and ethyl acetate, respectively. The aqueous portion was subjected to Amberlite XAD-II ($H_2O \rightarrow$MeOH), and 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_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 $C_{3\text{-}3}$ was subjected to HPLC [octadecyl silica (ODS), MeOH–H_2O (3 : 37)] to give four fractions (frs. $C_{3\text{-}3\text{-}1}$—$C_{3\text{-}3\text{-}4}$). Fraction $C_{3\text{-}3\text{-}3}$ was chromatographed over silica gel [$CHCl_3$–MeOH (20 : 1)] to give **1** (11 mg). Fraction $C_{3\text{-}5}$ was subjected to HPLC [ODS, MeOH–H_2O (1 : 3)] and then silica gel [$CHCl_3$–MeOH (20 : 1)] to give **2** (3 mg). Fraction C_5 (1.3 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 $C_{5\text{-}3}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (97 : 3)] to give **3** (2 mg). Fraction $C_{5\text{-}7}$[11)] was acetylated with Ac_2O and pyridine, and the acetylated fraction was 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 $C_{5\text{-}7\text{-}1}$ was deacetylated by heating in a water bath with 5% NH_4OH–MeOH for 2 h to give **7** (3 mg) in pure form. 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 $C_{5\text{-}9\text{-}3}$ was **6** (5 mg) in pure form. Fraction C_7 (0.7 g) was subjected to a Lobar RP-8 column [CH_3CN–H_2O (1 : 10$\rightarrow$3 : 17)] to give ten fractions (frs. $C_{7\text{-}1}$—$C_{7\text{-}10}$). Fraction $C_{7\text{-}7}$ was subjected to HPLC [carbohydrate analysis, CH_3CN–H_2O (14 : 1)] to give two fractions (frs. $C_{7\text{-}7\text{-}1}$ and $C_{7\text{-}7\text{-}2}$). Fraction

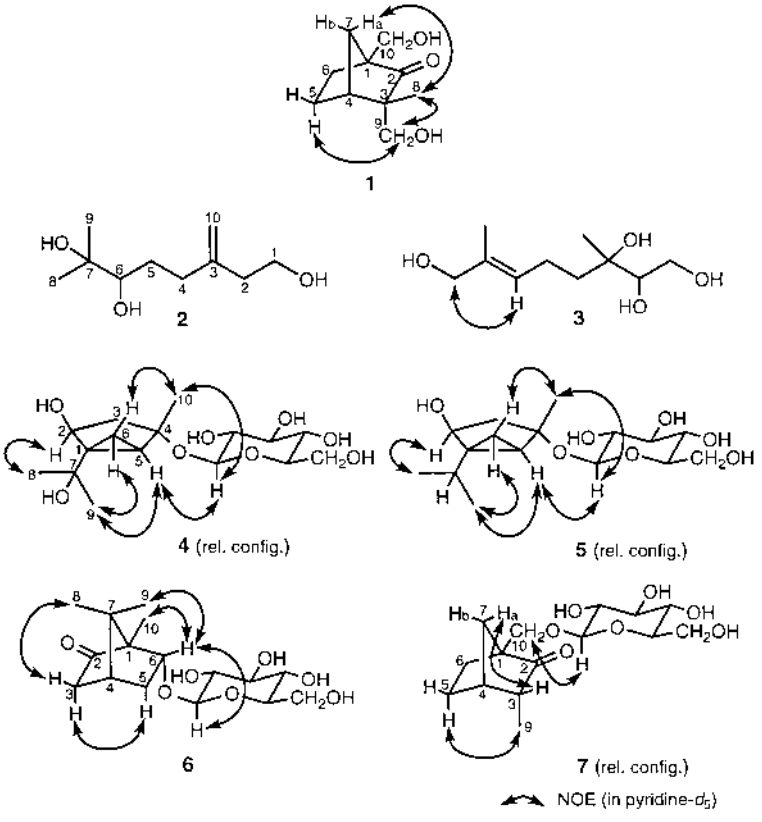

Fig. 1. Structures of **1**—**7** and NOE Interactions Observed in the NOESY Spectra of **1**, **3**—**7**

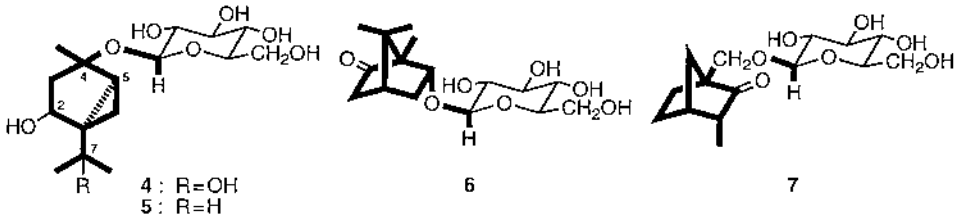

Fig. 2. Partial Structures of **4**—**7** Solved by HMBC Spectra (Heavy Lines)

$C_{7\text{-}7\text{-}1}$ was chromatographed over silica gel [$CHCl_3$–MeOH (17 : 3)] to give **5** (10 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 $C_{9\text{-}5}$[11] was acetylated with Ac_2O and pyridine, 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 $C_{9\text{-}5\text{-}3}$ was deacetylated by heating in a water bath with 10% NH_4OH–MeOH for 2 h, and then silica gel [$CHCl_3$–MeOH (17 : 3)] to give **4** (6 mg).

(1*S*,3*S*,4*R*)-9,10-Dihydroxyfenchone (1) An amorphous powder, $[\alpha]_D^{23}$ +4.6° (*c*=0.4, MeOH). Positive FAB-MS (NBA) *m/z*: 185.1159 $[M+H]^+$ (base, Calcd for $C_{10}H_{17}O_3$: 185.1177), 167 $[M-H_2O+H]^+$, 149 $[M-2H_2O+H]^+$ (base). CD: (*c*=0.0114 M, 95% EtOH) $\Delta\varepsilon$ (nm): +0.41 (288).

3,7-Dimethyloct-3(10)-ene-1,6,7-triol (2) An amorphous powder, $[\alpha]_D^{23}$ −23.0° (*c*=0.1, MeOH), $[\alpha]_D^{23}$ −30.0° (*c*=0.1, $CHCl_3$). Positive FAB-MS *m/z*: 211 $[M+Na]^+$, 189.1465 $[M+H]^+$ (Calcd for $C_{10}H_{21}O_3$: 189.1490), 171 $[M-H_2O+H]^+$ (base), 153 $[M-2H_2O+H]^+$.

(6*E*)-3,7-Dimethyloct-6-ene-1,2,3,8-tetrol (3) A colorless syrup, $[\alpha]_D^{23}$ −41.8° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 409 $[2M+H]^+$, 227 $[M+Na]^+$, 205.1451 $[M+H]^+$ (base, Calcd for $C_{10}H_{21}O_4$: 205.1440), 187 $[M-H_2O+H]^+$, 169 $[M-2H_2O+H]^+$, 151 $[M-3H_2O+H]^+$.

***trans*-Thujane-2β,4α,7-triol 4-*O*-β-D-Glucopyranoside (4)** An amorphous powder, $[\alpha]_D^{25}$ −30.0° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 697 $[2M+H]^+$, 371.1657 $[M+Na]^+$ (base, Calcd for $C_{16}H_{28}O_8Na$: 371.1681), 349.1866 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_8$: 349.1862), 331 $[M-H_2O+H]^+$, 169 $[M-C_6H_{12}O_6+H]^+$. Negative FAB-MS *m/z*: 347 $[M-H]^-$ (base).

***trans*-Thujane-2β,4α-diol 4-*O*-β-D-Glucopyranoside (5)** An amorphous powder, $[\alpha]_D^{25}$ −10.0° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 371 $[M+K]^+$, 355.1731 $[M+Na]^+$ (Calcd for $C_{16}H_{28}O_7Na$: 355.1731), 333.1941 $[M+H]^+$ (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*S*,4*R*,6*R*)-6-Hydroxycamphor β-D-Glucopyranoside (6) An amorphous powder, $[\alpha]_D^{23}$ −8.0° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 661 $[2M+H]^+$, 353 $[M+Na]^+$, 331.1741 $[M+H]^+$ (base, Calcd for $C_{16}H_{27}O_7$: 331.1757), 169 $[M-C_6H_{10}O_5+H]^+$.

10-Hydroxy-8-norfenchone β-D-Glucopyranoside (7) An amorphous powder, $[\alpha]_D^{23}$ −7.7° (*c*=0.1, MeOH). Positive FAB-MS *m/z*: 409 $[M+H+glycerol]^+$, 339 $[M+Na]^+$, 317.1595 $[M+H]^+$ (Calcd for $C_{15}H_{25}O_7$: 317.1600), 155 $[M-C_6H_{10}O_5+H]^+$ (base).

Acid Hydrolysis of 5 Compound **5** (5 mg) was dissolved in aq. 2 N H_2SO_4 and heated in a water bath for 3 h. The reaction mixture of hydrolysate was 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 was subjected to HPLC [column, carbohydrate analysis (3.9×300 mm); detector, JASCO OR-990 chiral detector; solv., CH_3CN–H_2O (17 : 3), 2 ml/min]; t_R 4.55 min (D-glucose, identical with standard sample).

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

References and Notes

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10) All reported ^{1}H-chemical shifts of **6** were about 0.13 ppm downfield from our data.
11) No acetoxyl group was detectable by NMR spectral data for these fractions.