Water-Soluble Constituents of Dill

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From the water-soluble portion of the methanol extract of dill (fruit of *Anethum graveolens* L.), which has been used as a spice and medicine, thirty-three compounds, including a new monoterpenoid, six new monoterpenoid glycosides, a new aromatic compound glucoside and a new alkyl glucoside were obtained. Their structures were clarified by spectral investigation.

Key words dill; *Anethum graveolens* fruit; *p*-menthane glucoside; tetrahydrocarvone; phenylpropanoid glucoside; alkyl glucoside

Dill [*Anethum graveolens* L.; Umbelliferae] has been cultivated in Europe since antiquity and used as a popular aromatic herb and spice. Its fruit has also been used for medicinal purposes in the relief of digestive problems and to stimulate milk for nursing mothers.[1] Dill water was believed to have a soothing effect on the digestive system and was given to babies to relieve hiccups and colic. The fruit contains essential oil (3—4%) rich in *d*-carvone (main; 50—60%), and *trans*- and *cis*-dihydrocarvone, *trans*- and *cis*-carveol, limonene, *d*-dihydrocarveol, *l*-dihydrocarveol, α- and γ-terpinene, α-phellandrene, β-terpineol, terpinene-4-ol *p*-cymene, thymol, carvacrol *et al.* were reported as other constituents.[2] However, only dillanoside has been published as a constituent of the water-soluble portion of this fruit.[3] In continuation of our studies on the water-soluble constituents of spices,[4] and to show the relationship between the essential oil and the water-soluble constituent, we undertook a detailed investigation of this fruit. In this paper, we discuss the isolation and structure elucidation of monoterpenoids, monoterpenoid glycosides, aromatic compound glycosides, alkyl glycosides, glucides and nucleosides.

The commercial dill was extracted with 70% methanol, and the methanolic extract was suspended in water and successively extracted with ether and ethyl acetate. The aqueous layer was chromatographed on Amberlite XAD-II to give water and methanol eluate fractions. These fractions were chromatographed on Sephadex LH-20, and subjected to a combination of silica gel, Lobar RP-8 column chromatography and HPLC to separate monoterpenoid ketodiols (**1** to **2**), monoterpenoid glycosides (**3** to **10**) and aromatic compound glycosides (**11** to **17**) from the methanol eluate fraction, and three alkyl glycosides (**18** to **20**), eleven glucides (**21** to **31**) and two nucleosides (**32**, **33**) from the water eluate fraction. Among them, **2**—**4**, **6**—**8**, **10**, **11** and **18** are new compounds. All new glucosides described in this paper were β-D-glucopyranosides as shown by their ^{1}H- and ^{13}C-NMR data (Tables 1, 2 and Experimental), and this was confirmed by hydrolysis to yield D-glucose or comparison of the $[\alpha]_D$ or $[M]_D$ values with those of their aglycones.[5] Their molecular formulae were suggested from the accurate mass number of the $[M+H]^+$ or $[M+Na]^+$ ion peak in the high-resolution positive FAB-MS.

Monoterpenoid ketodiol **1** ($C_{10}H_{16}O_3$, an amorphous powder, $[\alpha]_D^{25}$ −7°), monoterpenoid glycoside **5** ($C_{16}H_{28}O_7$, mp 154—156 °C, $[\alpha]_D^{25}$ +13°) and **9** ($C_{16}H_{30}O_8$, an amorphous powder, $[\alpha]_D^{25}$ −46°) were identified as (4*S*,8*S*)-8,9-dihydroxy-8,9-dihydrocarvone,[4] (1*S*,2*S*,4*R*)-*p*-menth-8-ene-1,2-diol 2-*O*-β-D-glucopyranoside[6] and (1*S*,2*R*,4*R*,8*S*)-*p*-menthane-2,8,9-triol 2-*O*-β-D-glucopyranoside,[6] respectively, by direct comparison with authentic samples isolated from caraway.

Monoterpenoid glycoside **3** ($C_{16}H_{26}O_8$, an amorphous powder, $[\alpha]_D^{24}$ −17°) showed an $[M+H]^+$ ion peak at *m*/*z* 347 and an $[M-C_6H_{12}O_6+H]^+$ ion peak at *m*/*z* 167 in the positive FAB-MS. The glycoside **3** was hydrolyzed with hesperidinase and, from the hydrolyzed mixtures, **1** and D-glucose were obtained. Consequently, **3** was a monoglucoside of **1**. The position of the β-glucosyl unit was proved to be C-9 by the down-field glycosylation shift of the C-9 (by 8.1 ppm) signal and up-field glycosylation shift of the C-8 (by 0.7 ppm) signal, and from the observed nuclear Overhauser effect (NOE) interaction between the glucosyl H-1/H_2-9 in the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum of **3**. So, **3** was characterized as (4*S*,8*S*)-8,9-dihydroxy-8,9-dihydrocarvone 9-*O*-β-D-glucopyranoside.

Monoterpenoid ketodiol **2** ($C_{10}H_{18}O_3$, an amorphous powder, $[\alpha]_D^{21}$ −23°) showed an $[M+H]^+$ ion peak at *m*/*z* 187 and was suggested to have one *tert*-methyl, one *sec*-methyl, one hydroxymethyl, three methylenes, two methine, one oxygenated quaternary carbon and one carbonyl group by the ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2). From the analysis of heteronuclear multiple-bond correlation (HMBC) spectral data (H-1_{ax}/C-2, C-6, C-7; H-3_{ax}/C-2, C-4, C-5, C-8; H-3_{eq}/C-2, C-4, C-5; H-4_{ax}/C-5, C-8, C-10; H-5_{ax}/C-1, C-3, C-4, C-6; H-5_{eq}/C-1, C-3, C-4; H-6_{ax}/C-1, C-4, C-5, C-7; H-6_{eq}/C-1, C-2, C-4, C-5, C-7; H_3-7/C-1, C-2, C-6; H_2-9/C-4, C-10; H_3-10/C-4, C-8, C-9), **2** was suggested to be 8,9-dihydroxytetrahydrocarvone (8,9-dihydroxy-*p*-menthan-2-one). The conformation of **2** was found to be 7,8-*trans* form from the observed NOE interactions between H-1/H-3_{ax}, H-5_{ax}, and between H-4/H-6_{ax} in the NOESY spectrum. Furthermore, the 1D-NOESY spectrum of **2** showed the NOE interactions between H_2-9/H-3_{eq}, H-4_{ax}, H-5_{eq}, and between H_3-10/H-3_{ax}, H-5_{eq}, H-5_{ax} (Fig. 1), the stereochemical relationship between C-4 and C-8 was believed to be 4*S**,8*S**.[6] It was also confirmed to give a mixture of C-2 equatorial and axial forms (5 : 4) of (1*S**,4*S**,8*S**)-*p*-menthane-2,8,9-triol[6] by $NaBH_4$ reduction of **2**. The absolute configuration of the C-4 was determined to be *S* from the results of circular dichroism (CD) spectra which showed a negative Cotton effect [291 nm for ($\Delta\varepsilon$ −0.70)] the same as **1** and *d*-carvone [250 nm for **1** ($\Delta\varepsilon$ −0.48) and 260 nm for *d*-carvone ($\Delta\varepsilon$ −0.41)].[4,7] Then, **2**

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Table 1. ^{1}H-NMR Chemical Shifts of **2**—**4**, **6**, **6a**, **7**, **8**, **8a**, **10** and **10a** (in Pyridine-d_5, 500 MHz)

	2	**3**	**4**
H-1_{ax}	2.33 m	—	2.26 m
H-3_{ax}	2.63 dd (13.0, 13.0)	2.53 dd (13.0, 13.0)	2.50 dd (13.0, 13.0)
H-3_{eq}	3.12 dd (2.0, 13.0)	3.09 dd (2.0, 13.0)	2.99 ddd (1.5, 3.0, 13.0)
H-4_{ax}	2.36 dddd (3.0, 3.0, 13.0, 13.0)	2.56 m	2.29 m
H-5_{ax}	1.70 dddd (3.0, 13.0, 13.0, 13.0)	2.31 ddd (4.5, 13.0, 14.0)	1.63 dddd (3.0, 13.0, 13.0, 13.0)
H-5_{eq}	2.02 dddd (3.0, 3.0, 3.0, 13.0)	2.40 ddd (4.5, 4.5, 14.0)	1.93 m
H-6	—	6.55 br d (4.5)	—
H-6_{ax}	1.23 dddd (3.0, 13.0, 13.0, 13.0)	—	1.15 dddd (3.0, 13.0, 13.0, 13.0)
H-6_{eq}	1.99 br ddd (3.0, 6.0, 13.0)	—	1.93 m
H_3-7	1.05 d (6.5)	1.77 s	1.00 d (6.5)
H_2-9	3.88 br s	3.82 d (10.5)	3.81 d (10.0)
	—	4.22 d (10.5)	4.19 d (10.0)
H_3-10	1.42 s	1.36 s	1.37 s
Glc-1	—	4.91 d (7.5)	4.90 d (8.0)

	6	**6a**	**7**
H-2_{eq}	4.17 dd (3.0, 3.0)	4.18 dd (3.0, 3.0)	4.27 dd (3.0, 3.0)
H-3_{ax}	2.45 ddd (3.0, 13.0, 13.0)	2.49 ddd (3.0, 13.0, 13.0)	2.63 ddd (3.0, 13.0, 13.0)
H-3_{eq}	2.51 ddd (3.0, 3.0, 13.0)	2.06 ddd (3.0, 3.0, 13.0)	2.00 ddd (3.0, 3.0, 13.0)
H-4_{ax}	2.69 dddd (3.0, 3.0, 13.0, 13.0)	2.83 dddd (3.0, 3.0, 13.0, 13.0)	2.78 dddd (3.0, 3.0, 13.0, 13.0)
H-5_{ax}	2.02 dddd (3.0, 13.0, 13.0, 13.0)	2.13 dddd (3.0, 13.0, 13.0, 13.0)	2.31 dddd (3.0, 13.0, 13.0, 13.0)
H-5_{eq}	1.61 m	1.70 m	1.67 dddd (3.0, 3.0, 3.0, 13.0)
H-6_{ax}	2.05 ddd (3.0, 13.0, 13.0)	2.24 ddd (3.0, 13.0, 13.0)	2.10 ddd (3.0, 13.0, 13.0)
H-6_{eq}	1.77 ddd (3.0, 3.0, 13.0)	1.85 ddd (3.0, 3.0, 13.0)	2.13 ddd (3.0, 3.0, 13.0)
H_3-7	1.80 s	1.78 s	1.80 s
H-9a	4.78 br s	4.81 br s	4.74 br s
H-9b	4.93 br s	4.92 br s	4.86 br s
H_3-10	1.79 s	1.70 s	1.72 s
Glc-1	4.97 d (8.0)	—	5.19 d (7.5)
Api-1	5.77 d (2.0)	—	—

	8	**8a**	**10**	**10a**
H-1_{eq}	2.49 m	2.28 m	—	—
H-2_{ax}	4.34 dd (4.5, 4.5, 11.0)	4.10 dd (4.0, 4.0, 11.0)	—	—
H-2_{eq}	—	—	4.21 dd (3.0, 3.0)	4.26 dd (3.0, 3.0)
H-3_{ax}	1.91 br ddd (11.0, 12.5, 12.5)	1.94 ddd (11.0, 12.0, 12.0)	2.34 ddd (3.0, 13.0, 13.0)	2.43 ddd (3.0, 12.5, 12.5)
H-3_{eq}	2.53 ddd (3.5, 4.5, 12.5)	2.48 ddd (3.5, 4.0, 12.0)	2.81 ddd (3.0, 3.0, 13.0)	2.36 ddd (3.0, 3.0, 12.5)
H-4_{ax}	1.92 br dd (12.5, 12.5)	2.06 dddd (3.5, 3.5, 12.0, 12.0)	2.42 dddd (3.0, 3.0, 13.0, 13.0)	2.48 dddd (3.0, 3.0, 12.5, 12.5)
H-5_{ax}	1.59 dddd (3.0, 12.5, 12.5, 12.5)	1.49 dddd (4.0, 12.0, 12.0, 12.0)	1.98 dddd (3.0, 13.0, 13.0, 13.0)	2.13 dddd (3.0, 12.5, 12.5, 12.5)
H-5_{eq}	1.92 m	1.65 m	1.75 ddd (3.0, 3.0, 13.0)	2.02 ddd (3.0, 3.0, 12.5)
H-6_{ax}	1.43 dddd (3.0, 3.0, 12.5, 12.5)	1.58 dddd (4.0, 4.0, 12.0, 12.0)	2.11 ddd (3.0, 13.0, 13.0)	2.27 ddd (3.0, 12.5, 12.5)
H-6_{eq}	1.60 dddd (3.0, 3.0, 3.0, 12.5)	1.67 dddd (4.0, 6.0, 12.0, 12.0)	1.85 ddd (3.0, 3.0, 13.0)	1.93 ddd (3.0, 3.0, 12.5)
H_3-7	1.22 d (7.0)	1.22 d (7.0)	1.83 s	1.69 s
H-9a	3.85 d (11.0)	3.92 d (11.0)	—	—
H-9b	3.88 d (11.0)	3.95 d (11.0)	—	—
H_3-9	—	—	1.42 s	1.44 s
H_3-10	1.38 s	1.44 s	1.36 s	1.44 s
Glc-1	5.06 d (7.5)	—	5.00 d (8.0)	—

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

was concluded to be (1*S*,4*S*,8*S*)-8,9-dihydroxytetrahydrocarvone.

Monoterpenoid glycoside **4** ($C_{16}H_{28}O_8$, an amorphous powder, $[\alpha]_D^{25}$ −28°) showed an $[M+H]^+$ ion peak at *m/z* 349 and an $[M-C_6H_{12}O_6+H]^+$ ion peak at *m/z* 169 in the positive FAB-MS. Enzymatic hydrolysis of **4** gave **2** and D-glucose, and **4** was suggested to be a monoglucoside of **2**. The position of the β-glucosyl unit of **4** was proved to be C-9 from the HMBC correlation of glucosyl H-1/C-9, and from the observed NOE interaction between the glucosyl H-1/H_2-9 in the NOESY spectrum. Therefore, **4** was characterized as (1*S*,4*S*,8*S*)-8,9-dihydroxytetrahydrocarvone 9-*O*-β-D-glucopyranoside.

Monoterpenoid glycoside **6** ($C_{21}H_{36}O_{11}$, an amorphous powder, $[\alpha]_D^{22}$ −33°) showed an $[M+H]^+$ ion peak at *m/z* 465, an $[M-C_5H_8O_4+H]^+$ ion peak at *m/z* 333 and an $[M-C_{11}H_{20}O_{10}+H]^+$ ion peak at *m/z* 153 in the positive FAB-MS. Enzymatic hydrolysis of **6** gave an aglycone (**6a**) which was identical to (1*S*,2*S*,4*R*)-*p*-menthane-8-ene-1,2-diol (aglycone of **5**),[4] and D-apiose and D-glucose were identified as sugar components. The ^{13}C-NMR spectral data of **6** showed the presence of one β-D-apiofuranosyl-(1→6)-β-D-

Table 2. ^{13}C-NMR Chemical Shifts of **1**—**10**, **6a**, **8a** and **10a** (in Pyridine-d_5, 125 MHz)

	1	**3**	**2**	**4**	**5**	**6**	**6a**
C-1	134.96	134.79	44.81	44.74	70.45 (−0.3)	70.45 (−0.3)	70.70
C-2	200.23	200.38	212.99	213.31	83.65 (+9.6)	83.92 (+9.9)	74.03
C-3	39.58	39.20	43.04	42.74	33.53 (−1.9)	33.66 (−1.7)	35.39
C-4	42.28	42.12	46.81	46.68	38.64	38.66	38.44
C-5	27.77	27.49	26.87	26.59	26.95	26.93	27.31
C-6	145.44	145.46	35.33	35.10	34.99	35.06	34.69
C-7	15.86	15.79	14.76	14.73	28.07	28.09	28.64
C-8	73.13	72.38 (−0.8)	73.54	72.89 (−0.7)	150.88	150.90	151.30
C-9	68.58	76.68 (+8.1)	68.85	77.04 (+8.2)	108.73	108.72	108.69
C-10	21.96	22.05	21.73	22.03	21.25	21.49	21.21
Glc-1		105.59		105.66	106.25	106.41	
Glc-2		75.11		75.14	75.64	75.57	
Glc-3		78.50		78.48	78.65	78.68	
Glc-4		71.55		71.55	71.74	71.83	
Glc-5		78.59		78.57	78.21	76.97	
Glc-6		62.64		62.65	62.85	68.85	
Api-1						111.12	
Api-2						77.82	
Api-3						80.52	
Api-4						75.10	
Api-5						65.85	

	7	**8**	**8a**	**9**	**10**	**10a**
C-1	78.58 (+7.9)	30.29 (−4.6)	34.91	30.32	70.18 (− 0.6)	70.82
C-2	71.54 (−2.5)	78.44 (+5.9)	72.58	78.61	85.23 (+10.7)	74.47
C-3	34.83	28.21 (−2.1)	30.29	29.15	28.95 (−2.5)	31.48
C-4	38.09	44.09	44.01	44.02	41.99	42.31
C-5	26.91	21.00	21.12	19.99	23.43	23.26
C-6	33.59 (−1.1)	30.88	31.27	30.78	35.34	34.97
C-7	23.35 (−5.3)	11.41	11.58	11.41	28.65	28.87
C-8	151.04	73.93	74.02	74.06	71.93	71.63
C-9	108.72	69.00	69.15	68.90	29.28	27.77[a)]
C-10	21.33	21.63	21.74	21.75	25.99	27.93[a)]
Glc-1	98.95	101.28		101.35	106.07	
Glc-2	75.43	75.45		75.42	75.72	
Glc-3	79.07	78.71		78.63	78.76	
Glc-4	71.97	71.73		71.75	72.19	
Glc-5	78.09	78.52		78.39	78.48	
Glc-6	63.11	62.75		62.75	63.39	

δ in ppm from TMS. $\Delta\delta$ (δ glucoside−δ aglycone) are given in parentheses. *a*) Assignments may be interchanged.

glucopyranosyl group.[8)] Comparison of the $[M]_D$ value of **6** with those of **5** ($[M]_D$ value of **6**−$[M]_D$ value of **5**=−173°)[9)] suggested that **6** was a β-D-apiofuranoside of **5**. Thus, **6** was characterized as (1*S*,2*S*,4*R*)-*p*-menth-8-ene-1,2-diol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Monoterpenoid glycoside **7** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{24}$ +7°) showed an $[M+H]^+$ ion peak at *m*/*z* 333 and an $[M-C_6H_{12}O_6+H]^+$ ion peak at *m*/*z* 153 in the positive FAB-MS. Enzymatic hydrolysis of **7** gave **6a** and D-glucose, and thus, **7** was suggested to be a monoglucoside of **6a**. The position of the β-glucosyl unit of **7** was proved to be C-1 by the down-field glycosylation shift of the C-1 (by 7.9 ppm) signal and up-field glycosylation shift of C-2, C-6 and C-7 (by 2.5, 1.1 and 5.2 ppm) signals.[10)] Therefore, **7** was characterized as (1*S*,2*S*,4*R*)-*p*-menth-8-ene-1,2-diol 1-*O*-β-D-glucopyranoside.

Monoterpenoid glycoside **8** ($C_{16}H_{30}O_8$, an amorphous powder, $[\alpha]_D^{22}$ −50°) showed an $[M+H]^+$ ion peak at *m*/*z* 351 and an $[M-C_6H_{10}O_5+H]^+$ ion peak at *m*/*z* 189 in the positive FAB-MS. Enzymatic hydrolysis of **8** gave (1*S*,2*R*,4*R*,8*R*)-*p*-menthane-2,8,9-triol (**8a**),[6)] which was isolated from caraway by us, and D-glucose. The position of attachment of the β-glucosyl unit was shown to be C-2 of **8a** from the H-C long-range correlation between the anomeric proton signal and the C-2 carbon in the HMBC spectrum. Therefore, **8** was characterized as (1*S*,2*R*,4*R*,8*R*)-*p*-menthane-2,8,9-triol 2-*O*-β-D-glucopyranoside. The glycoside **8** was the stereoisomer of **9** at C-8.

Monoterpenoid glycoside **10** ($C_{16}H_{30}O_8$, an amorphous powder, $[\alpha]_D^{21}$ +9°) showed the presence of one β-glucopyranosyl unit, three *tert*-methyls, three methylenes, two methines (one oxygenated) and two oxygenated quaternary carbons by the ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2). Analysis of the HMBC spectrum of **10** (H-2/C-3, C-4, C-6, C-7, Glc C-1; H-3_{ax}/C-1, C-2, C-4, C-5; H-3_{eq}/C-1, C-2, C-4, C-5; H-4_{ax}/C-3, C-8, C-10; H-5_{ax}/C-4, C-6; H-5_{eq}/C-1, C-3, C-4, C-6; H-6_{ax}/C-1, C-4, C-5, C-7; H-6_{eq}/C-2, C-4, C-5; H_2-7/C-1, C-2, C-6; H_3-9/C-4, C-8, C-10; H_3-10/C-4, C-8, C-9; Glc H-1/C-2) suggested that the planar structure of the aglycone was *p*-menthane-1,2,8-triol, and the glucosyl unit was attached to C-2 of the aglycone. As NOE interactions between H-4/H-6_{eq}, between H_3-7/H-2, H-6_{ax}, H-6_{eq}, between

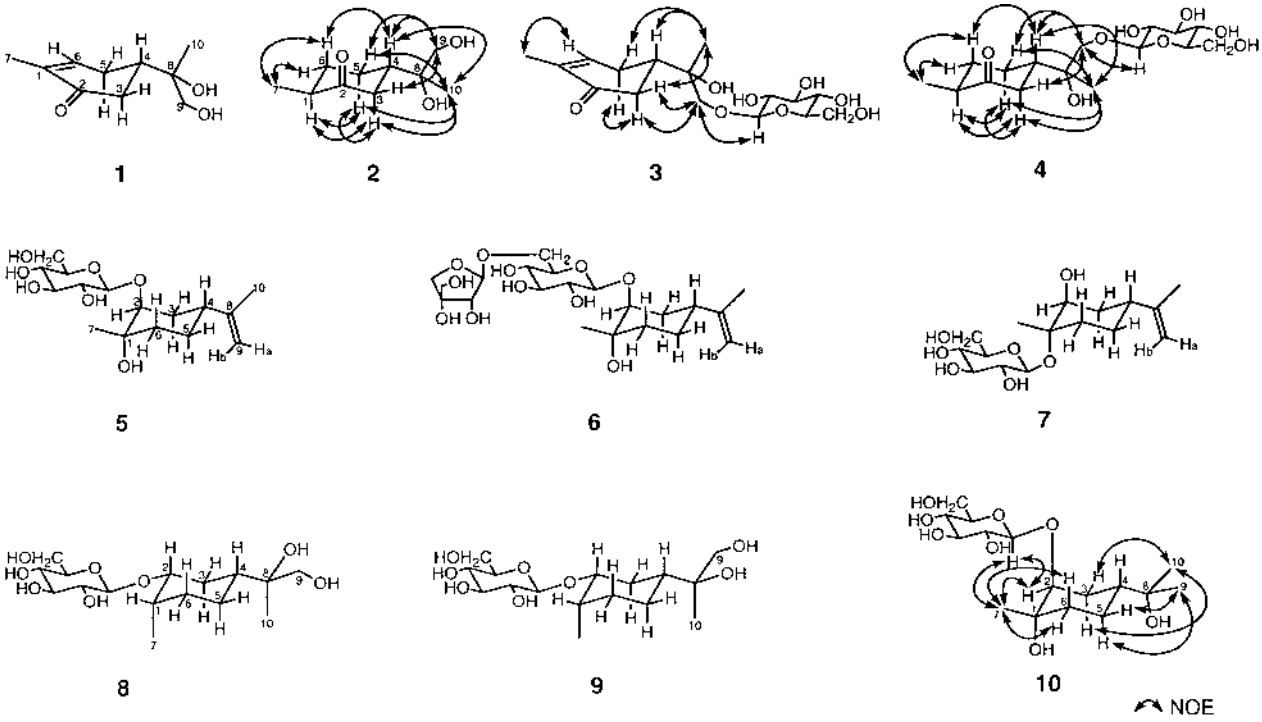

Fig. 1. Structures of **1**—**10** and NOE Correlations of **2**—**4** and **10**

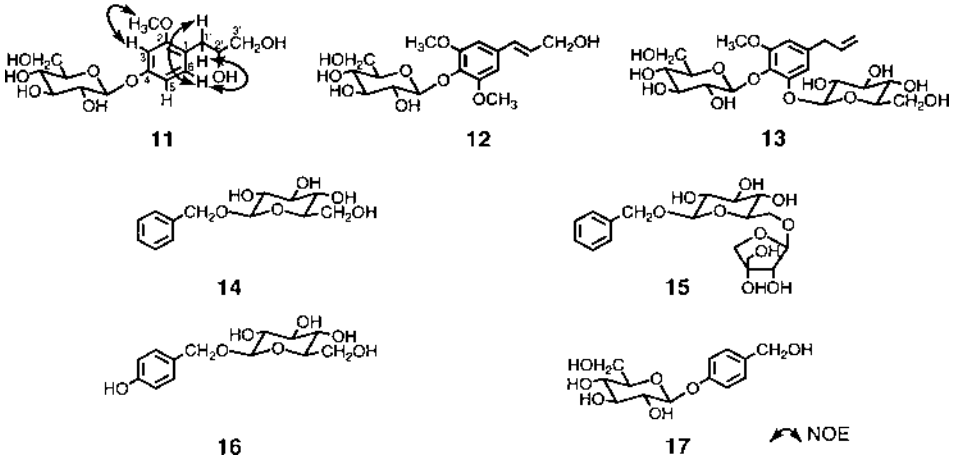

Fig. 2. Structures of **11**—**17** and NOE Correlations of **11**

H_3-9/H-5_{ax}, H-5_{eq}, and between H_3-9/H-3_{ax}, H-3_{eq} were observed in the NOESY spectrum of **10** (Fig. 1), and the H-2 signal was found as a narrow double doublet (J=3.0, 3.0 Hz), the conformation of the cyclohexane ring should be chair-form having 7—8 *trans* relation, and the configuration of C-2 hydroxyl group was axial. Enzymatic hydrolysis of **10** gave an aglycone (**10a**; $C_{10}H_{20}O_3$, an amorphous powder, $[\alpha]_D^{23}$ +25°) and D-glucose. The absolute configuration at C-2 of **10** was indicated as *S* by the values of the glycosylation shift of the α- and β-carbons [C-1 (β-pro-*S*): −0.6 ppm, C-2 (α): +10.7 ppm, C-3 (β-pro-*R*): −2.5 ppm] and the chemical shift of the anomeric carbon (δ 106.1).[10] Thus, **10** was characterized as (1*S*,2*S*,4*R*)-*p*-menthane-1,2,8-triol 2-*O*-β-D-glucopyranoside.

Aromatic compound glycosides **12**, **13**, **14**, **15**, **16** and **17** were identified as shashenoside I,[11] syringin,[12] benzyl β-D-glucopyranosides,[12] icariside F_2,[12] 4-hydroxybenzyl β-D-glucopyranosides[13] and 4-hydroxybenzyl alcohol 4-*O*-β-D-glucopyranosides,[14] respectively.

Aromatic compound glycoside **11** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{24}$ −29°) showed one peak by HPLC using ODS and Carbohydrate analysis column, but it was suggested to be an equivalent mixture of two diastereomeric compounds by NMR spectral data (see Experimental). Its positive FAB-MS showed the $[M+H]^+$ and $[M-C_6H_{10}O_5+H]^+$ ion peaks at *m*/*z* 361 and 199, and the ^{1}H- and ^{13}C-NMR data for **11** showed the presence of one β-glucopyranosyl, one 1,2,4-trisubstituted benzene, two methylenes (one oxygenated), one oxygenated methine and one methoxyl group. From the analysis of the HMBC spectrum (H-3/C-2, C-4; H-5/C-4; H-6/C-2, C-4, C-1′; H-1′a/C-1, C-2, C-6, C-2′, C-3′; H-1′b/C-1, C-2, C-6, C-2′, C-3′; O-CH_3/C-2; Glc H-1/C-4), aglycone of **11** was indicated to be 1′-(4-hydroxy-2-methoxyphenyl)propane-2′,3′-diol (an equivalent stereo-

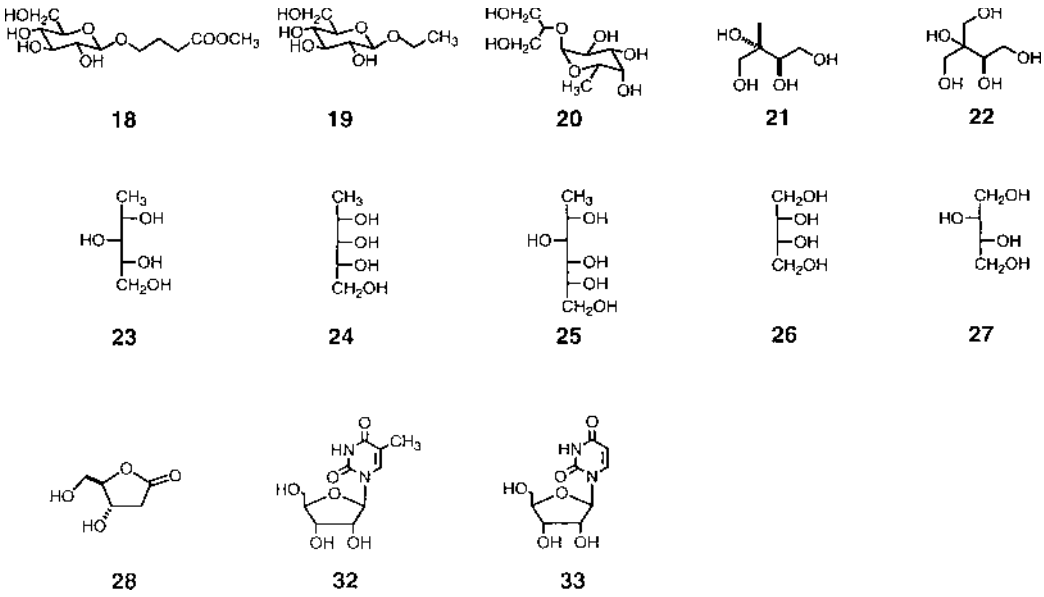

Fig. 3. Structures of **18**—**28**, **32** and **33**

isomeric mixture at C-2′), and the position of the glucosyl unit was C-4. This was also supported by the observed NOE interactions between O-CH_3/H-3 and between H_2-1′/H-6 in its NOESY spectrum (Fig. 2). Therefore, **11** was represented as an equivalent mixture of two stereoisomeric 1′-(4-hydroxy-2-methoxyphenyl)propane-2′,3′-diol 4-*O*-*β*-D-glucopyranosides.

Alkyl glycosides **19**, **20**, glucides **21**, **22**, **23**, **24**, **25**, **26**, **27**, **28**, **29**, **30**, **31**, and nucleosides **32** and **33** were identified as ethyl *β*-D-glucopyranoside,[15] glycerol 2-*O*-*α*-L-fucopyranoside,[16] 2-*C*-methyl-D-erythritol,[17] (3*R*)-2-hydroxymethylbutane-1,2,3,4-tetrol,[17] 1-deoxy-D-xylitol,[18] 1-deoxy-D-ribitol,[18] 1-deoxy-D-glucitol,[18] erythritol,[18] D-threitol,[18] 2-deoxy-D-ribono-1,4-lactone,[18] glycerol, D-glucose, D-fructose, thymidine[18] and uridine,[18] respectively.

Alkyl glucoside **18** ($C_{11}H_{20}O_8$, an amorphous powder, $[\alpha]_D^{24}$ −19°) showed $[M+H]^+$ and $[M-C_6H_{10}O_5+H]^+$ ion peaks at *m*/*z* 281 and 119 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR data for **18** showed the presence of two methylenes, one hydroxymethyl and one methoxycarbonyl group in addition to one *β*-glucopyranosyl residue. From the analysis of the HMBC spectrum (H_2-1/C-2, C-3, Glc C-1; H_2-2/C-1, C-3, C-4; H_2-3/C-1, C-2, C-4; H_3-5/C-4; Glc H-1/C-1), aglycone of **18** was indicated to be 3-(methoxycarbonyl)-propanol, and the position of the glucosyl unit was C-1. As the optical rotation of **18** showed a negative value, **18** was characterized as 3-(methoxycarbonyl)propyl *β*-D-glucopyranoside.

The ingrediential relationship between the essential oil and the water-soluble constituent was confirmed by the isolation of these monoterpenoids and glycosides which showed the biosynthetic relation to *d*-carbone.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. The CD spectra were recorded with a JASCO J-600 spectropolarimeter at 23 °C. FAB-MS were recorded with a JEOL HX-110 spectrometer using glycerol as matrix. ^{1}H- and ^{13}C-NMR spectra were taken on JEOL A-500 spectrometers with tetramethylsilane as an internal standard, and chemical shifts were recorded in δ value. ^{1}H–^{13}C COSY, HMBC, NOESY and one-dimensional (1D) NOESY spectra were obtained with the usual pulse sequence, and data processing was performed with standard JEOL software. Column chromatography (C. C.) was carried out under TLC monitoring using Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100 μm, Pharmacia), Lobar RP-8 column (Merck) and Amberlite XAD-II (Organo). TLC was performed on silica gel (Merck 5721) and spots were detected with *p*-anisaldehyde–H_2SO_4 reagent. HPLC separation was carried out with Symmetryprep C_{18} 7 μm [Waters; column size, 7.8×300 mm; ODS], carbohydrate analysis [Waters; column size, 3.9×300 mm; CHA] columns. Acetylation was done in the usual way using Ac_2O and pyridine. No acetoxyl group had been detected by NMR spectral analysis of the materials prior to acetylation.

Extraction and Separation Commercial dill (the fruit of *Anethum graveolens* L.; purchased from Asaoka Spices Ltd., Lot. No. 00011801; 2.0 kg) was extracted with 70% methanol (4 l×2), and the extract (278.0 g) was partitioned into ether–water and ethyl acetate–water, respectively. The aqueous portion (231.3 g) was chromatographed over Amberlite XAD-II (H_2O→MeOH) to give water eluate (181.1 g) and methanol eluate (50.2 g) fractions.

The methanol fraction was subjected to Sephadex LH-20 (MeOH) to give four fractions (frs. A—D). Fraction B (41.42 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1→7 : 3 : 0.5)→MeOH] to give seventeen fractions (frs. B_1—B_{17}). Fraction B_2 (1.26 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give five fractions (frs. $B_{2\text{-}1}$—$B_{2\text{-}5}$), and fr. $B_{2\text{-}2}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **1** (7 mg). Fraction $B_{2\text{-}3}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 9)] to give **2** (4 mg). Fraction B_6 (0.92 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give fourteen fractions (frs. $B_{6\text{-}1}$—$B_{6\text{-}14}$), and fr. $B_{6\text{-}2}$ was subjected to Sephadex LH-20 (MeOH) and silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to give **32** (12 mg). Fraction B_7 (3.51 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give thirteen fractions (frs. $B_{7\text{-}1}$—$B_{7\text{-}13}$), and fr. $B_{7\text{-}3}$ was passed through HPLC [CHA, MeCN–H_2O (24 : 1)] to give **18** (15 mg). Fraction $B_{7\text{-}5}$ was subjected to HPLC [CHA, MeCN–H_2O (24 : 1)] and then silica gel column chromatography [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2)] to give **13** (166 mg) and **3** (65 mg). Fraction $B_{7\text{-}7}$ (0.94 g) was passed through HPLC [ODS, MeCN–H_2O (1 : 9)] and silica gel column chromatography [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1)] to give **4** (217 mg). Fraction $B_{7\text{-}10}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 7)] to give **14** (12 mg) and **7** (8 mg). Fraction $B_{7\text{-}11}$ was subjected to HPLC [CHA, MeCN–H_2O (19 : 1)] to give **5** (118 mg). Fraction B_8 (1.35 g) was subjected to Sephadex LH-20 (MeOH) to give eight fractions (frs. $B_{8\text{-}1}$—$B_{8\text{-}8}$), and fr. $B_{8\text{-}2}$ was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] and HPLC [CHA, MeCN–H_2O (24 : 1)] to give **19** (9 mg). Fraction $B_{8\text{-}5}$ was subjected to HPLC [CHA, MeCN–H_2O (49 : 1)] to give **33** (12 mg). Fraction B_{10} (0.82 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give eight fractions (frs. $B_{10\text{-}1}$—$B_{10\text{-}8}$), and fr.

$B_{10\text{-}6}$ was subjected to HPLC [CHA, MeCN–H_2O (14 : 1)] to give **15** (9 mg). Fraction B_{12} (1.91 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give fourteen fractions (frs. $B_{12\text{-}1}$—$B_{12\text{-}14}$), and fr. $B_{12\text{-}3}$ was subjected to HPLC [CHA, MeCN–H_2O (24 : 1)] to give **17** (8 mg). Fraction $B_{12\text{-}4}$ was also subjected to HPLC [ODS, MeCN–H_2O (1 : 19)] to give **16** (5 mg), **10** (5 mg), **9** (72 mg) and **8** (12 mg), respectively. Fraction $B_{12\text{-}5}$ was passed through HPLC [ODS, MeCN–H_2O (1 : 19)], silica gel column chromatography [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2)] and then subjected to HPLC [CHA, MeCN–H_2O (9 : 1)] to give **11** (52 mg). Fraction $B_{12\text{-}6}$ was subjected to HPLC [CHA, MeCN–H_2O (14 : 1)] to give **6** (34 mg). Fraction B_{13} (0.74 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give eleven fractions (frs. $B_{13\text{-}1}$—$B_{13\text{-}11}$), and fr. $B_{13\text{-}7}$, **12** (10 mg) was isolated by HPLC [ODS, MeCN–H_2O (3 : 17)].

A part of the water eluate fraction (36.2 g) was subjected to Sephadex LH-20 (MeOH) to give four fractions (frs. E—H). Fraction G (32.0 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2→4 : 1 : 0.1→7 : 3 : 0.5)→MeOH] to give twenty-one fractions (frs. G_1—G_{21}). Fraction G_2 (0.06 g) was passed through Sephadex LH-20 (MeOH) to give **28** (32 mg). Fraction G_6 (0.13 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (1 : 99)] and HPLC [CHA, MeCN–H_2O (97 : 3)] to give **29** (82 mg). Fraction G_8 (0.50 g) was passed through a Lobar RP-8 column [MeCN–H_2O (1 : 99)] and HPLC [CHA, MeCN–H_2O (97 : 3)], and the thus-obtained glucide fraction was acetylated with Ac_2O and pyridine. The acetylated fraction was subjected to HPLC [ODS, MeOH–H_2O (9 : 11)] to give three fractions. These three fractions were deacetylated by heating in a water bath with 5% NH_4OH–MeOH for 2 h, and from these three fractions, **21** (3 mg), **23** (4 mg) and **24** (6 mg) were isolated after passing through Sephadex LH-20 (MeOH). Fraction G_{13} (0.16 g) was passed through a Lobar RP-8 column (H_2O) to give eight fractions (frs. $G_{13\text{-}1}$—$G_{13\text{-}8}$), and fr. $G_{13\text{-}6}$ was subjected to HPLC [CHA, MeCN–H_2O (97 : 3)] to give **20** (3 mg). Fraction $G_{13\text{-}2}$ was subjected to HPLC [CHA, MeCN–H_2O (97 : 3)], and the thus obtained glucide fraction was acetylated with Ac_2O and pyridine. The acetylated fraction was subjected to HPLC [ODS, MeOH–H_2O (1 : 1)] to give two fractions, and these two fractions were deacetylated by heating in a water bath with 5% NH_4OH–MeOH for 2 h. From these two fractions, **26** (46 mg) and **27** (8 mg) were isolated after passing through Sephadex LH-20 (MeOH). Fraction G_{14} (0.28 g) was passed through a Lobar RP-8 column (H_2O) and HPLC [CHA, MeCN–H_2O (97 : 3)] to give **25** (7 mg). Fraction G_8 (0.50 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (1 : 99)] and HPLC [CHA, MeCN–H_2O (97 : 3)] to give **22** (29 mg). Fraction G_{16} (0.66 g) was passed through a Lobar RP-8 column (H_2O) and HPLC [CHA, MeCN–H_2O (24 : 1)] to give **31** (115 mg) and **30** (5 mg).

The following compounds were identified by comparison with authentic compounds or published physical and spectral data. (4*S*,8*S*)-8,9-dihydroxy-8,9-dihydrocarvone (**1**), (1*S*,2*S*,4*R*)-*p*-menth-8-ene-1,2-diol 2-*O*-*β*-D-glucopyranoside (**5**), (1*S*,2*R*,4*R*,8*S*)-*p*-menthane-2,8,9-triol 2-*O*-*β*-D-glucopyranoside (**9**), shashenoside I (**12**), syringin (**13**), benzyl *β*-D-glucopyranosides (**14**), icariside F_2 (**15**), 4-hydroxybenzyl *β*-D-glucopyranosides (**16**), 4-hydroxybenzyl alcohol 4-*O*-*β*-D-glucopyranosides (**17**), ethyl *β*-D-glucopyranoside (**19**), glycerol 2-*O*-*α*-L-fucopyranoside (**20**), 2-*C*-methyl-D-erythritol (**21**), (3*R*)-2-hydroxymethylbutane-1,2,3,4-tetrol (**22**), 1-deoxy-D-xylitol (**23**), 1-deoxy-D-ribitol (**24**), 1-deoxy-D-glucitol (**25**), erythritol (**26**), D-threitol (**27**), 2-deoxy-D-ribono-1,4-lactone (**28**), glycerol (**29**), D-glucose (**30**), D-fructose (**31**), thymidine (**32**) and uridine (**33**).

(1*S*,4*S*,8*S*)-8,9-Dihydroxytetrahydrocarvone (2) An amorphous powder, $[\alpha]_D^{21}$ −23° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 373 $[2M+H]^+$, 187.1321 $[M+H]^+$ (base, Calcd for $C_{10}H_{19}O_3$; 187.1334), 169 $[M-H_2O+H]^+$, 151 $[M-2H_2O+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 2. CD: (*c*=0.0151 M, MeOH) *Δε* (nm): −0.70 (291).

$NaBH_4$ Reduction of 2 Monoterpenoid ketodiol **2** (6 mg) was dissolved in MeOH (5 ml) and stirred with $NaBH_4$ (5 mg) for 5 h at room temperature. After work-up, the residue was purified by silica gel [$CHCl_3$–MeOH (3 : 2)] to give a mixture of (1*S*,2*S*,4*S*,8*S*)- and (1*S*,2*R*,4*S*,8*S*)-*p*-menthane-2,8,9-triols (5 : 4; 5 mg).

(4*S*,8*S*)-8,9-Dihydroxy-8,9-dihydrocarvone 9-*O*-*β*-D-Glucopyranoside (3) An amorphous powder, $[\alpha]_D^{24}$ −17° (*c*=1.4, MeOH). Positive FAB-MS *m/z*: 369.1543 $[M+Na]^+$ (base, Calcd for $C_{16}H_{26}NaO_8$; 369.1526), 347 $[M+H]^+$, 167 $[M-C_6H_{12}O_6+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 2.

Enzymatic Hydrolysis of 3 A mixture of **3** (8 mg) and hesperidinase (5 mg, ICN Biomedicals Inc., Lot 72635) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was concentrated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1 and 1 : 1 : 0.1)] to afford **1** (2 mg) and a sugar fraction. The sugar fraction was passed through Sephadex LH-20 (MeOH) to give a syrup, and HPLC [carbohydrate analysis (Waters), detector; JASCO RI-930 detector and JASCO OR-990 chiral detector, solv.; MeCN–H_2O (17 : 3), 2 ml/min; t_R 4.50 min (same location as that of D-glucose)] show the presence of D-glucose.

(1*S*,4*S*,8*S*)-8,9-Dihydroxytetrahydrocarvone 9-*O*-*β*-D-Glucopyranoside (4) An amorphous powder, $[\alpha]_D^{25}$ −28° (*c*=3.5, MeOH). Positive FAB-MS *m/z*: 387 $[M+K]^+$, 371 $[M+Na]^+$ (base), 349.1865 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_8$; 349.1862), 169 $[M-C_6H_{12}O_6+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 2.

Enzymatic Hydrolysis of 4 A mixture of **4** (13 mg) and *β*-glucosidase (5 mg, TOYOBO Co., Ltd. Lot 52275) in water (5 ml) was shaken in a water bath at 37 °C for 30 d. The mixture was treated in the same way as described for **3** to afford **2** (6 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **3**.

(1*S*,2*S*,4*R*)-*p*-Menthane-8-ene-1,2-diol 2-*O*-*β*-D-Apiofuranosyl-(1→6)-*β*-D-glucopyranoside (6) An amorphous powder, $[\alpha]_D^{22}$ −33° (*c*=0.8, MeOH). Positive FAB-MS *m/z*: 503 $[M+K]^+$, 487 $[M+Na]^+$, 465.2340 $[M+H]^+$ (base, Calcd for $C_{21}H_{37}O_{11}$; 465.2335), 333 $[M-C_5H_8O_4+H]^+$, 153 $[M-C_{11}H_{20}O_{11}+H]^+$. ^{1}H-NMR (pyridine-$d_5$, 500 MHz) *δ*: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 2.

Enzymatic Hydrolysis of 6 A mixture of **6** (15 mg) and *β*-glucosidase (5 mg, TOYOBO Co., Ltd. Lot 52275) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was treated in the same way as described for **2** to afford (1*S*,2*S*,4*R*)-*p*-menthane-8-ene-1,2-diol (**6a**; 4 mg) and a sugar fraction. The sugar fraction was passed through Sephadex LH-20 (MeOH) to give a syrup, and HPLC [carbohydrate analysis (Waters), detector; JASCO RI-930 detector and JASCO OR-990 chiral detector, solv.; MeCN–H_2O (9 : 1), 2 ml/min; t_R 7.9 min (same location as that of D-apiose)] and t_R 10.6 min (same location as that of D-glucose)] show the presence of D-apiose and D-glucose.

(1*S*,2*S*,4*R*)-*p*-Menth-8-ene-1,2-diol 1-*O*-*β*-D-Glucopyranoside (7) An amorphous powder, $[\alpha]_D^{24}$ +7° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 371 $[M+K]^+$, 355 $[M+Na]^+$, 333.1909 $[M+H]^+$ (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}H-NMR (pyridine-d_5, 500 MHz) *δ*: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 2.

Enzymatic Hydrolysis of 7 A mixture of **7** (6 mg) and *β*-glucosidase in water (5 ml) was shaken in a water bath at 37 °C for 14 d. The mixture was treated in the same way as described for **3** to afford **6a** (2 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **3**.

(1*R*,2*R*,4*R*,8*R*)-*p*-Menthane-2,8,9-triol 2-*O*-*β*-D-Glucopyranoside (8) An amorphous powder, $[\alpha]_D^{22}$ −50° (*c*=0.2, MeOH). Positive FAB-MS *m/z*: 389 $[M+K]^+$, 373 $[M+Na]^+$, 351.2033 $[M+Na]^+$ (base, Calcd for $C_{16}H_{31}O_8$; 351.2019), 315 $[M-2H_2O+H]^+$, 189 $[M-C_6H_{10}O_5+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 2. HMBC Correlations: H-1_{eq}/C-2, C-5; H-2_{ax}/C-3, C-7, Glc-1; H-3_{ax}/C-1, C-2, C-4; H-3_{eq}/C-1, C-2, C-5; H-5_{ax}/C-3, C-4; H-5_{eq}/C-4; H-6_{ax}/C-2, C-7; H-6_{eq}/C-2, C-4; H_2-7/C-1, C-2, C-6; H_3-9/C-4, C-8, C-10; H_3-10/C-4, C-8, C-9; Glc H-1/C-2.

Enzymatic Hydrolysis of 8 A mixture of **8** (4 mg) and *β*-glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was treated in the same way as described for **3** to afford (1*S*,2*R*,4*R*,8*R*)-*p*-menthane-2,8,9-triol (**8a**; 1 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **3**.

(1*S*,2*S*,4*R*)-*p*-Menthane-1,2,8-triol 2-*O*-*β*-D-Glucopyranoside (10) An amorphous powder, $[\alpha]_D^{21}$ +9° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 351.2004 $[M+H]^+$ (Calcd for $C_{16}H_{31}O_8$; 351.2045), 333 $[M-H_2O+H]^+$ (base), 171 $[M-C_6H_{12}O_6+H]^+$). ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 2.

Enzymatic Hydrolysis of 10 A mixture of **10** (4 mg) and *β*-glucosidase in water (3 ml) was shaken in a water bath at 37 °C for 14 d. The mixture was treated in the same way as described for **3** to afford **10a** (1 mg) and a sugar fraction. From the sugar fraction, D-glucose was detected as described for **3**.

(1*S*,2*S*,4*R*)-*p*-Menthane-1,2,8-triol (10a) An amorphous powder, $[\alpha]_D^{23}$ +25° (*c*=0.1, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: 4.26 (1H, dd, *J*=3.0, 3.0 Hz, H-2_{eq}), 2.43 (1H, ddd, *J*=3.0, 12.5, 12.5 Hz, H-3_{ax}), 2.36 (1H, ddd, *J*=3.0, 3.0, 12.5 Hz, H-3_{eq}), 2.48 (1H, dddd, *J*=3.0, 3.0, 12.5, 12.5 Hz, H-4_{ax}), 2.12 (1H, dddd, *J*=3.0, 12.5, 12.5, 12.5 Hz, H-5_{ax}), 2.02 (1H, ddd, *J*=3.0, 3.0, 12.5 Hz, H-5_{eq}), 2.27 (1H, ddd, *J*=3.0, 12.5, 12.5 Hz,

H-6_{ax}), 1.93 (1H, ddd, J=3.0, 3.0, 12.5 Hz, H-6_{eq}), 1.73 (3H, s, H_3-7), 1.44 (6H, s, H_3-9, -10). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

1′-(4-Hydroxy-2-methoxyphenyl)propane-2′,3-diol 4-*O*-β-D-Glucopyranoside (11) An amorphous powder, $[\alpha]_D^{24}$ −29° (c=1.1, MeOH). Positive FAB-MS m/z: 399 $[M+K]^+$, 361.1519 $[M+H]^+$ (Calcd for $C_{16}H_{25}O_9$; 361.1499), 199 $[M-C_6H_{10}O_5+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 5.88 (1H, d, J=2.0 Hz, H-3), 5.87 (1H, dd J=2.0, 8.0 Hz, H-5), 6.83 (1H, d, J=8.0 Hz, H-6), 3.08, 3.27 (each 1H, dd, J=6.0, 13.5 Hz, H_2-1′), 4.43 (1H, m, H-2′), 4.05 (2H, m, H_2-3), 3.96 (3H, s, 2-*O*-CH_3), 6.09 (1H, d, J=7.5 Hz, Glc H-1); stereoisomeric compound [5.88 (1H, d, J=2.0 Hz, H-3), 5.87 (1H, dd J=2.0, 8.0 Hz, H-5), 6.83 (1H, d, J=8.0 Hz, H-6), 3.14, 3.24 (each 1H, dd, J=6.0, 13.5 Hz, H_2-1′), 4.43 (1H, m, H-2′), 4.04 (2H, m, H_2-3), 3.95 (3H, s, 2-*O*-CH_3), 6.09 (1H, d, J=7.5 Hz, Glc H-1)]. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 126.5 (C-1), 145.0 (C-2), 101.5 (C-3), 135.6 (C-4), 101.5 (C-5), 104.3 (C-6), 35.1 (C-1′), 73.5 (C-2′), 67.2 (C-3′), 61.3 (2-*O*-CH_3), 102.6 (Glc-1), 75.5 (Glc-2), 78.7 (Glc-3), 71.4 (Glc-4), 79.0 (Glc-5), 62.4 (Glc-6); stereoisomeric compound [126.4 (C-1), 144.9 (C-2), 101.5 (C-3), 135.6 (C-4), 101.5 (C-5), 104.3 (C-6), 35.1 (C-1′), 73.4 (C-2′), 67.0 (C-3′), 61.3 (2-*O*-CH_3), 102.6 (Glc-1), 75.5 (Glc-2), 78.7 (Glc-3), 71.4 (Glc-4), 79.0 (Glc-5), 62.4 (Glc-6)].

3-(Methoxycarbonyl)propyl β-D-Glucopyranoside (18) An amorphous powder, $[\alpha]_D^{24}$ −19° (c=0.4, MeOH). Positive FAB-MS m/z: 561 $[2M+H]^+$, 303 $[M+Na]^+$, 281.1229 $[M+H]^+$ (Calcd for $C_{11}H_{21}O_8$; 281.1236), 153 $[M-C_6H_{10}O_5+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.72, 4.10 (each 1H, ddd, J=6.5, 6.5, 10.5 Hz, H_2-1), 2.01 (2H, dq J=6.5, 7.5 Hz, H_2-2), 3.91 (2H, t, J=7.5 Hz, H_2-3), 3.55 (3H, s, H_3-5), 4.81 (1H, d, J=7.5 Hz, Glc H-1). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 68.6 (C-1), 25.7 (C-2), 30.9 (C-3), 173.8 (C-4), 51.3 (C-5), 104.7 (Glc-1), 75.2 (Glc-2), 78.6 (Glc-3), 71.7 (Glc-4), 78.5 (Glc-5), 62.8 (Glc-6).

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