Five New Monoterpene Glycosides and Other Compounds from Foeniculi Fructus (Fruit of *Foeniculum vulgare* MILLER)

Masateru ONO,*[,a] Yasuyuki ITO,[a] Thoru ISHIKAWA,[b] Junichi KITAJIMA,[b] Yasuko TANAKA,[b] Yujiro NIIHO,[c] and Toshihiro NOHARA[d]

Faculty of Research Institute of General Education, Kyushu Tokai University,[a] Choyo 5435, Aso, Kumamoto 869–14, Japan, Showa College of Pharmaceutical Sciences,[b] Higashi Tamagawa Gakuen 3–3165, Machida, Tokyo 154, Japan, Tsukuba Research Institute, Ohta's Isan Co., Ltd.,[c] Shishiko 957, Ushiku, Ibaraki 300–12, Japan, and Faculty of Pharmaceutical Sciences, Kumamoto University,[d] Oe-honmachi 5–1, Kumamoto 862, Japan.

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Five new monoterpene glycosides, foeniculosides V, VI, VII, VIII and IX, were isolated from Foeniculi Fructus (fruit of *Foeniculum vulgare* MILLER) along with seven known compounds, zizybeoside I, icaviside A_4, syringin, sinapyl alcohol 1,3′-di-*O*-β-D-glucopyranoside, adenosine, *threo*-anethole glycol and *erythro*-anethole glycol. The structures of foeniculosides V, VI, VII, VIII and IX were characterized as β-D-glucopyranosides of (1*S*,2*R*,4*S*)-2,4-dihydroxy-1,8-cineole-2-*O*-, (1*R*,4*R*,6*R*)-4,6-dihydroxy-1,8-cineole-6-*O*-, (1*R*,4*R*,6*R*)-4,6-dihydroxy-1,8-cineole-4-*O*-, (1*S*,2*R*,4*R*,6*S*)-2,6-dihydroxy-1,8-cineole-2-*O*- and (1*S*,2*R*,4*S*,5*R*)-2,5-dihydroxy-1,8-cineole-2-*O*-, respectively, on the basis of chemical and spectroscopic data.

Key words *Foeniculum vulgare*; monoterpene glucoside; 1,8-cineole; foeniculoside; Umbelliferae; Foeniculi Fructus

Foeniculum vulgare MILLER (Umbelliferae) is widely cultivated worldwide, and its fruit (Foeniculi Fructus) is used as flavoring, spice and in folk medicine.[1)]

We earlier reported[2)] the isolation and structure elucidation of four new glycosides of *cis*-miyabenol C, called foeniculosides I—IV, as well as two known compounds, miyabenol C and *cis*-miyabenol C from Foeniculi Fructus. The present paper describes the further isolation and structure elucidation of five new monoterpene glycosides (**1**—**5**) and seven other known compounds (**6**—**12**) from this fruit.

The fractions reported previously[2)] were subjected successively to silica gel column chromatography, Sephadex LH 20 column chromatography and high performance liquid chromatography (HPLC) on octadecyl silica (ODS) and silica gel to give twelve compounds (**1**—**12**).

Compound **1**, called foeniculoside V, was obtained as a white powder, $[\alpha]_D$ −56.9°, and it exhibited an $[M+Na]^+$ ion peak at *m/z* 371 together with a fragment ion peak at *m/z* 187 $[M+H-\text{hexose}]^+$ in the positive FAB-MS; the high-resolution (HR) positive FAB-MS indicated the molecular formula of **1** to be $C_{16}H_{28}O_8$. The ^{13}C-NMR spectrum of **1** showed the signals of three quaternary carbons (δ 77.5, 71.6, 69.5), one methine carbon (δ 76.7), three methylene carbons (δ 39.5, 32.1, 30.4) and three methyl carbons (δ 25.9, 25.0, 23.4) along with the signals of six glucopyranosyl carbons (δ 101.4, 74.7, 78.6, 71.9, 78.7, 63.1),[3)] suggesting **1** to be a mono-

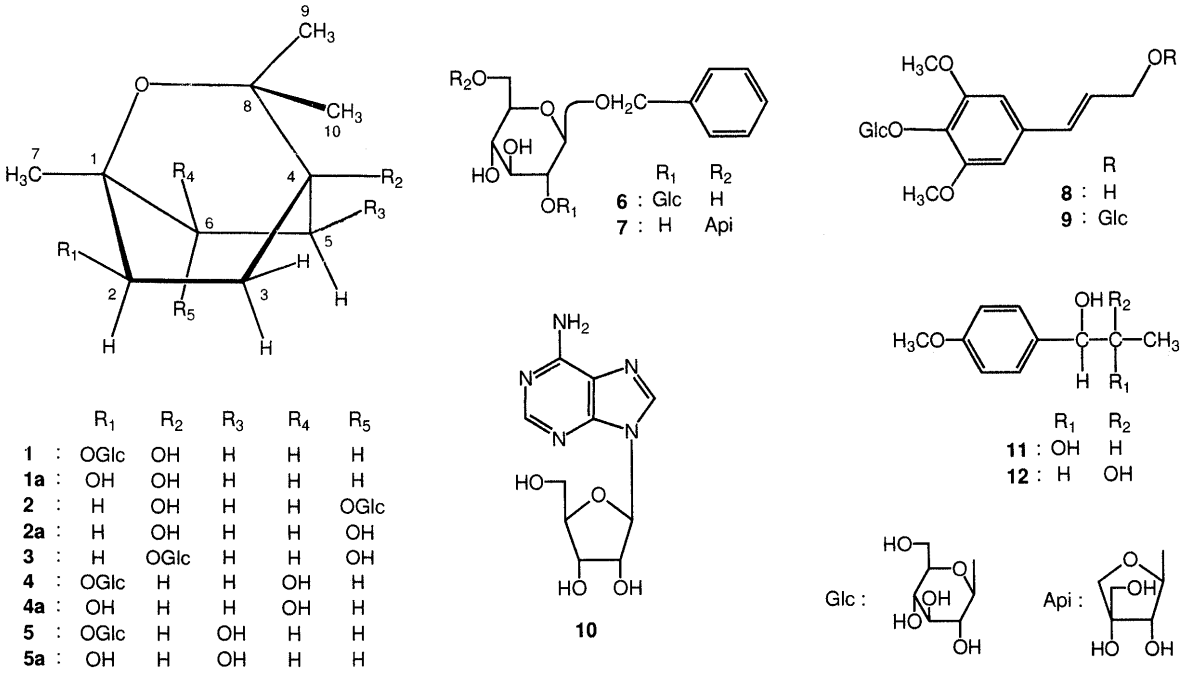

Fig. 1. Structures of **1**—**12**

* To whom correspondence should be addressed.

terpene glucoside. In the ^{1}H-NMR spectrum of **1**, the coupling constant of anomeric proton signal (δ 5.02, d, $J=7.7$ Hz) indicated the mode of glycosidic linkage of glucose (Glc) unit to be β.

Enzymatic hydrolysis of **1** with β-glucosidase from Almonds gave an aglycone (Ag) (**1a**) and Glc which was identified as D-form on the basis of gas chromatographic (GC) analysis according to Hara *et al.*[4]

The ^{1}H-NMR spectrum of **1a** exhibited the signals of two hydroxyl protons (δ 6.16, 5.93), one oxymethine proton (δ 4.02), six methylene protons (δ 2.58, 2.40, 2.25, 2.00, 1.75, 1.68) and three methyl groups (δ 1.74, 1.59, 1.38), and the ^{13}C-NMR spectrum showed ten signals (δ 77.5, 72.7, 72.1, 69.5, 43.4, 31.9, 30.7, 26.0, 25.1, 23.1), indicating **1a** to be a cineole type monoterpenoide. Further, **1a** was identified as 2β,4-dihydroxy-1,8-cineole by comparison of its ^{1}H- and ^{13}C-NMR data with those of a synthetic sample.[5]

To identify the location of the sugar linkage and the absolute configuration of Ag, the ^{1}H- and ^{13}C-NMR signals in **1** and **1a** were assigned with the aid of ^{1}H–^{1}H shift correlated 2D-NMR (COSY), nuclear Overhauser effect (NOE) difference, ^{1}H–^{13}C heteronuclear shift correlated 2D-NMR (HETCOR) and ^{1}H-detected heteronuclear multiple-bond multiple-quantum coherence (HMBC) (J_{C-H}, 10 Hz) spectra.

In the NOE difference spectrum, irradiation of the signal of anomeric proton gave enhancements of the signals of 2-H and 3-H$_\beta$ of Ag, and the HMBC spectrum showed the cross peak between anomeric proton and 2-C of Ag. Further, in the ^{13}C-NMR spectrum, glycosylation shifts[3] were observed at 1-C, 2-C and 3-C of Ag by -1.1, $+4.6$ and -3.9 ppm, respectively, in comparison with that of **1a**. These data indicated that Glc was attached to 2-C of Ag.

Kasai *et al.*[3] reported that the values of glycosylation shift of α-, β-(pro-*S* side) and β'-(pro-*R* side) carbons of secondary alcohols to which β-D-glucopyranose was attached, and anomeric carbon reflect the absolute configuration of the alcohols, and the α-carbon, β-methylene carbon and β'-quaternary carbon to *R*-alcohols showed the glycosylation shifts by *ca.* $+6$—$+8$, -3.7——4.9 and -0.6——0.8 ppm, respectively; in contrast, the α-carbon, β'-methylene carbon and β-quaternary carbon to the *S*-alcohols indicated the glycosylation shifts by *ca.* $+10$—$+11$, -1.2——2.2 and $+0.3$ ppm, respectively. It was further reported that the chirality at 2-C of the 2-*O*-β-D-glucopyranosides of (1*S*,2*S*,4*R*)-2-hydroxy-1,8-cineole and its enantiomer were determined by this empirical rule.[6] From the above evidence, the absolute configuration at 2-C of **1a** was determined to be *R*. Consequently, the structure of **1** was defined as (1*S*,2*R*,4*S*)-2,4-dihydroxy-1,8-cineole-2-*O*-β-D-glucopyranoside.

Compound **2**, called foeniculoside VI, was obtained as a white powder, $[\alpha]_D$ $-59.5°$, and its positive FAB-MS was quite similar to that of **1**, indicating an $[M+Na]^+$ ion peak at *m/z* 371. The ^{1}H- and ^{13}C-NMR spectra of **2** showed the signals due to the β-glucopyranoside of cineole type monoterpenoide.

On enzymatic hydrolysis, **2** furnished **2a** and D-Glc. Compound **2a** was identical with 2 (or 6) α,4-dihydroxy-1,8-cineole, by comparison of ^{1}H- and ^{13}C-NMR data with those of an authentic sample, which was a possum urinary metabolite of 1,8-cineole.[5] The proton and carbon signals in ^{1}H- and ^{13}C-NMR spectra of **2** and **2a** were assigned as shown in Tables 1 and 2. In comparing the chemical shifts of ^{13}C-NMR signals between **2** and **2a**, the signals of 1-C, 5-C and 6-C of Ag showed the glycosylation shift[3] by -1.6, -3.5 and $+5.7$ ppm, respectively. Therefore, the glycosidic linkage is located at 6-C of Ag, and the absolute configuration at 6-C is *R*. Accordingly, the structure of **2** was concluded to be (1*R*,4*R*,6*R*)-4,6-dihydroxy-1,8-cineole-6-*O*-β-D-glucopyranoside.

Compound **3**, called foeniculoside VII, $[\alpha]_D$ $-15.6°$, a white powder, showed the same $[M+Na]^+$ ion peak as those of **1** and **2** at *m/z* 371 in the positive FAB-MS, and the ^{1}H- and ^{13}C-NMR spectra were similar to those of **1** and **2**. Further, enzymatic hydrolysis of **3** gave **2a** and D-Glc. These data suggested **3** to be a positional isomer of **2** with Glc situated at 4-C of Ag. This suggestion was confirmed by the NOE difference spectra and ^{13}C-NMR data comparison with those of **2a**. In the NOE difference spectra, irradiations of the signals of 10-H$_3$ and 3-H$_\beta$ of Ag gave NOE enhancements of the signal of anomeric proton, respectively, and irradiation of the signal of anomeric proton showed NOE of the signal of 3-H$_\alpha$ and/or 5-H$_\alpha$ of Ag. Moreover, the ^{13}C-NMR spectrum of **3** exhibited, in comparison with that of **2a**, the glycosylation shift[3] by $+7.2$ ppm at 4-C of Ag. Consequently, the structure of **3** was concluded to be (1*R*,4*R*,6*R*)-4,6-dihydroxy-1,8-cineole-4-*O*-β-D-glucopyranoside.

Compound **4**, called foeniculoside VIII, $[\alpha]_D$ $-34.9°$, a white powder, showed an $[M+Na]^+$ ion peak at *m/z* 371, being the same as those of **1**—**3** in the positive FAB-MS.

The ^{1}H- and ^{13}C-NMR spectra of **4** were similar to those of **1**, in particular, the signals of sugar moiety were superimposable, and **4** on enzymatic hydrolysis gave **4a** and D-Glc.

The ^{1}H-NMR spectrum of **4a** showed the signals of two hydroxyl protons (δ 5.88 × 2), two oxymethine protons (δ 3.81 × 2), four methylene protons (δ 1.98 × 2, 2.26 × 2), three methyl groups (δ 1.61, 1.57 × 2) and one methine proton (δ 1.51); the ^{13}C-NMR spectrum of **4a** indicated seven signals (δ 76.6, 73.6, 68.9, 34.9, 34.0, 28.9, 19.3), which suggested **4a** to be a symmetrical di-hydroxy-1,8-cineole.

In the NOE difference spectra of **4**, the correlations were as illustrated in Fig. 2, which indicated **4** to be 2β,6β-dihydroxy-1,8-cineole-2-*O*-β-D-glucopyranoside.

In the ^{13}C-NMR spectrum of **4**, compared with that of **4a**, the signals of 1-C, 2-C and 3-C of Ag indicated the glycosylation shifts[3] by -0.9, $+4.7$ and -4.1 ppm, respectively. Consequently, **4** was characterized as (1*S*,2*R*,4*R*,6*S*)-2,6-dihydroxy-1,8-cineole-2-*O*-β-D-glucopyranoside.

Compound **5**, called foeniculoside IX, was obtained as a white powder, $[\alpha]_D$ $-65.9°$, and the ^{1}H- and ^{13}C-NMR spectra were similar to those of **1**—**4**. The positive FAB-MS of **5** exhibited the same $[M+Na]^+$ ion peak as those of **1**—**4** at *m/z* 371. Therefore, **5** was disclosed to be a cineole type monoterpene glycoside.

Table 1. ^{1}H-NMR Data for **1**, **1a**, **2**, **2a**, **3**, **4**, **4a**, **5** and **5a** (in Pyridine-d_5)

	1[a]	**1a**[b]	**2**[b]	**2a**[b]	**3**[b]
Ag-2-H$_\alpha$	4.33, dd (2.9, 9.9)	4.02, ddd (3.7, 6.1, 10.4)[c]	*ca.* 2.32	2.53, ddd (3.7, 12.5, 13.2)	2.52, ddd (3.5, 12.5, 12.5)
Ag-2-H$_\beta$			1.77, dddd (1.0, 6.1, 12.2, 12.2)	1.86, dddd (1.8, 4.3, 11.7, 13.2)	1.83, dddd (1.5, 6.1, 12.5, 12.5)
Ag-3-H$_\alpha$	*ca.* 2.25	2.40, dd (10.4, 13.4)	1.96, ddd (6.1, 12.2, 12.2)	2.03, ddd (4.3, 12.5, 13.2)	*ca.* 2.40
Ag-3-H$_\beta$	2.84, br d-like (13.2)	2.58, ddd (3.7, 3.7, 13.4)	2.16, dddd (3.1, 3.1, 12.2, 12.2)	2.29, dddd (3.7, 3.7, 11.7, 13.2)	2.26, dddd (3.5, 3.5, 12.5, 12.5)
Ag-5-H$_\alpha$	1.69, ddd (5.1, 12.5, 12.5)	1.75, ddd (5.0, 12.5, 12.5)	*ca.* 2.30	2.04, dd (3.7, 13.2)	*ca.* 2.41
Ag-5-H$_\beta$	*ca.* 2.21	2.25, dddd (3.7, 3.7, 12.5, 12.5)	2.86, ddd (3.1, 9.8, 13.0)	2.96, ddd (3.7, 9.5, 13.2)	3.07, ddd (3.5, 9.8, 14.0)
Ag-6-H$_\alpha$	1.60, dd-like (12.5, 12.5)	1.68, ddd (3.7, 12.5, 12.5)			
Ag-6-H$_\beta$	1.93, ddd (5.1, 12.5, 12.5)	2.00, ddd (5.0, 12.5, 12.5)	*ca.* 4.40	4.21, br d-like (8.5)	4.14, br d-like (9.8)
Ag-7-H$_3$	1.36, s	1.38, s	1.40, s	1.42, s	1.38, s
Ag-9-H$_3$	1.54, s	1.59, s	1.47, s	1.51, s	1.50, s
Ag-10-H$_3$	1.75, s	1.74, s	1.54, s	1.61, s	1.60, s
Glc-1-H	5.02, d (7.7)		5.03, d (7.3)		5.13, d (7.3)
Glc-2-H	4.01, dd (7.7, 8.8)		4.03, dd-like (8.2, 8.2)[d]		3.98, dd-like (7.9, 7.9)[d]
Glc-3-H	4.26, dd (8.8, 8.8)		*ca.* 4.25		*ca.* 4.23
Glc-4-H	4.18, dd (8.8, 8.8)		*ca.* 4.25		*ca.* 4.24
Glc-5-H	*ca.* 3.97		3.96, m		3.91, m
Glc-6-Ha	4.58, dd (2.2, 11.7)		4.54, dd (2.4, 11.6)		4.48, dd (2.4, 11.6)
Glc-6-Hb	4.37, dd (5.8, 11.7)		4.40, dd (5.5, 11.6)		4.36, dd (4.9, 11.6)

	4[a]	**4a**[b]	**5**[a]	**5a**[a]
Ag-2-H$_\alpha$	4.14, dd (2.6, 9.5)	3.81, br d-like (9.8)	4.11, dd (3.5, 9.5)	3.77, dd (3.5, 9.7)
Ag-3-H$_\alpha$	1.79, ddd (3.1, 9.5, 14.1)	1.98, ddd (3.1, 9.8, 14.7)	1.90, ddd (3.5, 9.5, 13.6)	2.08, ddd (3.5, 9.7, 13.9)
Ag-3-H$_\beta$	2.49, br dd-like (2.6, 14.1)	2.26, dddd (3.1, 3.1, 3.1, 14.7)	2.44, br d-like (13.6)	2.23, ddd (3.5, 3.5, 13.9)
Ag-4-H	1.49, br dd-like (3.1, 3.1)	1.51, dddd (3.1, 3.1, 3.1, 3.1)	*ca.* 1.81	1.81, br d-like (3.5)
Ag-5-H$_\alpha$	1.91, ddd (2.6, 10.1, 14.1)	1.98, ddd (3.1, 9.8, 14.7)	*ca.* 4.25	4.36, br dd-like (8.5, 8.5)
Ag-5-H$_\beta$	2.23, br dd-like (2.6, 14.1)	2.26, dd-like (3.1, 14.7)		
Ag-6-H$_\alpha$	3.69, dd (2.6, 10.1)	3.81, d-like (9.8)	2.05, dd (9.9, 13.9)	*ca.* 2.16
Ag-6-H$_\beta$			2.11, dd (6.6, 13.9)	*ca.* 2.18
Ag-7-H$_3$	1.60, s	1.61, s	1.38, s	1.39, s
Ag-9-H$_3$	1.52, s	1.57, s	1.83, s	1.88, s
Ag-10-H$_3$	1.59, s	1.57, s	1.50, s	1.51, s
Glc-1-H	5.03, d (7.7)		4.98, d (7.7)	
Glc-2-H	4.03, dd (7.7, 9.0)		3.99, dd (7.7, 8.8)	
Glc-3-H	4.31, dd (9.0, 9.0)		4.31, dd (8.8, 8.8)	
Glc-4-H	4.21, dd (9.0, 9.0)		4.20, dd (8.8, 8.8)	
Glc-5-H	*ca.* 4.03		*ca.* 4.00	
Glc-6-Ha	4.59, dd (2.2, 11.7)		4.60, dd (0.8, 11.4)	
Glc-6-Hb	4.38, dd (5.5, 11.7)		4.39, dd (5.5, 11.4)	

δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses). *a*) 400 MHz; *b*) 500 MHz. *c*) $J=6.1$ arose from coupling of hydroxyl proton at δ 5.93. *d*) Signals were deformed by virtual coupling.

Table 2. ^{13}C-NMR Data for **1**, **1a**, **2**, **2a**, **3**, **4**, **4a**, **5** and **5a** (in Pyridine-d_5)

	1[a]	**1a**[b]	$\Delta\delta$ (**1**−**1a**)	**2**[b]	**2a**[b]	$\Delta\delta$ (**2**−**2a**)	**3**[b]	$\Delta\delta$ (**3**−**2a**)	**4**[a]	**4a**[a]	$\Delta\delta$ (**4**−**4a**)	**5**[a]	**5a**[a]	$\Delta\delta$ (**5**−**5a**)
Ag-1-C	71.6	72.7	−1.1	71.6	73.2	−1.6	73.0	−0.2	75.7	76.6	−0.9	72.6	73.5	−0.9
Ag-2-C	76.7	72.1	+4.6	29.3	28.7	+0.6	28.3	−0.4	73.6	68.9	+4.7	74.2	69.6	+4.6
Ag-3-C	39.5	43.4	−3.9	30.6	31.0	−0.4	26.3	−4.7	30.8	34.9	−4.1	30.2	34.1	−3.9
Ag-4-C	69.5	69.5	±0.0	69.9	70.0	−0.1	77.2	+7.2	33.7	34.0	−0.3	42.1	42.6	−0.5
Ag-5-C	30.4	30.7	−0.3	40.1	43.6	−3.5	41.3	−2.3	34.8	34.9	−0.1	69.0	69.2	−0.2
Ag-6-C	32.1	31.9	+0.2	78.1	72.4	+5.7	72.2	−0.2	68.9	68.9	±0.0	42.4	41.9	+0.5
Ag-7-C	23.4	23.1	+0.3	24.5	24.4	+0.1	24.3	−0.1	19.5	19.3	+0.2	23.6	23.4	+0.2
Ag-8-C	77.5	77.5	±0.0	76.9	76.9	±0.0	76.5	−0.4	73.6	73.6	±0.0	73.9	73.8	+0.1
Ag-9-C	25.9	26.0	−0.1	25.7[d]	26.0	−0.3	26.3	+0.3	28.9	28.9	±0.0	31.6	31.6	±0.0
Ag-10-C	25.0	25.1	−0.1	25.6[d]	25.7	−0.1	26.0	+0.3	28.9	28.9	±0.0	30.5	30.5	±0.0
Glc-1-C	101.4			102.3			98.6		101.5			101.5		
Glc-2-C	74.7			75.2			75.3		74.8			74.7		
Glc-3-C	78.6[c]			78.5[c]			78.1[c]		78.7[c]			78.7		
Glc-4-C	71.9			71.9			71.8		72.0			71.9		
Glc-5-C	78.7[c]			78.7[c]			78.9[c]		78.8[c]			78.7		
Glc-6-C	63.1			63.0			63.0		63.1			63.1		

δ in ppm from TMS. *a*) 100 MHz. *b*) 125 MHz. *c*, *d*) Assignments may be interchanged in each column.

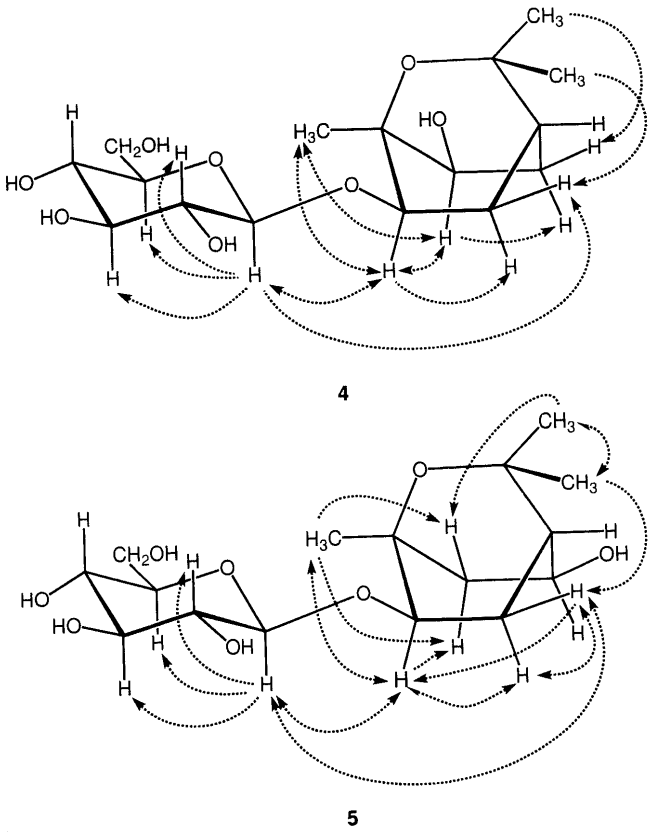

Fig. 2. NOE's Observed in the NOE Difference Spectra of **4** and **5** (in Pyridine-d_5, 400 MHz)

Enzymatic hydrolysis of **5** afforded **5a** and D-Glc, and the signals of ^{1}H- and ^{13}C-NMR spectra of **5a** and **5** were assigned as shown in Tables 1 and 2 by techniques similar to those of **1**. Based on these data, **5** was deduced to be a positional isomer of **1**, that is, the hydroxyl group at 4-C of Ag in **1** was transferred to β position of 5-C of Ag in **5**.

This assumption was confirmed by the ^{13}C-NMR data and the NOE difference spectra. In comparing the chemical shifts of the signals in the ^{13}C-NMR spectra of **5** and **5a**, glycosylation shifts[3] were observed at 1-C, 2-C and 3-C of Ag by -0.9, $+4.6$ and -3.9 ppm, respectively; the NOE difference spectra of **5** showed correlations between the respective protons as illustrated in Fig. 2. The structure of **5** was therefore defined as (1*S*,2*R*,4*S*,5*R*)-2,5-dihydroxy-1,8-cineole-2-*O*-β-D-glucopyranoside.

Compounds **6**—**12** were identified with zizybeoside I,[7] icaviside A_4,[8] syringin,[9] sinapyl alcohol 1,3′-di-*O*-β-D-glucopyranoside,[10] adenosine, *threo*-anethole glycol[11] and *erythro*-anethole glycol,[11] respectively, with respect to the physical data, spectral data and ^{1}H-NMR data of the acetates[12] of **11** and **12**.

Compounds **1**—**5** are novel monoterpene glycosides and **6**—**12** are the first examples of the isolation from the Foeniculi Fructus. Foeniculosides I—IV, miyabenol C and *cis*-miyabenol C, which were previously reported,[2] showed stronger antioxidative activity than *tert*-butyl-4-hydroxyanisole by the ferric thiocyanate method.[13]

Experimental

All instruments and materials used were the same as cited in the preceding report[2] unless otherwise specified.

Isolation of 1—12 The fraction (fr.) 2[2] (5.10 g) was chromatographed over silica gel [Merck, Art. 9385, $CHCl_3$–MeOH–H_2O (10:2:0.1→8:2:0.2→7:3:0.5→6:4:1→4:6:1)→MeOH] furnished fr. 32 (27 mg), fr. 33 (51 mg), fr. 34 (33 mg), fr. 35 (39 mg), fr. 36 (29 mg), fr. 37 (18 mg), fr. 38 (21 mg), fr. 39 (98 mg), fr. 40 (1480 mg), fr. 41 (862 mg), fr. 42 (643 mg), fr. 43 (282 mg), fr. 44 (905 mg), fr. 45 (443 mg) and fr. 46 (157 mg). Fractions 40 and 42 were each crystallized from MeOH giving **8** (963 mg) from fr. 40, and **9** (238 mg) from fr. 42, respectively. Fraction 41 was subjected to Sephadex LH 20 chromatography (MeOH) to afford fr. 47 (435 mg), fr. 48 (298 mg), fr. 49 (68 mg) and **10** (52 mg). Fraction 47 was chromatographed over silica gel [Merck, Art. 9385, $CHCl_3$–MeOH–H_2O (10:2:0.1→8:2:0.2→7:3:0.5)→MeOH] to give fr. 50 (22 mg), fr. 51 (192 mg), fr. 52 (41 mg) and fr. 53 (67 mg). HPLC (YMC-pack S-5 120A ODS, 20 mm i.d. × 250 mm, 30% MeOH) of fr. 51 gave **5** (23 mg), **3** (10 mg), fr. 54 (54 mg) and fr. 55 (57 mg). HPLC (YMC-pack S-5 120A ODS, 20 mm i.d. × 250 mm, 15% MeOH) of fr. 54 afforded **4** (15 mg) and fr. 56 (8 mg). Fraction 55 was subjected to HPLC on Kusano C.I.G. prepacked Si-gel column (22 mm i.d. × 300 mm, $CHCl_3$–MeOH–H_2O (8:2:0.2) to give **1** (33 mg) and **2** (14 mg). Fraction 48 was subjected to HPLC (YMC-pack S-5 120A ODS, 20 mm i.d. × 250 mm, 29% MeOH) to afford **8** (22 mg), **7** (71 mg) and **6** (13 mg). HPLC (Inertsil ODS, 22 mm i.d. × 250 mm, 35% MeOH) of fr. 7[2] furnished **11** (318 mg) and **12** (84 mg).

1: A white powder, $[\alpha]_D^{29}$ $-56.9°$ (c=3.6, MeOH). HR positive FAB-MS m/z: 371.1684 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_8$: 371.1682). Positive FAB-MS m/z (%): 371 (100) $[M+Na]^+$, 349 (6) $[M+H]^+$, 187 (42) $[M+H-\text{hexose}]^+$. ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2. NOEs were observed between the following sets of protons: Ag-7-H_3→Ag-2-H and Ag-6-H_β; Ag-9-H_3→Ag-5-H_β, Ag-6-H_β and Ag-10-H_3; Ag-10-H_3→Ag-3-H_β and Ag-9-H_3; Glc-1-H→Ag-2-H, Ag-3-H_β, Glc-2-H, Glc-3-H and Glc-5-H (in pyridine-d_5, 400 MHz).

2: A white powder, $[\alpha]_D^{27}$ $-59.5°$ (c=0.1, MeOH). HR positive FAB-MS m/z: 371.1685 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_8$: 371.1682). Positive FAB-MS m/z (%): 371 (100) $[M+Na]^+$, 349 (30) $[M+H]^+$. ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2. NOEs were observed between the following sets of protons: Ag-2-H_β→Ag-2-H_α and Ag-7-H_3; Ag-3-H_α→Ag-3-H_β and Ag-2-H_α; Ag-3-H_β→Ag-2-H_β, Ag-3-H_α and Ag-10-H_3; Ag-5-H_β→Ag-5-H_α, Ag-6-H and Ag-9-H_3; Ag-7-H_3→Ag-6-H; Ag-9-H_3→Ag-5-H_β, Ag-6-H and Ag-10-H_3; Ag-10-H_3→Ag-3-H_β and Ag-9-H_3; Glc-1-H→Ag-6-H, Glc-2-H, Glc-3-H and Glc-5-H (in pyridine-d_5, 400 MHz).

3: A white powder, $[\alpha]_D^{27}$ $-15.6°$ (c=1.2, MeOH). HR positive FAB-MS m/z: 371.1681 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_8$: 371.1682). Positive FAB-MS m/z: 371 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2. NOEs were observed between the following sets of protons: Ag-2-H_α→Ag-2-H_β and Ag-7-H_3; Ag-2-H_β→Ag-2-H_α, Ag-3-H_β and Ag-7-H_3; Ag-3-H_β→Ag-2-H_β, Ag-3-H_α, Ag-10-H_3 and Glc-1-H; Ag-5-H_β→Ag-5-H_α, Ag-6-H and Ag-9-H_3; Ag-6-H→Ag-5-H_β, Ag-7-H_3 and Ag-9-H_3, Ag-7-H_3→Ag-2-H_α, Ag-2-H_β and Ag-6-H; Ag-9-H_3→Ag-5-H_β, Ag-6-H and Ag-10-H_3; Ag-10-H_3→Ag-2-H_β, Ag-3-H_β, Ag-9-H_3 and Glc-1-H; Glc-1-H→Ag-3-H_α, Glc-2-H, Glc-3-H and Glc-5-H (in pyridine-d_5, 400 MHz).

4: A white powder, $[\alpha]_D^{29}$ $-34.9°$ (c=1.6, MeOH). HR positive FAB-MS m/z: 371.1682 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_8$: 371.1682). Positive FAB-MS m/z (%): 371 (100) $[M+Na]^+$, 349 (4) $[M+H]^+$, 187 (25) $[M+H-\text{hexose}]^+$. ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2.

5: A white powder, $[\alpha]_D^{29}$ $-65.9°$ (c=2.5, MeOH). HR positive FAB-MS m/z: 371.1684 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_8$: 371.1682). Positive FAB-MS m/z (%): 371 (100) $[M+Na]^+$, 349 (13) $[M+H]^+$, 187 (85) $[M+H-\text{hexose}]^+$. ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2.

6: A white powder, $[\alpha]_D^{28}$ $-31.5°$ (c=1.0, H_2O). Negative FAB-MS m/z: 431 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5, 400 MHz) δ: 7.70 (2H, d, J=7.3 Hz, Ag-2(6)-H), 7.40 (2H, dd, J=7.3, 7.3 Hz, Ag-3(5)-H), 7.25 (1H, t, J=7.3 Hz, Ag-4-H), 5.38 (1H, d, J=7.7 Hz, Glc′-1-H), 5.17 (1H, d, J=11.7 Hz, Ag-1′-Ha), 5.04 (1H, d, J=7.3 Hz, Glc-1-H), 4.82 (1H, d, J=11.7 Hz, Ag-1′-Hb). ^{13}C-NMR (in pyridine-d_5, 100 MHz) δ: 138.8 (Ag-1-C), 128.5 (Ag-3(5)-C), 127.8 (Ag-2(6)-C), 127.6 (Ag-4-C), 106.6 (Glc′-1-C), 102.3 (Glc-1-C), 84.3 (Glc-2-C), 78.6, 78.4 (Glc-5-C, Glc′-5-C), 78.0 (Glc-3-C), 78.0 (Glc′-3-C), 76.8 (Glc′-2-C), 71.3, 71.1 (Glc-4-C, Glc′-4-C), 70.8 (Ag-1′-C), 62.5, 62.4 (Glc-6-C, Glc′-6-C).

7: A white powder, $[\alpha]_D^{23}$ $-98.1°$ (c=0.9, MeOH). Negative FAB-MS m/z: 401 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5, 400 MHz) δ: 7.55 (2H, d, J=7.0 Hz, Ag-2(6)-H), 7.30 (2H, dd, J=7.0, 7.0 Hz, Ag-3(5)-H), 7.27

(1H, t, J=7.0 Hz, Ag-4-H), 5.84 (1H, d, J=2.6 Hz, apiose (Api)-1-H), 5.19 (1H, d, J=11.7 Hz, Ag-1'-Ha), 4.92 (1H, d, J=7.7 Hz, Glc-1-H), 4.84 (1H, d, J=11.7 Hz, Ag-1'-Hb), 4.80 (1H, d, J=2.6 Hz, Api-2-H), 4.61 (1H, d, J=9.2 Hz, Api-4-Ha), 4.37 (1H, d, J=9.2 Hz, Api-4-Hb). ^{13}C-NMR (in pyridine-d_5, 100 MHz) δ: 138.6 (Ag-1-C), 128.4 (Ag-2(6)-C, Ag-3(5)-C), 127.7 (Ag-4-C), 111.1 (Api-1-C), 103.5 (Glc-1-C), 80.3 (Api-3-C), 78.3 (Glc-3-C), 77.7 (Api-2-C), 77.1 (Glc-5-C), 75.0 (Glc-2-C), 74.9 (Api-4-C), 71.7 (Glc-4-C), 70.7 (Ag-1'-C), 68.8 (Glc-6-C), 65.4 (Api-5-C).

8: Colorless needles (MeOH), mp 196—197 °C, $[\alpha]_D^{28}$ −15.4° (c=1.8, H_2O). Negative FAB-MS m/z (%): 371 (16) $[M-H]^-$, 209 (100) $[371-\text{hexose}]^-$. ^{1}H-NMR (in pyridine-d_5, 400 MHz) δ: 6.89 (1H, d, J=15.8 Hz, Ag-1'-H), 6.89 (2H, s, Ag-2(6)-H), 6.63 (1H, ddd, J=15.8, 5.1, 5.1 Hz, Ag-2'-H), 5.79 (1H, Signal was deformed by virtual coupling, Glc-1-H), *ca.* 4.60 (2H, Ag-3'-H_2), 3.78 (6H, s, $OCH_3\times2$). ^{13}C-NMR (in pyridine-d_5, 67.8 MHz) δ: 153.8 (Ag-3(5)-C), 135.8 (Ag-4-C), 133.9 (Ag-1-C), 131.0 (Ag-1'-C), 129.3 (Ag-2'-C), 105.1 (Glc-1-C), 104.8 (Ag-2(6)-C), 78.6, 78.3 (Glc-3-C, Glc-5-C), 76.0 (Glc-2-C), 71.5 (Glc-4-C), 62.7, 62.5 (Glc-6-C, Ag-3'-C).

9: Colorless needles (MeOH), mp 197—201 °C, $[\alpha]_D^{28}$ −43.0° (c=1.0, H_2O). Negative FAB-MS m/z (%): 533 $[M-H]^-$. Positive FAB-MS m/z: 557 $[M+Na]^+$. ^{1}H-NMR (in pyridine-d_5, 400 MHz) δ: 6.79 (2H, s, Ag-2(6)-H), 6.74 (1H, d, J=15.8 Hz, Ag-1'-H), 6.45 (1H, ddd, J=15.8, 5.5, 6.0 Hz, Ag-2'-H), 5.81 (1H, Signal was deformed by virtual coupling, Glc-1-H), 5.00 (1H, d, J=8.1 Hz, Glc'-1-H), 4.79 (1H, dd, J=13.0, 5.5 Hz, Ag-3'-Ha), 4.53 (1H, dd, J=13.0, 6.0 Hz, Ag-3'-Hb), 3.76 (6H, s, $OCH_3\times2$). ^{13}C-NMR (in pyridine-d_5, 67.8 MHz) δ: 153.7 (Ag-3(5)-C), 135.8 (Ag-4-C), 133.2 (Ag-1-C), 132.1 (Ag-1'-C), 126.1 (Ag-2'-C), 105.1 (Ag-2(6)-C), 104.6 (Glc-1-C), 103.8 (Glc'-1-C), 78.7, 78.5 (Glc-5-C, Glc-5'-C), 78.5, 78.3 (Glc-3-C, Glc-3'-C), 75.9 (Glc-2-C), 75.2 (Glc'-2-C), 71.6, 71.4 (Glc-4-C, Glc'-4-C), 69.6 (Ag-3'-C), 62.7, 62.5 (Glc-6-C, Glc'-6-C).

10: A white powder, $[\alpha]_D^{28}$ −57.3° (c=1.3, H_2O). EI-MS m/z: 267 $[M]^+$. ^{1}H-NMR (in DMSO-d_6, 400 MHz) δ: 8.36 (1H, s, Ag-2-H), 8.15 (1H, s, Ag-8-H), 7.36 (2H, s, NH_2), 5.89 (1H, d, J=6.6 Hz, ribose(Rib)-1-H). ^{13}C-NMR (in DMSO-d_6, 100 MHz) δ: 156.2 (Ag-6-C), 152.4 (Ag-2-C), 149.1 (Ag-4-C), 140.0 (Ag-8-C), 119.4 (Ag-5-C), 87.9 (Rib-1-C), 85.9 (Rib-4-C), 73.5 (Rib-2-C), 70.7 (Rib-3-C), 61.7 (Rib-5-C).

11: Colorless needles (MeOH–H_2O), mp 62—63 °C, $[\alpha]_D^{28}$ 0° (c=1.3, MeOH). EI-MS m/z: 182 $[M]^+$. ^{1}H-NMR (in DMSO-d_6, 400 MHz) δ: 7.22 (2H, d, J=8.8 Hz, 2(6)-H), 6.86 (2H, d, J=8.8 Hz, 3(5)-H), 5.07 (1H, d, J=4.0 Hz, 1'-OH), 4.57 (1H, d, J=4.0 Hz, 2'-OH), 4.22 (1H, dd, J=3.0, 4.0 Hz, 1'-H), 3.72 (3H, s, OCH_3), 3.62 (1H, m, 2'-H), 0.82 (1H, d, J=6.6 Hz, 3'-H_3). ^{13}C-NMR (in DMSO-d_6, 67.8 MHz) δ: 158.2 (4-C), 134.9 (1-C), 128.1 (2-C, 6-C), 113.0 (3-C, 5-C), 77.3 (1'-C), 70.8 (2'-C), 55.0 (OCH_3), 18.8 (3'-C).

12: Colorless needles (MeOH–H_2O), mp 118—119 °C, $[\alpha]_D^{28}$ 0° (c=1.0, MeOH). EI-MS m/z: 182 $[M]^+$. ^{1}H-NMR (in DMSO-d_6, 400 MHz) δ: 7.23 (2H, d, J=8.8 Hz, 2(6)-H), 6.85 (2H, d, J=8.8 Hz, 3(5)-H), 5.02 (1H, br s, 1'-OH), 4.38 (1H, br s, 2'-OH), 4.30 (1H, d-like, J=4.0 Hz, 1'-H), 3.72 (3H, s, OCH_3), 3.63 (1H, m, 2'-H), 0.98 (1H, d, J=6.6 Hz, 3'-H_3). ^{13}C-NMR (in DMSO-d_6, 67.8 MHz) δ: 158.1 (4-C), 135.6 (1-C), 127.9 (2-C, 6-C), 113.0 (3-C, 5-C), 76.6 (1'-C), 70.6 (2'-C), 55.0 (OCH_3), 18.5 (3'-C).

Enzymatic Hydrolysis of 1—5 Compounds **1** (9.7 mg), **2** (11.8 mg), **3** (5.4 mg), **4** (6.7 mg) and **5** (13.3 mg) were each dissolved in AcOH–AcONa buffer solution (pH 5.0, 3.0 ml), and β-glucosidase (from Almonds Lot 102H4008, Sigma Chemical Co., 2.5—3.5 mg) was added, respectively. The mixture was left to stand at 37 °C for 10—30 d. After removal of the solvent under reduced pressure, the residue was extracted with MeOH, and the MeOH extract was chromatographed over silica gel [Merck Art. 9385, $CHCl_3$–MeOH–H_2O (14:2:0.1→10:2:0.1→8:2:0.2→7:3:0.5→6:4:1)] to give aglycone [**1a** (3.0 mg) from **1**, **2a** (4.0 mg) from **2**, **2a** (0.9 mg) from **3**, **4a** (2.0 mg) from **4**, **5a** (5.4 mg) from **5**] and sugar fraction.

Each sugar fraction of **1—5** was subjected to HPTLC analysis [Rf: 0.33 (glucose) for **1—5**]. Each one was then converted into trimethylsilyl ether of the methyl thiazolidine 4(R)-carboxylate derivatives and subjected to GC analysis according to Hara *et al.*[4] [t_R (min): 20.61—20.99 (D-glucose) for **1—5**].

1a: A white powder. $[\alpha]_D^{26}$ −31.2° (c=0.2, MeOH). ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2. ^{1}H-NMR (in $CDCl_3$, 500 MHz) δ: 3.68 (1H, dd like, J=9.2, 7.3 Hz, 2-H), 2.19 (1H, br d like, 9.8 Hz, 3-H$_\beta$), 2.07 (1H, dd, J=9.2, 13.4 Hz, 3-H$_\alpha$), *ca.* 1.97 (2H, 5-H$_\alpha$, 6-H$_\beta$). 1.68 (1H, dd, J=11.0, 12.2 Hz, 5-H$_\beta$), 1.48 (1H, ddd, J=3.7, 6.1, 12.2 Hz, 6-H$_\alpha$), 1.31 (3H, s, 9-H_3 or 10-H_3), 1.29 (3H, s, 10-H_3 or 9-H_3), 1.11 (3H, s, 7-H_3) ^{13}C-NMR (in $CDCl_3$, 67.5 MHz) δ: 77.0 (8-C), 72.4 (1-C), 72.1 (2-C), 70.1 (4-C), 42.5 (3-C), 30.4, 29.7 (5-C, 6-C), 25.0, 24.2 (9-C, 10-C), 22.4 (7-C). NOEs were observed between the following sets of protons: Ag-2-H→Ag-7-H_3, Ag-3-H$_\beta$ and Ag-3-H$_\alpha$; Ag-3-H$_\beta$→Ag-2-H and Ag-3-H$_\alpha$; Ag-3-H$_\alpha$→Ag-3-H$_\beta$ and Ag-2-H; Ag-6-H$_\beta$→Ag-6-H$_\alpha$ and Ag-5-H$_\beta$; Ag-7-H_3→Ag-2-H, Ag-6-H$_\alpha$ and Ag-6-H$_\beta$; Ag-9-H_3→Ag-5-H$_\beta$, Ag-6-H$_\beta$ and Ag-10-H_3; Ag-10-H_3→Ag-3-H$_\beta$ and Ag-9-H_3 (in pyridine-d_5, 400 MHz).

2a: A white powder. $[\alpha]_D^{26}$ −23.0° (c=0.2, MeOH). ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2. ^{1}H-NMR (in $CDCl_3$, 500 MHz) δ: 3.81 (1H, br d, J=9.8 Hz, 6-H), 2.50 (1H, ddd, J=4.0, 9.8, 13.5 Hz, 5-H$_\beta$), 2.10 (1H, m, 2-H$_\alpha$), 1.93 (1H, dddd, J=4.0, 4.0, 13.5, 13.5 Hz, 3-H$_\beta$), *ca.* 1.70 (1H, 2-H$_\beta$), *ca.* 1.65 (1H, 3-H$_\alpha$), 1.46 (1H, dd, J=4.0, 13.5 Hz, 5-H$_\alpha$), 1.29 (3H, s, 10-H_3), 1.21 (3H, s, 9-H_3), 1.11 (3H, s, 7-H_3). ^{13}C-NMR (in $CDCl_3$, 125 MHz) δ: 76.3 (8-C), 72.5 (6-C), 72.4 (1-C), 70.6 (4-C), 41.8 (5-C), 29.9 (3-C), 27.6 (2-C), 24.6, 24.8 (9-C, 10-C), 23.3 (7-C). NOEs were observed between the following sets of protons: Ag-2-H$_\alpha$→Ag-2-H$_\beta$ and Ag-3-H$_\alpha$; Ag-2-H$_\beta$→Ag-2-H$_\alpha$, Ag-3-H$_\beta$ and Ag-7-H_3; Ag-3-H$_\beta$→Ag-2-H$_\alpha$, Ag-3-H$_\alpha$ and Ag-10-H_3; Ag-5-H$_\beta$→Ag-5-H$_\alpha$, Ag-6-H and Ag-9-H_3; Ag-6-H→Ag-5-H$_\alpha$, Ag-5-H$_\beta$ and Ag-7-H_3; Ag-7-H_3→Ag-2-H$_\alpha$, Ag-2-H$_\beta$ and Ag-6-H; Ag-9-H_3→Ag-5-H$_\beta$, Ag-6-H and Ag-10-H_3; Ag-10-H_3→Ag-2-H$_\beta$, Ag-3-H$_\beta$ and Ag-9-H_3 (in pyridine-d_5, 400 MHz).

4a: A white powder. ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2. NOEs were observed between the following sets of protons: Ag-2(6)-H→Ag-7-H_3, Ag-3(5)-H$_\beta$ and Ag-3(5)-H$_\alpha$; Ag-4-H→Ag-3(5)-H$_\beta$ and Ag-3(5)-H$_\alpha$; Ag-7-H_3→Ag-2(6)-H; Ag-9(10)-H_3→Ag-3(5)-H$_\beta$ and Ag-4-H (in pyridine-d_5, 400 MHz).

5a: A white powder. $[\alpha]_D^{26}$ −62.2° (c=0.5, MeOH). ^{1}H- and ^{13}C-NMR δ: see Tables 1 and 2. ^{1}H-NMR (in $CDCl_3$, 500 MHz) δ: 4.02 (ddd, J=1.8, 6.7, 9.5 Hz, 5-H), 3.44 (1H, br dd, J=4.9, 7.9 Hz, 2-H), 2.03 (1H, dd, J=9.5, 14.6 Hz, 6-H$_\alpha$), *ca.* 1.93 (2H, 3-H$_\alpha$, 3-H$_\beta$), 1.84 (1H, dd, J=6.7, 14.6 Hz, 6-H$_\beta$), 1.58 (1H, br s-like, 4-H), 1.47 (3H, s, 9-H_3), 1.30 (3H, s, 10-H_3), 1.13 (3H, s, 7-H_3). ^{13}C-NMR (in $CDCl_3$, 125 MHz) δ: 73.8, 72.9 (1-C, 8-C), 69.8, 69.6 (2-C, 5-C), 41.6 (4-C), 39.9 (6-C), 33.7 (3-C), 30.8, 29.9 (9-C, 10-C), 22.7 (7-C). NOEs were observed between the following sets of protons: Ag-2-H→Ag-3-H$_\beta$, Ag-3-H$_\alpha$, Ag-5-H and Ag-6-H$_\alpha$; Ag-3-H$_\alpha$→Ag-2-H, Ag-3-H$_\beta$ and Ag-5-H; Ag-4-H→Ag-3-H$_\alpha$, Ag-3-H$_\beta$, Ag-5-H and Ag-10-H_3; Ag-5-H→Ag-2-H, Ag-3-H$_\alpha$, Ag-4-H, Ag-6-H$_\alpha$ and Ag-6-H$_\beta$; Ag-7-H_3→Ag-2-H, Ag-6-H$_\alpha$ and Ag-6-H$_\beta$; Ag-9-H_3→Ag-6-H$_\beta$ and Ag-10-H_3; Ag-10-H_3→Ag-3-H$_\beta$, Ag-4-H and Ag-9-H_3 (in pyridine-d_5, 400 MHz).

Acetylation of 11 and 12 Compounds **11** (6 mg) and **12** (5 mg) in Ac_2O–pyridine (1:1, 0.2 ml) were each left to stand at room temperature overnight. After removal of the reagent under a stream of N_2, the residue was partitioned between ether (0.5 ml) and H_2O (0.5 ml). The ether layer was concentrated to afford a white powder, [acetate of **11** (7 mg), ^{1}H-NMR (in $CDCl_3$, 500 MHz) δ: 7.29 (2H, d, J=8.5 Hz, 2(6)-H), 6.89 (2H, d, J=8.5 Hz, 3(5)-H), 5.73 (1H, d, J=7.3 Hz, 1'-H), 5.27 (1H, dq, J=7.3, 6.1 Hz, 2'-H), 3.82 (3H, s, OCH_3), 2.07 (3H, s, $COCH_3$), 2.05 (3H, s, $COCH_3$), 1.09 (3H, d, J=6.1 Hz, 3'-H_3); acetate of **12** (6 mg), ^{1}H-NMR (in $CDCl_3$, 500 MHz) δ: 7.29 (2H, d, J=8.5 Hz, 2(6)-H), 6.89 (2H, d, J=8.5 Hz, 3(5)-H), 5.86 (1H, d, J=4.3 Hz, 1'-H), 5.23 (1H, dq, J=4.3, 6.1 Hz, 2'-H), 3.82 (3H, s, OCH_3), 2.13 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 1.20 (3H, d, J=6.1 Hz, 3'-H_3).

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