

Water-Soluble Constituents of Ajowan

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From the water-soluble portion of the methanol extract of the fruit of *Carum ajowan* (ajowan), which has been used as a spice and medicine, 25 compounds, including five new monoterpenoid glucosides, a new monoterpenoid, two new aromatic compound glucosides, and two new glucides, were obtained. Their structures were clarified by spectral investigation.

Key words ajowan; *Carum ajowan* fruit; hydroxythymol glucoside; menthane-type monoterpenoid; aromatic compound; glucide

Ajowan [*Carum ajowan* (Umbelliferae)] is mainly cultivated in southern India, and is known as a popular aromatic herb and spice. Its fruit has been used as much for medicine as in cooking, and used to primarily control flatulence and indigestion. It is prescribed for colic, diarrhea and other bowel disorders, and in the treatment of asthma.¹⁾ The main ingredient of its essential oil is thymol,²⁾ a germicide and antiseptic; also 6-hydroxycarvacrol 2-*O*- β -D-glucopyranoside, 3,5-dihydroxytoluene 3-*O*- β -D-galactopyranoside were reported as glycosyl constituents.³⁾ In continuation of our studies on the water-soluble constituents of spices,⁴⁾ and with the hope of isolating hydroxythymols and their glycosides, which can be expected to possess sterilizing property, we undertook a detailed investigation of this fruit and consequently isolated 25 compounds. In this paper, we discuss their structures.

The commercial ajowan was extracted with ether to remove the essential oil, and the residue was extracted with methanol. The methanol extract was suspended in water and extracted with ether, and the aqueous layer was chromatographed on Amberlite XAD-II to give water and methanol eluate fractions. The fractions were subjected to Sephadex LH-20, silica gel and Lobar RP-8 column chromatography, and finally, HPLC was used for purification of the compounds. Then, two monoterpenoids (**1**, **10**), light monoterpenoid glucosides (**2**–**9**), one alkyl glucoside (**11**), one aromatic compound (**13**), three aromatic compound glucosides (**12**, **14**, **15**), two nucleosides (**16**, **17**), and eight glucides (**18**–**25**) were obtained from the methanol extract. Among them, monoterpenoid and monoterpenoid glucosides **5** to **10**, and aromatic compound glucosides **14** and **15** are new compounds, while glucides **20** and **21** are newly isolated compounds from natural sources. All glucosides described in this paper were β -D-glucopyranosides, as shown by their ¹³C-NMR data, and this was confirmed by hydrolysis to yield D-glucose, or by 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 $[M+H]^+$ or $[M+Na]^+$ ion peaks in the high-resolution positive FAB-MS.

Monoterpenoid **1**, monoterpenoid glycoside **2**, **3** and **4** were identified as 3,7-dimethyloct-3(10)-ene-1,2,6,7-tetrol (a mixture of two stereoisomers), (2*S*,6*ζ*)-3,7-dimethyloct-3(10)-ene-1,2,6,7-tetrol 1-*O*- β -D-glucopyranoside,⁶⁾ 6-hydroxythymol 6-*O*- β -D-glucopyranoside⁷⁾ and 6-hydroxythymol 3-*O*- β -D-glucopyranoside,⁷⁾ respectively.

Monoterpenoid glucosides **5** (C₁₆H₂₄O₇, an amorphous powder, $[\alpha]_D^{25} -60^\circ$) and **6** (C₂₂H₃₄O₁₂, an amorphous pow-

der, $[\alpha]_D^{23} -62^\circ$) were glucosides of hydroxythymol and their ¹³C-NMR data are listed in Table 1. Glucoside **5** showed $[M+Na]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m/z* 351 and 149 in the positive FAB-MS, and had a 1,3,4-trisubstituted benzene ring, one hydroxymethyl and one isopropyl group, in addition to the β -glucopyranosyl moiety. From analysis of the heteronuclear multiplet-bond correlation (HMBC) spectral data (correlations: H-3/C-1, C-3, C-4, C-6, C-7; H-5/C-1, C-3, C-4, C-8; H-6/C-1, C-2, C-4, C-7; H₂-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; H₃-9/C-4, C-8, C-10; H₃-10/C-4, C-8, C-9; Glc H-1/C-3), the aglycone was clarified to be 7-hydroxythymol, and the location of the glucosyl group was indicated to be C-3. Thus, **5** was characterized as 7-hydroxythymol 3-*O*- β -D-glucopyranoside. Glucoside **6** showed $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 513 and 491 in the positive FAB-MS, and had the two β -glucopyranosyl moieties. Comparison of its ¹H- and ¹³C-NMR (Table 1) spectral data with those of **3** and **4** suggested that **6** is a diglucopyranoside of 6-hydroxythymol. The positions of the glucosyl units were confirmed to be C-3 and C-6 from the HMBC spectral data (correlations: H-2/C-4, C-6, C-7; H-5/C-1, C-3, C-8; H₃-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; H₃-9/C-4, C-8, C-10; H₃-10/C-4, C-8, C-9; Glc H-1/C-3; Glc H-1'/C-6), therefore, **6** was concluded to be 6-hydroxythymol 3,6-di-*O*- β -D-glucopyranoside.

Monoterpenoid glucoside **7** (C₁₆H₂₈O₇, an amorphous powder, $[\alpha]_D^{24} -15^\circ$) showed the presence of one β -glucopyranosyl unit, two *sec*-methyls, four methylenes (one of them was oxygenated), one methine, one oxygenated quaternary carbon and one trisubstituted double bond by the ¹H- and ¹³C-NMR spectral data. Analysis of cross-peaks of the HMBC spectrum of **7** (H-2/C-3, C-4, C-6, C-7; H-3_{ax}/C-1, C-2; H-3_{eq}/C-1, C-2, C-4; H-5_{ax}/C-1, C-3, C-4, C-6; H-5_{eq}/C-1, C-3, C-4, C-6, C-8; H-6_{ax}/C-1, C-2, C-4, C-5, C-7; H-6_{eq}/C-1, C-2, C-5; H₂-7/C-1, C-2, C-6; H-8/C-3, C-4, C-5, C-9, C-10; H₃-9/C-4, C-8, C-10; H₃-10/C-4, C-8, C-9; Glc H-1/C-4) suggested that the planar structure of the aglycone was *p*-menth-1-ene-4,7-diol, and the glucosyl unit was attached to the C-4 of the aglycone. Enzymatic hydrolysis of **7** gave an aglycone (**7a**; C₁₀H₁₈O₂, an amorphous powder, $[\alpha]_D^{21} +18^\circ$), which had a positive optical rotation, and D-glucose. Since the 4*S* form of *p*-menth-1-en-4-ol showed a positive optical rotation ($[\alpha]_D +24.5^\circ$) contrary to that of the 4*R* form ($[\alpha]_D -36^\circ$),⁸⁾ the configuration at C-4 of **7a** should be *S*. Thus, **7** was characterized as (4*S*)-*p*-menth-1-ene-4,7-diol 4-*O*- β -D-glucopyranoside.

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Monoterpenoid glucoside **8** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{24} -29^\circ$) was also a glucoside of *p*-menth-1-enediol. From the results of 1H -, ^{13}C -NMR and the HMBC spec-

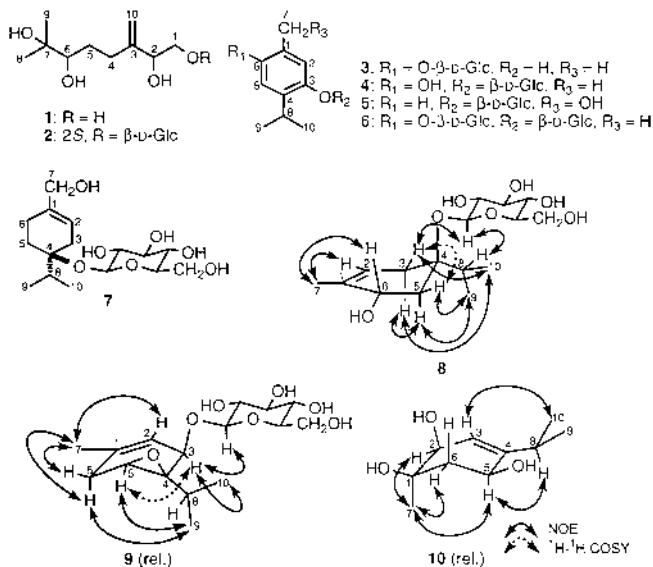


Fig. 1. Structures of **1**—**10**, and NOE and 1H - 1H COSY Correlations of **8**—**10**

tral data (correlations: H-2/C-4, C-6, C-7; H-3_{ax}/C-1, C-2; H-5_{ax}/C-1, C-3, C-6; H-5_{eq}/C-1, C-3, C-4, C-6, C-8; H-6_{eq}/C-1; H₃-7/C-1, C-2, C-6; H₃-9/C-4, C-8, C-10; H₃-10/C-4, C-8, C-9; Glc H-1/C-4), the positions of the hydroxyl groups were indicated to be C-4 and C-6, and the location of the glucosyl unit was the C-4 of the aglycone. As a cross-peak based on long-range W-type coupling was observed between H-3_{eq} and H-5_{eq} in the H-H correlation spectroscopy (COSY) spectrum, and the nuclear Overhauser effect (NOE) interactions shown in Fig. 1 were observed in the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum, the conformation of **8** could be described as Fig. 1. The configuration of C-6 hydroxyl was concluded to be equatorial by the coupling constant (dd, $J=5.0, 9.0$ Hz) of the H-6 signal. So, **8** was confirmed to be 4-*O*- β -D-glucopyranoside of *p*-menth-1-ene-4 β ,6 α -diol. As the glycosylation shift of C-3, C-4, C-5 and C-8 of **8** showed almost identical values to those of **7** (Table 1), the configuration at C-4 of **8** was suggested to be *R*. Therefore, **8** was characterized as (4*R*,6*S*)-*p*-menth-1-ene-4,6-diol 4-*O*- β -D-glucopyranoside.

Monoterpenoid glucoside **9** ($C_{16}H_{26}O_7$, an amorphous powder, $[\alpha]_D^{24} +45^\circ$) had one *tert*-methyl, two *sec*-methyls, one methylene, three methines (two of them were oxygenated), one oxygenated quaternary carbon and one trisubstituted double bond, in addition to the β -glucopyranosyl

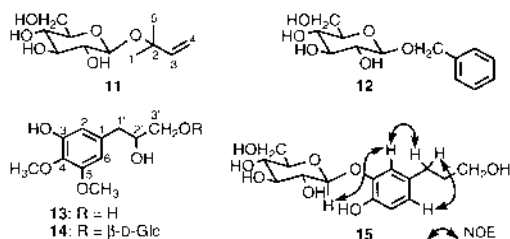


Fig. 2. Structures of **11**—**15**, and NOE Interactions Observed in the NOESY Spectrum of **15**

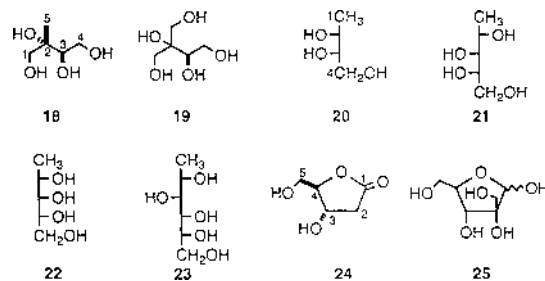


Fig. 3. Structures of **18**—**25**

Table 1. ^{13}C -NMR Chemical Shifts of **3**—**10**, and **7a**—**9a** (in Pyridine- d_5)

	3	4	5	6	7 $\delta_{(7-7a)}$	7a	8 $\delta_{(8-8a)}$	8a	9 $\delta_{(9-9a)}$	9a	10
C-1	126.35	122.91	142.49	126.21	139.14	138.16	139.32	138.72	132.15	129.55	73.32
C-2	117.79	120.28	114.43	119.08	120.18	120.92	119.17	119.48	120.80 (-3.0)	123.82	74.80
C-3	150.85	148.87	155.97	150.90	31.02 (-4.5)	35.53	31.30 (-4.0)	35.29	74.05 (+8.8)	65.26	124.43
C-4	133.83	137.31	136.60	136.98	82.44 (+8.6)	73.87	79.75 (+8.4)	71.36	62.59 (-0.3)	62.89	147.42
C-5	116.19	112.98	126.28	114.90	40.70 (-1.8)	42.48	29.41 (-2.4)	31.84	56.23	55.90	67.55
C-6	150.32	152.18	120.81	152.31	67.95	68.35	23.91	23.67	31.40	31.26	44.83
C-7	16.44	16.58	64.32	16.47	19.90	19.89	66.23	66.49	23.19	23.15	23.05
C-8	27.56	26.56	26.81	26.80	35.04 (-3.9)	38.98	34.04 (-3.4)	37.47	26.51	28.76	29.90
C-9	23.01 ^{a)}	23.40 ^{a)}	23.03 ^{a)}	23.21 ^{a)}	18.15	17.30	17.32	17.35	17.26	17.37	21.49
C-10	23.14 ^{a)}	23.67 ^{a)}	23.40 ^{a)}	23.32 ^{a)}	17.28	17.28	17.72	17.39	18.10	18.43	22.68
Glc-1	104.73	104.75	102.89	104.00	98.81		99.12		104.32		
Glc-2	75.23	75.32	75.13	75.19 ^{b)}	75.59		75.59		75.48		
Glc-3	78.82	78.83	78.76	78.77 ^{c)}	78.75		78.83		78.74		
Glc-4	71.60	71.53	71.23	71.38 ^{d)}	71.97		72.09		71.96		
Glc-5	78.68	78.63	78.59	78.74 ^{e)}	77.94		78.12		78.58		
Glc-6	62.63	62.60	62.36	62.46 ^{f)}	63.06		63.17		63.11		
Glc-1'				103.98							
Glc-2'				75.10 ^{b)}							
Glc-3'				78.57 ^{c)}							
Glc-4'				71.47 ^{d)}							
Glc-5'				78.64 ^{e)}							
Glc-6'				62.49 ^{f)}							

δ in ppm from TMS. a-f) Assignments may be interchanged in each column.

moiety. From the analysis of HMBC spectral data (correlations: H-2/C-3, C-4, C-6, C-7; H-3_{eq}/C-1, C-2, C-4, C-5, Glc C-1; H-5_{eq}/C-1, C-4, C-6, C-8; H-6_{ax}/C-1, C-2, C-4, C-5, C-7; H-6_{eq}/C-1, C-2, C-5; H₃-7/C-1, C-2, C-6; H₃-9/C-4, C-8, C-10; H₃-10/C-4, C-8, C-9; Glc H-1/C-3), **9** was clarified to be a glucopyranoside of a menth-1-ene type monoterpene having oxygenated functions at C-3, C-4 and C-5. The position of the glucosyl unit was revealed to be C-3 from the H-C long-range correlation between Glc H-1 and the C-3 carbon in the HMBC spectrum, and the NOE interactions between Glc H-1 and H-3 in the NOESY spectrum. Enzymatic hydrolysis of **9** gave an aglycone (**9a**; C₁₀H₁₆O₂, an amorphous powder, [α]_D²² +53°) and D-glucose, and from the molecular formula of **9**, an epoxy ring should be formed between C-4 and C-5. The relative configuration was examined by the ¹H-¹H COSY and NOESY spectra of **9**. Since a cross-peak between H-3_{eq} and H-5_{eq}, which was based on long-range W-type coupling, was observed in the ¹H-¹H COSY spectrum, and NOE interactions between H-5_{eq} and H₃-9, H-6_{ax} and H₃-9 were observed in the NOESY spectrum, the relative configuration of **9** was suggested to be as described in Fig. 1. However, the glycosylation shift values of the α - and β -pro-*S*-side carbons and the chemical shift of glucosyl C-1 could not be adapted to the empirical rule [C-3 (α -carbon): $\Delta\delta$ +8.8, *R*-alcohols, about $\Delta\delta$ +4 to +7, *S*-alcohols, about $\Delta\delta$ +9 to +11; C-2 (β -carbon): $\Delta\delta$ -3.0, β -pro-*S*-side carbon of *R*-alcohols, about $\Delta\delta$ -4 to -5, β -pro-*S*-side carbon of *S*-alcohols, about $\Delta\delta$ 0 to -2; glucosyl C-1: δ 104.32, *R*-alcohols, about δ 102, *S*-alcohols, about δ 106; (Table 1)],⁹ the absolute configuration at C-3 could not be revealed. So, **9** was represented as 3 β -hydroxy-*p*-menth-1-en-4 β ,5 β -oxide 3-*O*- β -D-glucopyranoside.

Monoterpene **10** (C₁₀H₁₈O₃, an amorphous powder, [α]_D²³ +2°) showed [M+Na]⁺ and [M+H]⁺ ion peaks at *m/z* 209 and 187 in the positive FAB-MS. The ¹H- and ¹³C-NMR spectral data revealed the presence of one *tert*-methyl, two *sec*-methyls, one methylene, three methines (two of them were oxygenated), one oxygenated quaternary carbon and one trisubstituted double bond. From the analysis of HMBC spectral data (correlations: H-3/C-1, C-5, C-8; H₂-6/C-1, C-2, C-4, C-5, C-7; H₃-7/C-1, C-2, C-6; H₃-9/C-4, C-8, C-10; H₃-10/C-4, C-8, C-9), **10** was suggested to be *p*-menth-3-ene-1,2,5-triol. As NOE interactions between H-2_{eq} and H₃-7, H-5_{ax} and H₃-7, and between H-6_{eq} and H₃-7 were observed in the NOESY spectrum of **10**, the orientation of H-2_{eq}, H-5_{ax}, H-6_{eq} and H₃-7 should be the same. So, **10** was concluded to be *p*-menth-3-ene-1 β ,2 β ,5 β -triol.

Alkyl glucoside **11**, aromatic compound glucoside **12** and aromatic compound **13** were identified as 2-methyl-3-buten-2-ol β -D-glucopyranoside,¹⁰ benzyl β -D-glucopyranoside¹¹ and 1'-(3-hydroxy-4,5-dimethoxyphenyl)-propane-2',3'-diol,¹² respectively.

Aromatic compound glucoside **14** (C₁₇H₂₆O₁₀, an amorphous powder, [α]_D²³ -6°) was suggested to be a β -glucopyranoside of **13** by the ¹H- and ¹³C-NMR spectral data (Table 2). The position of the glucosyl unit was indicated to be C-3' from the downfield glycosylation shift of the C-3 carbon ($\Delta\delta$ +7.7).⁹ Thus, **14** was characterized as 1'-(3-hydroxy-4,5-dimethoxyphenyl)-propane-2',3'-diol 3'-*O*- β -D-glucopyranoside.

Aromatic compound glucoside **15** (C₁₅H₂₂O₈, an amor-

Table 2. ¹³C-NMR Chemical Shifts of **13**—**15** (in Pyridine-*d*₅)

	13	14 $\delta_{(14-13)}$	15
C-1	136.03	135.98	134.25
C-2	111.72	111.90	120.14
C-3	136.41	136.13	146.63
C-4	151.89 ^{a)}	151.87 ^{a)}	147.55
C-5	153.82 ^{a)}	153.85 ^{a)}	117.12
C-6	105.45	105.54	124.53
C-1'	41.32	41.40	32.03
C-2'	74.04	71.72 (-2.3)	35.62
C-3'	66.88	74.61 (+7.7)	61.34
4-OCH ₃	60.39	60.42	—
5-OCH ₃	55.79	55.89	—
Glc-1		105.21	105.09
Glc-2		75.31	75.11
Glc-3		78.58	78.35
Glc-4		71.61	71.19
Glc-5		78.61	79.02
Glc-6		62.66	62.27

δ in ppm from TMS. a) Assignments may be interchanged in each column.

phous powder, [α]_D²³ -41°) showed the presence of one 1,3,4-trisubstituted benzene ring, one hydroxypropyl group in addition to the β -glucopyranosyl unit by the ¹H- and ¹³C-NMR spectral data (Table 2). As cross-peaks between H-2 and H-1', H-6 and H-1', and between H-2 and Glc H-1 were observed in the NOESY spectrum (Fig. 2), **15** was characterized as 3,4-dihydroxyphenylpropanol 3-*O*- β -D-glucopyranoside.

Nucleosides **16** and **17**, and glucides **18** and **19** were identified as adenosine,⁴ uridine,⁴ (2*S*,3*R*)-2-methylbutane-1,2,3,4-tetrol¹²) and (3*R*)-2-hydroxymethylbutane-1,2,3,4-tetrol,¹²) respectively.

Glucide **20** (C₄H₁₀O₃, an amorphous powder, [α]_D²⁴ -30°) was made up of one *sec*-methyl, one hydroxylated methylene, and two hydroxylated methines, and showed identical ¹H- and ¹³C-NMR spectral data with those of 1-deoxyerythritol, which was obtained as an epimeric mixture of 1-deoxythreitol from fennel.⁴) As **20** showed a minus optical rotation value opposite that of synthetic 1-deoxy-D-erythritol ([α]_D +16°),¹³) **20** was concluded to be 1-deoxy-L-erythritol.

Glucide **21** (C₅H₁₂O₄, an amorphous powder, [α]_D²⁴ -3°) was indicated to be 1-deoxypentitol by the ¹H- and ¹³C-NMR spectral data. Comparison of these data with those of four possible 1-deoxypentitol, three natural products, 1-deoxy-ribitol,⁴) 1-deoxy-xylitol⁴) and 1-deoxy-lyxitol^{6b)} do not give concordant data, but synthetic 1-deoxy-arabinitol¹³) showed identical spectral data. As 1-deoxy-L-arabinitol ([α]_D -1°)¹³) showed minus optical rotation, the same as **21**, glucide **21** was identified as 1-deoxy-L-arabinitol.

Glucide **22**, **23**, **24** and **25** were identical with 1-deoxy-D-ribitol,⁴) 1-deoxy-D-glucitol,⁴) 2-deoxy-D-ribino-1,4-lactone⁴) and D-hamamelose,¹⁴) respectively.

As the water-soluble constituent of ajowan, four hydroxythymol glucosides (**3** to **6**) were obtained in more than 1% yield from the methanol extract.

Experimental

The instruments used and the experimental conditions for obtaining spectral data and for chromatography were the same as in the previous paper.^{6b)} HPLC separation was carried out with Symmetryprep C18 7 μ m [Waters; column size, 7.8 \times 300 mm; ODS], Carbohydrate Analysis [Waters; column size, 3.9 \times 300 mm; CHA], Wakobeads T-100s [Wako; column size,

6.0×150 mm; WBT] and Wakosil 5NH₂ [Wako; column size, 4.0×300 mm] columns. Acetylation was done in the usual way using Ac₂O and pyridine, and no acetoxy group was detected by NMR spectral data for those acetylated fractions.

Extraction and Separation Commercial ajowan (the fruit of *Carum ajowan*; purchased from Asaoka Spices, Ltd., Lot. No. 93010; 1.95 kg) were extracted with ether (41×2) at room temperature. After removing the ether extract portion (52.0 g) which contained the essential oil, the residue was extracted with methanol (41×3) at room temperature. After evaporation of the solvent, the residue (65.3 g) was partitioned into ether–water, and the aqueous portion (40.6 g) was subjected to Amberlite XAD-II (H₂O→MeOH). The methanol eluate (17.0 g) was chromatographed over Sephadex LH-20 (MeOH) to give seven fractions (frs. A–G). Fraction D (7.87 g) was chromatographed over silica gel [CHCl₃–MeOH–H₂O (17:3:0.2→4:1:0.1→7:3:0.5)→MeOH] to give 28 fractions (frs. D₁–D₂₈). Fraction D₃ (61 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give seven fractions (frs. D_{3,1}–D_{3,7}). Fraction D_{3,3} was subjected to HPLC [ODS, MeCN–H₂O (3:37)] to give **10** (5 mg) and **13** (2 mg). Fraction D₄ (67 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give nine fractions (frs. D_{4,1}–D_{4,9}). Fraction D_{4,4} was subjected to Sephadex LH-20 (MeOH) and HPLC [ODS, MeCN–H₂O (1:9)] to give **12** (4 mg). Fraction D_{4,5} was subjected to HPLC [ODS, MeCN–H₂O (1:9)] to give **9** (10 mg). Fraction D₇ (1.40 g) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give eight fractions (frs. D_{7,1}–D_{7,8}). Fraction D_{7,2} was subjected to HPLC [CHA, MeCN–H₂O (49:1)] to give **1** (5 mg) and **11** (2 mg). Fraction D_{7,4} was subjected to HPLC [CHA, MeCN–H₂O (97:3)] to give **8** (25 mg), and fr. D_{7,6} was subjected to HPLC [ODS, MeCN–H₂O (3:17)] to give **17** (10 mg), **4** (34 mg), **3** (822 mg) and **7** (21 mg). Fraction D₁₀ (417 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give 17 fractions (frs. D_{10,1}–D_{10,17}), and from fr. D_{10,14}: **5** (25 mg) was isolated by HPLC [ODS, MeCN–H₂O (1:4)]. Fraction D₁₃ (156 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give 17 fractions (frs. D_{13,1}–D_{13,17}), and from fr. D_{13,5}: **16** (5 mg) was isolated by HPLC [ODS, MeCN–H₂O (3:37)] and Sephadex LH-20 (MeOH). Fraction D₁₄ (233 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give 12 fractions (frs. D_{14,1}–D_{14,12}), and from fr. D_{14,5}: **14** (3 mg) and **15** (3 mg) were isolated by HPLC [Wakosil 5NH₂, MeCN–H₂O (9:1)]. Fraction D₁₈ (355 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give nine fractions (frs. D_{18,1}–D_{18,9}), and from fr. D_{18,2}: **2** (5 mg) was isolated by HPLC [ODS, MeCN–H₂O (1:19)]. Fraction D₂₂ (250 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (3:17)] to give seven fractions (frs. D_{22,1}–D_{22,7}), and from fr. D_{22,3}: **6** (8 mg) was isolated by HPLC [ODS, MeCN–H₂O (3:37)].

The water eluate (23.2 g) was chromatographed over Sephadex LH-20 [MeOH–H₂O (9:1)] to give four fractions (frs. H–K). Fraction I (19.5 g) was chromatographed over silica gel [CHCl₃–MeOH–H₂O (17:3:0.2→4:1:0.1→7:3:0.5→6:4:0.5)→MeOH] to give 23 fractions (frs. I₁–I₂₃). Fraction I₄ (50 mg) was subjected to Sephadex LH-20 (MeOH) and HPLC [CHA, MeCN–H₂O (99:1)] to give **24** (25 mg). Fraction I₇ (62 mg) was passed through a Lobar RP-8 column [MeCN–H₂O (1:99)] to give six fractions (frs. I_{7,1}–I_{7,6}), and from fr. I_{7,3}: **20** (6 mg) was isolated by HPLC [CHA, MeCN–H₂O (99:1)]. Fraction I₉ (758 mg) was passed through a Lobar RP-8 column (H₂O) to give six fractions (frs. I_{9,1}–I_{9,6}), and fr. I_{9,6} was subjected to HPLC [CHA, MeCN–H₂O (97:3)]. The main fraction was acetylated with Ac₂O and pyridine, and the acetylated fraction was subjected to HPLC [ODS, MeCN–H₂O (1:1)] to give two fractions (frs. I_{9,3a} and I_{9,3b}). These two fractions were deacetylated by heating in a water bath with 5% NH₄OH–MeOH for 2 h, and passed through Sephadex LH-20 (MeOH) to give **18** (40 mg) and a mixture of **21** and **22** (120 mg). A part of this mixture (12 mg) was subjected to HPLC [WBT×2, MeCN–H₂O (17:3)] to give **21** (11 mg) and **22** (1 mg), respectively. Fraction I₁₄ (662 mg) was passed through a Lobar RP-8 column (H₂O) to give 12 fractions (frs. I_{14,1}–I_{14,12}). Fraction I_{14,4} and fr. I_{14,6} were subjected to HPLC [CHA, MeCN–H₂O (24:1)] to give **19** (13 mg) and **23** (30 mg), respectively. Fraction I₁₆ (494 mg) was passed through a Lobar RP-8 column (H₂O) to give eight fractions (frs. I_{16,1}–I_{16,8}), and from fr. I_{16,3}: **25** (51 mg) was isolated by HPLC [CHA, MeCN–H₂O (14:1)].

The following compounds were identified by comparison with authentic compounds or published physical and spectral data. 3,7-Dimethyloct-3(10)-ene-1,2,6,7-tetrol (**1**), (2*S*,6*ζ*)-3,7-dimethyloct-3(10)-ene-1,2,6,7-tetrol 1-*O*-β-D-glucopyranoside (**2**), 6-Hydroxythymol 6-*O*-β-D-glucopyranoside (**3**), 6-hydroxythymol 3-*O*-β-D-glucopyranoside (**4**), 2-methyl-3-buten-2-ol β-D-glucopyranoside (**11**), benzyl β-D-glucopyranoside (**12**), 1'-(3-hydroxy-4,5-dimethoxyphenyl)-propane-2',3'-diol (**13**), adenosine (**16**), uridine (**17**),

(2*S*,3*R*)-2-methylbutane-1,2,3,4-tetrol (**18**), (3*R*)-2-hydroxymethylbutane-1,2,3,4-tetrol (**19**), 1-deoxy-D-ribose (**22**), 1-deoxy-D-glucitol (**23**), 2-deoxy-D-ribose-1,4-lactone (**24**) and D-hamamelose (**25**).

7-Hydroxythymol 3-*O*-β-D-Glucopyranoside (**5**): An amorphous powder, [α]_D²⁵ –60° (*c*=1.9, MeOH). Positive FAB-MS *m/z*: 657 [2M+H]⁺, 351.1440 [M+Na]⁺ (Calcd for C₁₆H₂₄O₇Na; 351.1420), 311 [M–H₂O+H]⁺, 167 [M–C₆H₁₀O₅+H]⁺, 149 [M–C₆H₁₂O₆+H]⁺ (base). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ: 7.83 (1H, s, H-2), 7.32 (1H, d, *J*=8.0 Hz, H-5), 7.35 (1H, d, *J*=8.0 Hz, H-6), 4.94, 4.97 (each 2H, d, *J*=13.5 Hz, H₂-7), 3.76 (1H, sept, *J*=7.0 Hz, H-8), 1.26 (6H, d, *J*=7.0 Hz, H₃-9, H₃-10), 5.59 (1H, d, *J*=7.0 Hz, Glc H-1), 4.33–4.38 (3H, m, Glc H-2, Glc H-4, Glc H-6a), 4.30 (1H, t, *J*=9.0 Hz, Glc H-3), 3.99 (1H, m, Glc H-5), 4.48 (1H, dd, *J*=2.0, 12.0 Hz, Glc H-6b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ: Table 1.

6-Hydroxythymol 3,6-Di-*O*-β-D-glucopyranoside (**6**): An amorphous powder, [α]_D²⁵ –62° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 513.1945 [M+Na]⁺ (Calcd for C₂₂H₃₄O₁₂Na; 513.1948), 491.2124 [M+H]⁺ (Calcd for C₂₂H₃₅O₁₂; 491.2129), 131 [M–2(C₆H₁₂O₆+H)]⁺ (base). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ: 7.52 (1H, s, H-2), 7.63 (1H, s, H-5), 2.40 (3H, s, H₃-7), 3.81 (1H, sept, *J*=7.0 Hz, H-8), 1.24, 1.30 (each 3H, d, *J*=7.0 Hz, H₃-9, H₃-10), 5.51 (1H, d, *J*=7.0 Hz, Glc H-1), 5.52 (1H, d, *J*=7.0 Hz, Glc H-1'), 4.34–4.38 (6H, m, Glc H-2, Glc H-2', Glc H-3, Glc H-3', Glc H-4, Glc H-4'), 4.09 (2H, m, Glc H-5, Glc H-5'), 4.41 (2H, dd, *J*=5.0, 11.5 Hz, Glc H-6a, Glc H-6a'), 4.55, 4.57 (each 1H, dd, *J*=2.0, 11.5 Hz, Glc H-6b, Glc H-6b'). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ: Table 1.

(4*S*)-*p*-Menth-1-ene-4,7-diol 4-*O*-β-D-Glucopyranoside (**7**): An amorphous powder, [α]_D²⁴ –15° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 665 [2M+H]⁺, 355.1732 [M+Na]⁺ (Calcd for C₁₆H₂₈O₇Na; 355.1733), 333.1909 [M+H]⁺ (Calcd for C₁₆H₂₉O₇; 333.1913), 315 [M–H₂O+H]⁺, 153 [M–C₆H₁₂O₆+H]⁺ (base). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ: 5.88 (1H, brs, H-2), 2.36 (1H, brd, *J*=18.0 Hz, H-3_{ax}), 2.61 (1H, brd, *J*=18.0 Hz, H-3_{eq}), 1.75 (1H, ddd, *J*=5.5, 8.5, 13.5 Hz, H-5_{ax}), 2.08 (1H, ddd, *J*=5.5, 5.5, 13.5 Hz, H-5_{eq}), 2.85 (1H, ddd, *J*=5.5, 8.5, 18.0 Hz, H-6_{ax}), 2.21 (1H, ddd, *J*=5.5, 5.5, 18.0 Hz, H-6_{eq}), 4.30 (2H, brs, H₂-7), 2.14 (1H, sept, *J*=7.0 Hz, H-8), 1.07 (3H, d, *J*=7.0 Hz, H₃-9), 1.05 (3H, d, *J*=7.0 Hz, H₃-10), 5.03 (1H, d, *J*=7.0 Hz, Glc H-1), 3.99 (1H, dd, *J*=7.0, 9.0 Hz, Glc H-2), 4.23 (1H, t, *J*=9.0 Hz, Glc H-3), 4.19 (1H, t, *J*=9.0 Hz, Glc H-4), 3.91 (1H, m, Glc H-5), 4.33 (1H, dd, *J*=5.5, 11.5 Hz, Glc H-6a), 4.52 (1H, dd, *J*=2.5, 11.5 Hz, Glc H-6b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ: Table 1.

Enzymatic Hydrolysis of 7 A mixture of **7** (11 mg) and hesperidinase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was evaporated *in vacuo* to dryness and the residue was chromatographed over silica gel [CHCl₃–MeOH–H₂O (4:1:0.1 and 7:3:0.5)] to afford **7a** (3.5 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–H₂O (17:3), 2 ml/min; *t*_R 4.20 min (same location as that of D-glucose)] showed the presence of D-glucose.

(4*S*)-*p*-Menth-1-ene-4,7-diol (**7a**): An amorphous powder, [α]_D²¹ +18° (*c*=0.3, MeOH). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ: 5.90 (1H, brs, H-2), 2.18–2.38 (3H, m, H-3_{ax}, H-3_{eq}, H-6_{eq}), 1.67 (1H, dd, *J*=6.0, 10.5, 13.0 Hz, H-5_{ax}), 1.89 (1H, ddd, *J*=6.0, 6.0, 13.0 Hz, H-5_{eq}), 2.63 (1H, ddd, *J*=6.0, 10.5, 18.0 Hz, H-6_{ax}), 4.34 (2H, brs, H₂-7), 1.80 (1H, sept, *J*=7.0 Hz, H-8), 1.10 (3H, d, *J*=7.0 Hz, H₃-9), 1.05 (3H, d, *J*=7.0 Hz, H₃-10). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ: Table 1.

(4*R*,6*S*)-*p*-Menth-1-ene-4,6-diol 4-*O*-β-D-Glucopyranoside (**8**): An amorphous powder, [α]_D²⁴ –29° (*c*=1.8, MeOH). Positive FAB-MS *m/z*: 355.1735 [M+Na]⁺ (Calcd for C₁₆H₂₈O₇Na; 355.1733), 315 [M–H₂O+H]⁺ (base), 153 [M–C₆H₁₂O₆+H]⁺. ¹H-NMR (pyridine-*d*₅, 500 MHz) δ: 5.51 (1H, brs, H-2), 2.30 (1H, brd, *J*=17.0 Hz, H-3_{ax}), 2.43 (1H, brd, *J*=17.0 Hz, H-3_{eq}), 2.01 (1H, dd, *J*=9.0, 13.0 Hz, H-5_{ax}), 2.68 (1H, dd, *J*=5.0, 13.0 Hz, H-5_{eq}), 5.30 (1H, dd, *J*=5.0, 9.0 Hz, H-6_{ax}), 2.02 (3H, s, H₃-7), 2.24 (1H, sept, *J*=7.0 Hz, H-8), 1.00, 1.08 (each 3H, d, *J*=7.0 Hz, H₃-9, H₃-10), 5.06 (1H, d, *J*=7.0 Hz, Glc H-1), 3.98 (1H, dd, *J*=7.0, 9.0 Hz, Glc H-2), 4.23 (1H, t, *J*=9.0 Hz, Glc H-3), 4.16 (1H, t, *J*=9.0 Hz, Glc H-4), 3.94 (1H, m, Glc H-5), 4.30 (1H, dd, *J*=5.0, 11.5 Hz, Glc H-6a), 4.53 (1H, dd, *J*=2.0, 11.5 Hz, Glc H-6b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ: Table 1.

Enzymatic Hydrolysis of 8 A mixture of **8** (9 mg) and hesperidinase (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 described for **7** to afford **8a** (3.0 mg) and a sugar fraction. From the sugar fraction, the presence of D-glucose was revealed as **7**.

(4*R*,6*S*)-*p*-Menth-1-ene-4,6-diol (**8a**): An amorphous powder, [α]_D²¹ –20° (*c*=0.2, MeOH). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ: 5.53 (1H, brs, H-2), 2.20 (1H, brd, *J*=18.0 Hz, H-3_{ax}), 2.28 (1H, brd, *J*=18.0 Hz, H-3_{eq}), 1.94

(1H, dd, $J=9.0$, 12.5 Hz, H-5_{ax}), 2.57 (1H, dd, $J=5.0$, 12.5 Hz, H-5_{eq}), 4.97 (1H, dd, $J=5.5$, 9.0 Hz, H-6_{ax}), 2.07 (3H, s, H₃₋₇), 1.81 (1H, sept, $J=7.0$ Hz, H-8), 1.04, 1.11 (each 3H, d, $J=7.0$ Hz, H₃₋₉, H₃₋₁₀). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : Table 1.

3 β -Hydroxy-*p*-menth-1-en-4 β ,5 β -oxide 3-*O*- β -D-Glucopyranoside (9): An amorphous powder, $[\alpha]_D^{24} +45^\circ$ ($c=0.5$, MeOH). Positive FAB-MS m/z : 353 [M+Na]⁺, 331.1777 [M+H]⁺ (Calcd for C₁₆H₂₇O₇; 333.1757), 313 [M-H₂O+H]⁺, 151 [M-C₆H₁₂O₆+H]⁺ (base). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 5.85 (1H, br d, $J=5.0$ Hz, H-2), 4.90 (1H, br d, $J=5.0$ Hz, H-3), 3.42 (1H, br dd, $J=2.0$, 3.0 Hz, H-5), 2.42 (1H, br d, $J=19.0$ Hz, H-6_{ax}), 2.55 (1H, br d, $J=19.0$ Hz, H-6_{eq}), 1.46 (3H, s, H₃₋₇), 3.11 (1H, sept, $J=7.0$ Hz, H-8), 0.87 (3H, d, $J=7.0$ Hz, H₃₋₉), 1.24 (3H, d, $J=7.0$ Hz, H₃₋₁₀), 5.09 (1H, d, $J=8.0$ Hz, Glc H-1), 4.08 (1H, dd, $J=8.0$, 9.0 Hz, Glc H-2), 4.28 (1H, t, $J=9.0$ Hz, Glc H-3), 4.21 (1H, t, $J=9.0$ Hz, Glc H-4), 3.98 (1H, m, Glc H-5), 4.37 (1H, dd, $J=5.5$, 11.5 Hz, Glc H-6a), 4.59 (1H, dd, $J=2.5$, 11.5 Hz, Glc H-6b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : Table 1.

Enzymatic Hydrolysis of 9 A mixture of **9** (5 mg) and β -glucosidase (5 mg) in water (5 ml) was shaken in a water bath at 37 °C for 15 d. The mixture was treated in the same way described for **7** to afford **9a** (2 mg) and a sugar fraction. From the sugar fraction, the presence of *D*-glucose was revealed as **7**.

3 β -Hydroxy-*p*-menth-1-en-4 β ,5 β -oxide (9a): An amorphous powder, $[\alpha]_D^{22} +53^\circ$ ($c=0.1$, MeOH). Positive FAB-MS m/z : 169 [M+H]⁺, 151 [M-H₂O+H]⁺ (base). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 5.72 (1H, br s, H-2), 4.78 (1H, br s, H-3_{eq}), 3.30 (1H, br dd, $J=1.5$, 2.5 Hz, H-5_{eq}), 2.21 (1H, br d, $J=19.0$ Hz, H-6_{ax}), 2.39 (1H, br d, $J=19.0$ Hz, H-6_{eq}), 1.56 (3H, s, H₃₋₇), 2.74 (1H, sept, $J=7.0$ Hz, H-8), 1.04 (3H, d, $J=7.0$ Hz, H₃₋₉), 1.28 (3H, d, $J=7.0$ Hz, H₃₋₁₀). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : Table 1.

***p*-Menth-3-ene-1 β ,2 β ,5 β -triol (10):** An amorphous powder, $[\alpha]_D^{23} +2^\circ$ ($c=0.2$, MeOH). Positive FAB-MS m/z : 373 [2M+H]⁺, 225 [M+K]⁺, 209.1161 [M+Na]⁺ (base, Calcd for C₄₀H₁₈O₃Na; 209.1154), 187 [M+H]⁺, 169 [M-H₂O+H]⁺, 151 [M-2H₂O+H]⁺ (base). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 4.73 (1H, br s, H-2), 5.89 (1H, br s, H-3), 4.66 (1H, dd, $J=5.5$, 7.5 Hz, H-5), 2.37 (1H, dd, $J=7.5$, 13.0 Hz, H-6_{ax}), 2.62 (1H, dd, $J=5.5$, 13.0 Hz, H-6_{eq}), 1.67 (3H, s, H₃₋₇), 2.97 (1H, sept, $J=7.0$ Hz, H-8), 1.17 (3H, d, $J=7.0$ Hz, H₃₋₉), 1.18 (3H, d, $J=7.0$ Hz, H₃₋₁₀). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : Table 1.

1'-(3-Hydroxy-4,5-dimethoxyphenyl)-propane-2',3'-diol (13): ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 7.12 (1H, d, $J=1.8$ Hz, H-2), 6.73 (1H, d, $J=1.8$ Hz, H-6), 3.08 (1H, dd, $J=8.0$, 13.5 Hz, H-1'a), 3.22 (1H, dd, $J=5.0$, 13.5 Hz, H-1'b), 4.44 (1H, m, H-2'), 4.08 (2H, m, H₂₋₃), 3.89 (3H, s, 4-OCH₃), 3.73 (3H, s, 5-OCH₃). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : Table 2.

1'-(3-Hydroxy-4,5-dimethoxyphenyl)-propane-2',3'-diol 3'-*O*- β -D-Glucopyranoside (14): An amorphous powder, $[\alpha]_D^{23} -6^\circ$ ($c=0.1$, MeOH). Positive FAB-MS m/z : 413 [M+Na]⁺, 391.1616 [M+H]⁺ (Calcd for C₁₇H₂₇O₁₀; 391.1604), 229 [M-C₆H₁₀O₅+H]⁺ (base). ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 7.09 (1H, d, $J=1.5$ Hz, H-2), 6.69 (1H, d, $J=1.5$ Hz, H-6), 3.03 (1H, dd, $J=7.5$, 13.5 Hz, H-1'a), 3.13 (1H, dd, $J=5.0$, 13.5 Hz, H-1'b), 4.51 (1H, m, H-2'), 4.04 (1H, dd, $J=4.5$, 10.0 Hz, H-3'a), 4.35 (1H, dd, $J=6.0$, 10.0 Hz, H-3'b), 3.89 (3H, s, 4-OCH₃), 3.74 (3H, s, 5-OCH₃), 4.99 (1H, d, $J=7.5$ Hz, Glc H-1), 4.11 (1H, dd, $J=7.5$, 8.5 Hz, Glc H-2), 4.27 (2H, m, Glc H-3, Glc H-4), 3.96 (1H, m, Glc H-5), 4.40 (1H, dd, $J=5.0$, 12.0 Hz, Glc H-6a), 4.56 (1H, dd, $J=2.5$, 12.0 Hz, Glc H-6b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : Table 2.

3,4-Dihydroxyphenylpropanol β -D-Glucopyranoside (15): An amorphous powder, $[\alpha]_D^{23} -41^\circ$ ($c=0.2$, MeOH). Positive FAB-MS m/z : 331.1375 [M+H]⁺ (base, Calcd for C₁₅H₂₃O₈; 331.1393), 169 [M-C₆H₁₀O₅+H]⁺. ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 7.55 (1H, d, $J=2.0$ Hz, H-2), 7.21 (1H, d, $J=8.5$ Hz, H-5), 6.99 (1H, dd, $J=2.0$, 8.5 Hz, H-6), 2.77 (2H, t, $J=7.5$ Hz, H_{2-1'}), 2.00 (2H, dddd, $J=6.5$, 6.5, 7.5, 7.5 Hz, H_{2-2'}), 3.85 (2H, br t, $J=6.5$ Hz, H_{2-3'}), 5.47 (1H, d, $J=7.5$ Hz, Glc H-1), 4.26—4.34 (3H, m, Glc

H-2, Glc H-3, Glc H-4), 4.40 (1H, dd, $J=5.0$, 12.0 Hz, Glc H-6a), 4.53 (1H, dd, $J=2.0$, 12.0 Hz, Glc H-6b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : Table 2.

1-Deoxy-L-erythritol (20): An amorphous powder, $[\alpha]_D^{23} -30^\circ$ ($c=0.3$, H₂O). Positive FAB-MS m/z : 129.0520 [M+Na]⁺ (base, Calcd for C₄H₁₀O₃Na; 129.0528), 71 [M-H₂O+H]⁺, 53 [M-3H₂O+H]⁺. ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 1.65 (3H, d, $J=6.5$ Hz, H₃₋₁), 4.37 (1H, dq, $J=6.5$, 6.5 Hz, H-2), 4.17 (1H, ddd, $J=4.5$, 6.5, 6.5 Hz, H-3), 4.29 (1H, dd, $J=6.5$, 11.0 Hz, H-4a), 4.38 (1H, dd, $J=4.5$, 11.0 Hz, H-4b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : 20.34 (C-1), 69.43 (C-2), 77.17 (C-3), 65.13 (C-4).

1-Deoxy-L-arabinitol (21): An amorphous powder, $[\alpha]_D^{24} -3^\circ$ ($c=0.5$, H₂O). Positive FAB-MS m/z : 159 [M+Na]⁺, 137.0806 [M+H]⁺ (base, Calcd for C₅H₁₃O₄; 137.0814), 119 [M-H₂O+H]⁺, 101 [M-2H₂O+H]⁺. ¹H-NMR (pyridine-*d*₅, 500 MHz) δ : 1.60 (3H, d, $J=6.5$ Hz, H₃₋₁), 4.71 (1H, dq, $J=2.5$, 6.5 Hz, H-2), 4.07 (1H, dd, $J=2.5$, 7.0 Hz, H-3), 4.52 (1H, ddd, $J=4.0$, 5.5, 7.0 Hz, H-4), 4.36 (1H, dd, $J=5.5$, 11.0 Hz, H-5a), 4.48 (1H, dd, $J=4.0$, 11.0 Hz, H-5b). ¹³C-NMR (pyridine-*d*₅, 125 MHz) δ : 20.65 (C-1), 67.48 (C-2), 76.07 (C-3), 73.57 (C-4), 65.27 (C-5).

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