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 ^{13}C-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*,6ζ)-3,7-dimethyloct-3(10)-ene-1,2,6,7-tetrol 1-*O*-β-D-glucopyranoside,[6] 6-hydroxythymol 6-*O*-β-D-glucopyranoside[7] and 6-hydroxythymol 3-*O*-β-D-glucopyranoside,[7] respectively.

Monoterpenoid glucosides **5** ($C_{16}H_{24}O_7$, an amorphous powder, $[\alpha]_D^{25}$ −60°) and **6** ($C_{22}H_{34}O_{12}$, an amorphous powder, $[\alpha]_D^{23}$ −62°) were glucosides of hydroxythymol and their ^{13}C-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; H_2-7/C-1, C-2, C-6; H-8/C-3, C-4. C-5, C-9, C-10; H_3-9/C-4, C-8, C-10; H_3-10/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 ^{1}H- and ^{13}C-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; H_3-7/C-1, C-2, C-6; H-8/C-3, C-4. C-5, C-9, C-10; H_3-9/C-4, C-8, C-10; H_3-10/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** ($C_{16}H_{28}O_7$, an amorphous powder, $[\alpha]_D^{24}$ −15°) 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 ^{1}H- and ^{13}C-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; H_2-7/C-1, C-2, C-6; H-8/C-3, C-4. C-5, C-9, C-10; H_3-9/C-4, C-8, C-10; H_3-10/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**; $C_{10}H_{18}O_2$, an amorphous powder, $[\alpha]_D^{21}$ +18°), 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°) contrary to that of the 4*R* form ($[\alpha]_D$ −36°),[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°) was also a glucoside of *p*-menth-1-ene-diol. From the results of ^{1}H-, ^{13}C-NMR and the HMBC spectral 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; H_3-7/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-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-4β,6α-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°) 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

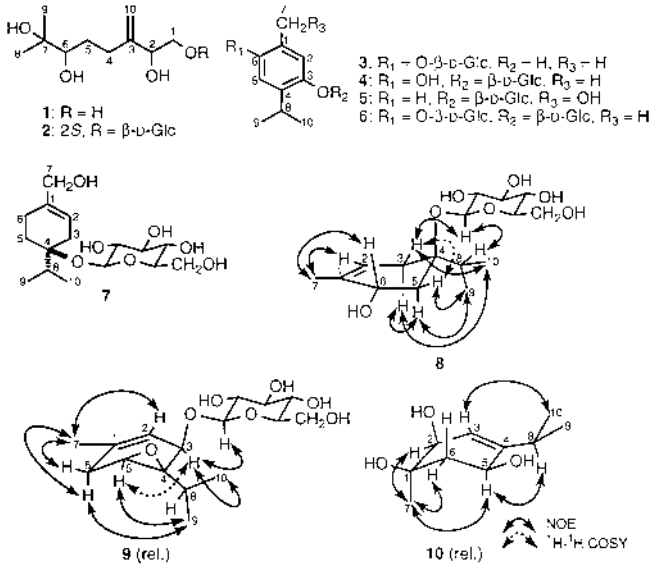

Fig. 1. Structures of **1**—**10**, and NOE and ^{1}H–^{1}H COSY Correlations of **8**—**10**

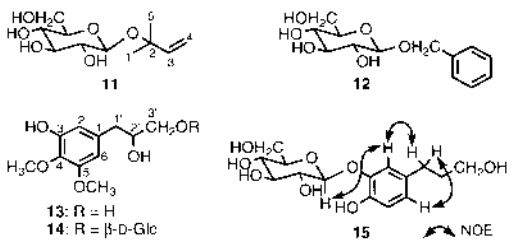

Fig. 2. Structures of **11**—**15**, and NOE Interactions Observed in the NOESY Spectrum of **15**

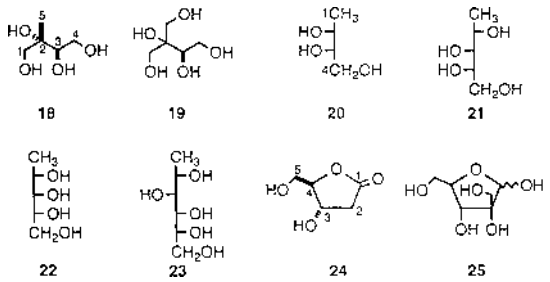

Fig. 3. Structures of **18**—**25**

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; H_3-7/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-3), **9** was clarified to be a glucopyranoside of a menth-1-ene type monoterpenoid 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**; $C_{10}H_{16}O_2$, an amorphous powder, $[\alpha]_D^{22}$ +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 H_3-9, H-6_{ax} and H_3-9 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 3β-hydroxy-*p*-menth-1-en-4β,5β-oxide 3-*O*-β-D-glucopyranoside.

Monoterpenoid **10** ($C_{10}H_{18}O_3$, an amorphous powder, $[\alpha]_D^{23}$ +2°) showed $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 209 and 187 in the positive FAB-MS. The ^1H- and ^{13}C-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; H_2-6/C-1, C-2, C-4, C-5, C-7; H_3-7/C-1, C-2, C-6; H_3-9/C-4, C-8, C-10; H_3-10/C-4, C-8, C-9), **10** was suggested to be *p*-menth-3-ene-1,2,5-triol. As NOE interactions between H-2_{eq} and H_3-7, H-5_{ax} and H_3-7, and between H-6_{eq} and H_3-7 were observed in the NOESY spectrum of **10**, the orientation of H-2_{eq}, H-5_{ax}, H-6_{eq} and H_3-7 should be the same. So, **10** was concluded to be *p*-menth-3-ene-1β,2β,5β-triol.

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

Aromatic compound glucoside **14** ($C_{17}H_{26}O_{10}$, an amorphous powder, $[\alpha]_D^{23}$ −6°) was suggested to be a β-glucopyranoside of **13** by the ^1H- and ^{13}C-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** ($C_{15}H_{22}O_8$, an amorphous powder, $[\alpha]_D^{23}$ −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 ^{13}C-NMR spectal 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.

Table 2. ^{13}C-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.

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-tetrol[12] and (3*R*)-2-hydroxymethylbutane-1,2,3,4-tetrol,[12] respectively.

Glucide **20** ($C_4H_{10}O_3$, an amorphous powder, $[\alpha]_D^{24}$ −30°) was made up of one *sec*-methyl, one hydroxylated methylene, and two hydroxylated methines, and showed identical ^1H- and ^{13}C-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 ($[\alpha]_D$ +16°),[13] **20** was concluded to be 1-deoxy-L-erythritol.

Glucide **21** ($C_5H_{12}O_4$, an amorphous powder, $[\alpha]_D^{24}$ −3°) was indicated to be 1-deoxypentitol by the ^1H- and ^{13}C-NMR spectral data. Comparison of these data with those of four possible 1-deoxypentitol, three natural products, 1-deoxy-ribitol,[4] 1-deoxy-xylitol[4] and 1-deoxy-lyxitol[6b)] do not give concordant data, but synthetic 1-deoxy-arabinitol[13] showed identical spectral data. As 1-deoxy-L-arabinitol ($[\alpha]_D$ −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-lactone[4] 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 μm [Waters; column size, 7.8×300 mm; ODS], Carbohydrate Analysis [Waters; column size, 3.9×300 mm; CHA], Wakobeads T-100s [Wako; column size,

6.0×150 mm; WBT] and Wakosil 5NH_2 [Wako; column size, 4.0×300 mm] columns. Acetylation was done in the usual way using Ac_2O and pyridine, and no acetoxyl 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 (4 l×2) at room temperature. After removing the ether extract portion (52.0 g) which contained the essential oil, the residue was extracted with methanol (4 l×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 (H_2O→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 [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2→4 : 1 : 0.1→7 : 3 : 0.5)→MeOH] to give 28 fractions (frs. D_1—D_{28}). Fraction D_3 (61 mg) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give seven fractions (frs. $D_{3\text{-}1}$—$D_{3\text{-}7}$). Fraction $D_{3\text{-}3}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 37)] to give **10** (5 mg) and **13** (2 mg). Fraction D_4 (67 mg) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give nine fractions (frs. $D_{4\text{-}1}$—$D_{4\text{-}9}$). Fraction $D_{4\text{-}4}$ was subjected to Sephadex LH-20 (MeOH) and HPLC [ODS, MeCN–H_2O (1 : 9)] to give **12** (4 mg). Fraction $D_{4\text{-}5}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 9)] to give **9** (10 mg). Fraction D_7 (1.40 g) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give eight fractions (frs. $D_{7\text{-}1}$—$D_{7\text{-}8}$). Fraction $D_{7\text{-}2}$ was subjected to HPLC [CHA, MeCN–H_2O (49 : 1)] to give **1** (5 mg) and **11** (2 mg). Fraction $D_{7\text{-}4}$ was subjected to HPLC [CHA, MeCN–H_2O (97 : 3)] to give **8** (25 mg), and fr. $D_{7\text{-}6}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **17** (10 mg), **4** (34 mg), **3** (822 mg) and **7** (21 mg). Fraction D_{10} (417 mg) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 17 fractions (frs. $D_{10\text{-}1}$—$D_{10\text{-}17}$), and from fr. $D_{10\text{-}14}$, **5** (25 mg) was isolated by HPLC [ODS, MeCN–H_2O (1 : 4)]. Fraction D_{13} (156 mg) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 17 fractions (frs. $D_{13\text{-}1}$—$B_{13\text{-}17}$), and from fr. $D_{13\text{-}5}$, **16** (5 mg) was isolated by HPLC [ODS, MeCN–H_2O (3 : 37)] and Sephadex LH-20 (MeOH). Fraction D_{14} (233 mg) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give 12 fractions (frs. $D_{14\text{-}1}$—$B_{14\text{-}12}$), and from fr. $D_{14\text{-}5}$, **14** (3 mg) and **15** (3 mg) were isolated by HPLC [Wakosil 5NH_2, MeCN–H_2O (9 : 1)]. Fraction D_{18} (355 mg) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give nine fractions (frs. $D_{18\text{-}1}$—$B_{18\text{-}9}$), and from fr. $D_{18\text{-}2}$, **2** (5 mg) was isolated by HPLC [ODS, MeCN–H_2O (1 : 19)]. Fraction D_{22} (250 mg) was passed through a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give seven fractions (frs. $D_{22\text{-}1}$—$B_{22\text{-}7}$), and from fr. $D_{22\text{-}3}$, **6** (8 mg) was isolated by HPLC [ODS, MeCN–H_2O (3 : 37)].

The water eluate (23.2 g) was chromatographed over Sephadex LH-20 [MeOH–H_2O (9 : 1)] to give four fractions (frs. H—K). Fraction I (19.5 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (17 : 3 : 0.2→4 : 1 : 0.1→7 : 3 : 0.5→6 : 4 : 0.5)→MeOH] to give 23 fractions (frs. I_1—I_{23}). Fraction I_4 (50 mg) was subjected to Sephadex LH-20 (MeOH) and HPLC [CHA, MeCN–H_2O (99 : 1)] to give **24** (25 mg). Fraction I_7 (62 mg) was passed through a Lobar RP-8 colum [MeCN–H_2O (1 : 99)] to give six fractions (frs. $I_{7\text{-}1}$—$I_{7\text{-}6}$), and from fr. $I_{7\text{-}3}$, **20** (6 mg) was isolated by HPLC [CHA, MeCN–H_2O (99 : 1)]. Fraction I_9 (758 mg) was passed through a Lobar RP-8 colum (H_2O) to give six fractions (frs. $I_{9\text{-}1}$—$I_{9\text{-}6}$), and fr. $I_{9\text{-}6}$ was subjected to HPLC [CHA, MeCN–H_2O (97 : 3)]. The main fraction was acetylated with Ac_2O and pyridine, and the acetylated fraction was subjected to HPLC [ODS, MeCN–H_2O (1 : 1)] to give two fractions (frs. $I_{9\text{-}3a}$ and $I_{9\text{-}3b}$). These two fractions were deacetylated by heating in a water bath with 5% NH_4OH–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–H_2O (17 : 3)] to give **21** (11 mg) and **22** (1 mg), respectively. Fraction I_{14} (662 mg) was passed through a Lobar RP-8 column (H_2O) to give 12 fractions (frs. $I_{14\text{-}1}$—$I_{14\text{-}12}$). Fraction $I_{14\text{-}4}$ and fr. $I_{14\text{-}6}$ were subjected to HPLC [CHA, MeCN–H_2O (24 : 1)] to give **19** (13 mg) and **23** (30 mg), respectively. Fraction I_{16} (494 mg) was passed through a Lobar RP-8 column (H_2O) to give eight fractions (frs. $I_{16\text{-}1}$—$I_{16\text{-}8}$), and from fr. $I_{16\text{-}3}$, **25** (51 mg) was isolated by HPLC [CHA, MeCN–H_2O (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*,6ζ)-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-ribitol (**22**), 1-deoxy-D-glucitol (**23**), 2-deoxy-D-ribino-1,4-lactone (**24**) and D-hamamelose (**25**).

7-Hydroxythymol 3-*O*-*β*-D-Glucopyranoside (**5**): An amorphous powder, $[\alpha]_D^{25}$ −60° (*c*=1.9, MeOH). Positive FAB-MS *m/z*: 657 $[2M+H]^+$, 351.1440 $[M+Na]^+$ (Calcd for $C_{16}H_{24}O_7Na$; 351.1420), 311 $[M-H_2O+H]^+$, 167 $[M-C_6H_{10}O_5+H]^+$, 149 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-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, H_2-7), 3.76 (1H, sept, *J*=7.0 Hz, H-8), 1.26 (6H, d, *J*=7.0 Hz, H_3-9, H_3-10), 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). ^{13}C-NMR (pyridine-d_5, 125 MHz) *δ*: Table 1.

6-Hydroxythymol 3,6-Di-*O*-*β*-D-glucopyranoside (**6**): An amorphous powder, $[\alpha]_D^{23}$ −62° (*c*=0.3, MeOH). Positive FAB-MS *m/z*: 513.1945 $[M+Na]^+$ (Calcd for $C_{22}H_{34}O_{12}Na$; 513.1948), 491.2124 $[M+H]^+$ (Calcd for $C_{22}H_{35}O_{12}$; 491.2129), 131 $[M-2(C_6H_{12}O_6)+H]^+$ (base). ^{1}H-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, H_3-9, H_3-10), 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′). ^{13}C-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, $[\alpha]_D^{24}$ −15° (*c*=0.5, MeOH). Positive FAB-MS *m/z*: 665 $[2M+H]^+$, 355.1732 $[M+Na]^+$ (Calcd for $C_{16}H_{28}O_7Na$; 355.1733), 333.1909 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$; 355.1913), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: 5.88 (1H, br s, H-2), 2.36 (1H, br d, *J*=18.0 Hz, H-3_{ax}), 2.61 (1H, br d, *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, br s, H_2-7), 2.14 (1H, sept, *J*=7.0 Hz, H-8), 1.07 (3H, d, *J*=7.0 Hz, H_3-9), 1.05 (3H, d, *J*=7.0 Hz, H_3-10), 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). ^{13}C-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 [$CHCl_3$–MeOH–H_2O (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–H_2O (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, $[\alpha]_D^{21}$ +18° (*c*=0.3, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: 5.90 (1H, br s, H-2), 2.18—2.38 (3H, m, H-3_{ax}, H-3_{eq}, H-6_{eq}), 1.67 (1H, ddd, *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, br s, H_2-7), 1.80 (1H, sept, *J*=7.0 Hz, H-8), 1.10 (3H, d, *J*=7.0 Hz, H_3-9), 1.05 (3H, d, *J*=7.0 Hz, H_3-10). ^{13}C-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, $[\alpha]_D^{24}$ −29° (*c*=1.8, MeOH). Positive FAB-MS *m/z*: 355.1735 $[M+Na]^+$ (Calcd for $C_{16}H_{28}O_7Na$; 355.1733), 315 $[M-H_2O+H]^+$ (base), 153 $[M-C_6H_{12}O_6+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: 5.51 (1H, br s, H-2), 2.30 (1H, br d, *J*=17.0 Hz, H-3_{ax}), 2.43 (1H, br d, *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, H_3-7), 2.24 (1H, sept, *J*=7.0 Hz, H-8), 1.00, 1.08 (each 3H, d, *J*=7.0 Hz, H_3-9, H_3-10), 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). ^{13}C-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, $[\alpha]_D^{21}$ −20° (*c*=0.2, MeOH). ^{1}H-NMR (pyridine-d_5, 500 MHz) *δ*: 5.53 (1H, br s, H-2), 2.20 (1H, br d, *J*=18.0 Hz, H-3_{ax}), 2.28 (1H, br d, *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, H_3-7), 1.81 (1H, sept, J=7.0 Hz, H-8), 1.04, 1.11 (each 3H, d, J=7.0 Hz, H_3-9, H_3-10). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 1.

3β-Hydroxy-*p*-menth-1-en-4β,5β-oxide 3-*O*-β-D-Glucopyranoside (**9**): An amorphous powder, $[\alpha]_D^{24}$ +45° (c=0.5, MeOH). Positive FAB-MS *m/z*: 353 $[M+Na]^+$, 331.1777 $[M+H]^+$ (Calcd for $C_{16}H_{27}O_7$; 333.1757), 313 $[M-H_2O+H]^+$, 151 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-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, H_3-7), 3.11 (1H, sept, J=7.0 Hz, H-8), 0.87 (3H, d, J=7.0 Hz, H_3-9), 1.24 (3H, d, J=7.0 Hz, H_3-10), 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). ^{13}C-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**.

3β-Hydroxy-*p*-menth-1-en-4β,5β-oxide (**9a**): An amorphous powder, $[\alpha]_D^{22}$ +53° (c=0.1, MeOH). Positive FAB-MS *m/z*: 169 $[M+H]^+$, 151 $[M-H_2O+H]^+$ (base). ^{1}H-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, H_3-7), 2.74 (1H, sept, J=7.0 Hz, H-8), 1.04 (3H, d, J=7.0 Hz, H_3-9), 1.28 (3H, d, J=7.0 Hz, H_3-10). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 1.

p-Menth-3-ene-1β,2β,5β-triol (**10**): An amorphous powder, $[\alpha]_D^{23}$ +2° (c=0.2, MeOH). Positive FAB-MS *m/z*: 373 $[2M+H]^+$, 225 $[M+K]^+$, 209.1161 $[M+Na]^+$ (base, Calcd for $C_{40}H_{18}O_3Na$; 209.1154), 187 $[M+H]^+$, 169 $[M-H_2O+H]^+$, 151 $[M-2H_2O+H]^+$. ^{1}H-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_{ax}), 1.67 (3H, s, H_3-7), 2.97 (1H, sept, J=7.0 Hz, H-8), 1.17 (3H, d, J=7.0 Hz, H_3-9), 1.18 (3H, d, J=7.0 Hz, H_3-10). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 1.

1′-(3-Hydroxy-4,5-dimethoxyphenyl)-propane-2′,3′-diol (**13**): ^{1}H-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, H_2-3), 3.89 (3H, s, 4-OCH_3), 3.73 (3H, s, 5-OCH_3). ^{13}C-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° (c=0.1, MeOH). Positive FAB-MS *m/z*: 413 $[M+Na]^+$; 391.1616 $[M+H]^+$ (Calcd for $C_{17}H_{27}O_{10}$, 391.1604), 229 $[M-C_6H_{10}O_5]^+$ (base). ^{1}H-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-OCH_3), 3.74 (3H, s, 5-OCH_3), 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). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

3,4-Dihydroxyphenylpropanol β-D-Glucopyranoside (**15**): An amorphous powder, $[\alpha]_D^{23}$ −41° (c=0.2, MeOH). Positive FAB-MS *m/z*: 331.1375 $[M+H]^+$ (base, Calcd for $C_{15}H_{23}O_8$; 331.1393), 169 $[M-C_6H_{10}O_5+H]^+$. ^{1}H-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). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

1-Deoxy-L-erythritol (**20**): An amorphous powder, $[\alpha]_D^{23}$ −30° (c=0.3, H_2O). Positive FAB-MS *m/z*: 129.0520 $[M+Na]^+$ (base, Calcd for $C_4H_{10}O_3Na$; 129.0528), 71 $[M-H_2O+H]^+$, 53 $[M-3H_2O+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 1.65 (3H, d, J=6.5 Hz, H_3-1), 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). ^{13}C-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° (c=0.5, H_2O). Positive FAB-MS *m/z*: 159 $[M+Na]^+$, 137.0806 $[M+H]^+$ (base, Calcd for $C_5H_{13}O_4$; 137.0814), 119 $[M-H_2O+H]^+$, 101 $[M-2H_2O+H]^+$. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 1.60 (3H, d, J=6.5 Hz, H_3-1), 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). ^{13}C-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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