Water-Soluble Constituents of Amomum Seed

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From the water-soluble portion of the methanolic extract of the amomum seed (seed of *Amomum xanthioides* WALL.), which has been used as a medicine for stomachic and digestive disorders, ten compounds, including two new and three newly isolated monoterpenoid glucosides and a newly isolated octane-tetrol, were isolated. Their structures were determined by spectral investigation.

Key words amomum seed; *Amomum xanthioides* seed; Zingiberaceae; monoterpenoid glucoside; bornane-type; octane-tetrol

The seed of the Amomum plant is one of the most ancient and highly valued spices in the world. The seed of *Amomum xanthioides* WALL. (Zingiberaceae) has also been used for medicinal purposes, and is prescribed in traditional medicine for aromatic stomachic and digestive disorders.[1)] It is listed in Japanese Pharmacopoeia as "amomum seed," and contains essential oil (1—1.5%) rich in monoterpenoids (borneol, bornylacetate, linalool, *d*-camphor, camphene, α- and β-pinene, cineole and nerolidol).[2)] However, no report has been published on the constituents of the water-soluble portion of this seed. In continuation of our studies on the water-soluble constituents of spices,[3)] and to learn the relationship between the essential oil and the water-soluble constituent, we undertook an investigation of this seed. In this paper, we discuss the isolation and structure elucidation of monoterpenoid glycosides, aromatic compound glycosides, octane-tetrol and nucleoside.

The commercial amomum seed was extracted with 70% methanol, and the methanolic extract was suspended in water and successively extracted with ether and ethyl acetate. The aqueous layer was chromatographed on Amberlite XAD-II to give water and methanol eluate fractions. The methanol eluate fraction was chromatographed on Sephadex LH-20, and subjected to a combination of silica gel, Lobar RP-8 column chromatography and HPLC. Then, six monoterpenoid glucosides (**1** to **6**), two aromatic compound glucosides (**7**, **8**), an octane-tetrol (**9**) and adenosine (**10**) were isolated. Among them, two monoterpenoid glucosides (**1**, **4**) are new, and three monoterpenoid glucosides (**3**, **5**, **6**) and an octane-tetrol (**9**) are newly isolated from the plant. The new glucosides **1** and **4** are β-D-glucopyranosides as shown by their ^{13}C-NMR data (Table 2 and Experimental), and this was confirmed by

Table 1. ^{1}H-NMR Chemical Shifts of **1**, **3**—**6** and **1a** (in Pyridine-d_5, 500 MHz)

	1	**1a**	**3**	**4**
H-2*exo*	4.40 ddd (2.0, 3.5, 9.0)	4.49 br d (10.0)	4.53 dd (3.5, 9.5)	4.37 dd (3.5, 10.0)
H-3*endo*	1.35 br dd (3.5, 13.0)	1.41 br dd (3.0, 13.0)	1.44 br dd (3.5, 13.0)	1.49 br dd (3.5, 13.5)
exo	2.55 ddd (4.5, 9.0, 13.0)	2.57 m	2.31 dddd (3.5, 4.5, 9.5, 13.0)	2.37 dddd (3.5, 4.5, 10.0, 13.5)
H-4	2.23 br dd (4.5, 4.5)	2.21 br dd (4.5, 4.5)	1.75 br dd (4.5, 4.5)	1.70 br dd (4.5, 4.5)
H-5*endo*	1.41 br ddd (4.5, 9.0, 13.0)	1.48 br ddd (4.5, 9.0, 13.0)	2.01 br dd (8.0, 12.5)	1.97 br dd (8.0, 12.5)
exo	1.74 dddd (4.5, 9.0, 13.0, 13.0)	1.85 dddd (4.5, 9.0, 13.0, 13.0)	2.08 ddd (4.5, 7.5, 12.5)	2.08 ddd (4.5, 7.5, 12.5)
H-6*endo*	2.53 ddd (4.5, 9.0, 13.0)	2.60 ddd (4.5, 9.0, 13.0)	5.06 dd (7.5, 8.0)	5.08 dd (7.5, 8.0)
exo	1.31 dddd (2.0, 4.5, 13.0, 13.0)	1.41 dddd (2.0, 4.5, 13.0, 13.0)	—	—
H_3-8	1.19 s	1.29 s	1.30 s	1.32 s
H-9a	3.86 d (10.0)	3.77 d (10.5)	—	—
b	4.13 d (10.0)	4.03 d (10.5)	—	—
H_3-9	—	—	0.84 s	0.85 s
H_3-10	1.05 s	1.18 s	1.46 s	1.46 s
Glc H-1	4.86 d (7.5)	—	4.90 d (7.5)	4.98 d (7.5)

	5	**6**
H-3*endo*	1.98 br d (18.0)	1.74 br d (18.0)
exo	2.33 ddd (3.5, 4.5, 18.0)	2.26 ddd (4.0, 4.0, 18.0)
H-4	1.90 br dd (4.5, 4.5)	2.04 br dd (4.0, 4.0)
H-5*endo*	1.85 br dd (3.0, 14.0)	2.03 br dd (8.0, 13.0)
exo	2.49 dddd (3.0, 4.5, 10.0, 14.0)	2.37 dddd (4.0, 4.0, 4.0, 13.0)
H-6*endo*	—	4.00 dd (4.0, 4.0)
exo	4.39 br dd (3.0, 10.0)	—
H_3-8	0.82 s	1.20 s
H_3-9	0.70 s	0.73 s
H_3-10	1.22 s	1.37 s
Glc H-1	4.84 d (7.5)	4.76 d (8.0)

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

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

	1	1a	2	3	4	5	6
C-1	52.98	50.58	50.89	53.35	53.87	63.42	64.16
C-2	76.01	76.28	85.17	82.89	84.89	215.40	217.58
C-3	39.44	39.48	35.77	35.86	37.49	43.49	42.74
C-4	42.85	42.71	53.42	45.11	45.22	41.83	43.14
C-5	28.86	29.03	74.80	41.65	41.82	36.90	40.19
C-6	27.08	27.48	40.11	70.13	70.26	84.60	80.98
C-7	50.91 (−3.3)	54.23	47.61	48.29	47.89	47.85	47.62
C-8	15.88	15.57	21.35	21.76	21.70	19.82	21.55
C-9	73.10 (+8.7)	64.40	20.18	20.28	20.24	20.20	20.63
C-10	14.69	14.87	13.89	10.42	10.83	8.31	6.72
Glc-1	105.52		106.28	103.64	105.99	106.48	106.25
Glc-2	75.40		75.56	75.36	75.61	75.23	75.48
Glc-3	78.65		78.63	78.73	78.76	78.42	78.41
Glc-4	71.76		71.68	71.95	71.72	71.44	71.61
Glc-5	78.52		78.33	78.36	78.35	78.52	78.68
Glc-6	62.87		62.87	63.02	62.86	62.85	62.83

δ in ppm from TMS. $\Delta\delta$ (δ glucoside−aglycone) are given in parentheses.

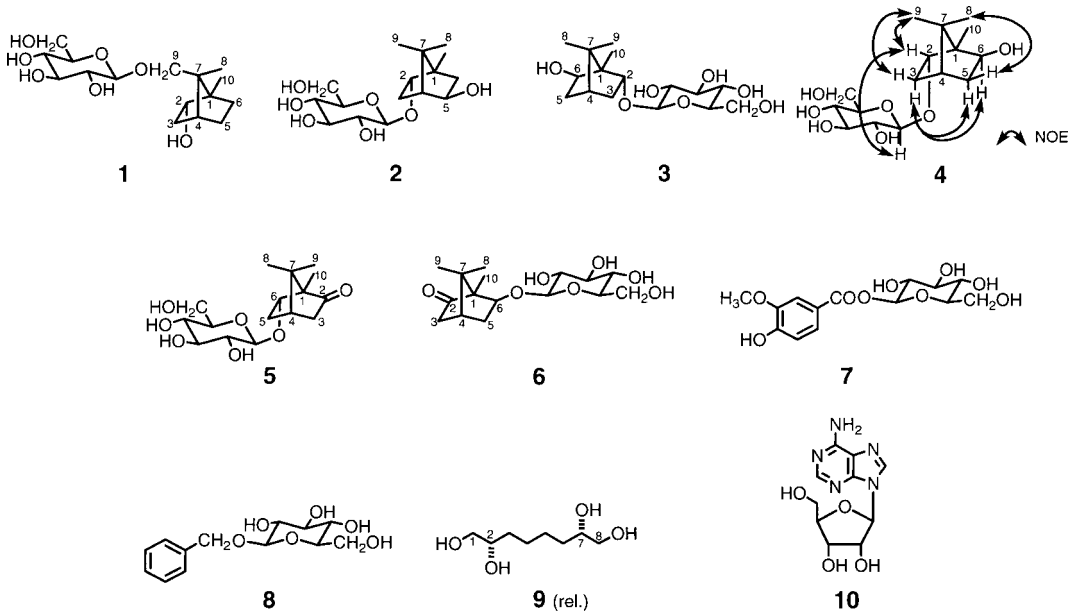

Fig. 1. Structures of **1**—**10**, and NOE Correlations of **4**

hydrolysis to yield D-glucose or by comparison of the $[\alpha]_D$ or $[M]_D$ values with those of their aglycones.[4,5] The molecular formulae of the new and newly isolated compounds were suggested from the accurate mass number of $[M+H]^+$ and/or $[M+Na]^+$ ion peak in the high-resolution positive FAB-MS.

Glucoside **1**, $C_{16}H_{28}O_7$, showed $[M+K]^+$, $[M+Na]^+$, $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 369, 355, 333 and 153 in the positive FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) of **1** showed the presence of two *tert*-methyls, three methylenes, one methine, two quaternary carbons, one hydroxylated methylene and one hydroxylated methine, in addition to the β-D-glucopyranosyl moiety. From analysis of the heteronuclear multiple-bond correlation (HMBC) spectrum (see Experimental), the aglycone of **1** was clarified as vicodiol (bornane-2,9-diol) and the location of the glucosyl group was C-9. Enzymatic hydrolysis of **1** gave an aglycone **1a**, $C_{10}H_{16}O_2$, and D-glucose, and the NMR spectra of **1a** were identical with those of vicodiol first isolated from the *Vicoa indica*.[6] As the vicodiol, which has the 1*S*,2*R*,4*S*,7*R* configuration, showed a minus $[\alpha]_D$ value in contrast to that of **1a** (+16°), **1a** was concluded to have the 1*R*,2*S*,4*R*,7*S* configuration. So, **1** was characterized as (1*R*,2*S*,4*R*,7*S*)-vicodiol 9-*O*-β-D-glucopyranoside.

Glucoside **2**, $C_{16}H_{28}O_7$, was identified as (1*R*,2*S*,4*S*,5*R*)-angelicoidenol 2-*O*-β-D-glucopyranoside by its physical and NMR spectral data.[7]

Glycoside **3**, $C_{16}H_{28}O_7$, and **4**, $C_{16}H_{28}O_7$, showed $[M+Na]^+$, $[M+H]^+$ and $[M-C_6H_{12}O_6+H]^+$ ion peaks at *m*/*z* 355, 333 and 153 in their positive FAB-MS. Their ^{1}H- and ^{13}C-NMR spectral data (Tables 1, 2) showed the presence of one β-D-glucopyranosyl, three *tert*-methyls, two methylenes, one methine, two quaternary carbons, and two hydroxylated methines. From the results of the HMBC experiment of **4**, **3** and **4** were indicated to be glucosides of bornane-2,6-diol, and the position of the glucosyl group was C-2. As nuclear Overhauser effect (NOE) interactions between H-3ax/H-6 and between H-2/H_3-9 were observed in their NOE spectroscopy (NOESY) spectra (Fig. 1), the configuration of

H-2 and H-6 of **3** and **4** should be *exo* and *endo*, respectively. So, they were represented as bornane-2*exo*,6*endo*-diol 2-*O*-*β*-D-glucopyranoside, respectively. Further, glucoside **3** was identified as (1*R*,2*R*,4*S*,6*R*)-bornane-2,6-diol 2-*O*-*β*-D-glucopyranoside, which was reported as a biotransformation product from a cell suspension culture of *Eucalypus perriniana* following administration of (−)-borneol,[8] by comparison of its physical and NMR spectral data with those reported. Consequently, **4** was suggested to be a glucoside having stereoisomeric aglycone of **3**. This was supported by comparison of their ^{13}C-chemical shift values (Table 2). As the ^{13}C chemical shift values of C-2 and glucosyl C-1 of **3** [C-2 (δ 82.89), glucosyl C-1 (δ 103.64)] showed an obvious up-field than that of **4** [C-2 (δ 84.89), glucosyl C-1 (δ 105.99)], the absolute configurations at C-2 of **3** and **4** were defined to be *R* and *S*, respectively.[9] Therefore, **4** was characterized as (1*S*,2*S*,4*R*,6*S*)-bornane-2,6-diol 2-*O*-*β*-D-glucopyranoside.

Glycoside **5**, $C_{16}H_{26}O_7$, and **6**, $C_{16}H_{26}O_7$, were suggested to be 6-hydroxycamphor 6-*O*-*β*-D-glucopyranoside by their FAB-MS and NMR spectral data. They were identified as (1*R*,4*S*,6*S*)-6-hydroxycamphor *β*-D-glucopyranoside and (1*S*,4*R*,6*S*)-6-hydroxycamphor *β*-D-glucopyranoside, respectively, which were obtained as biotransformation products from a cell suspension culture of *Eucalypus perriniana* following administration of (+)-camphor.[10]

Glycoside **7**, $C_{14}H_{18}O_9$, and **8**, $C_{13}H_{18}O_6$, were identified as vanillic acid *β*-D-glucopyranosyl ester[11] and benzyl *β*-D-glucopyranoside,[12] respectively, by comparison with an authentic compound or the results of spectral analysis.

Octane-tetrol **9**, $C_8H_{18}O_4$, showed $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 201 and 179 in their positive FAB-MS. Its ^{13}C-NMR spectrum showed only four signals, but analysis of ^{1}H- and ^{13}C–^{1}H correlation spectroscopy (COSY) NMR spectral data revealed the presence of two pairs of methylenes, one pair of hydroxylated methylene and one pair of hydroxylated methine. So, **9** was suggested to be octane-1,2,7,8-tetrol, which has an intramolecular symmetry plane or center. This was also supported by the result of HMBC experiment (see Experimental). Since **9** showed a negative optical rotation as D-threitol, and cannot be considered to be a meso form, the stereochemical relation-ship between C-2 and C-7 should be 2*S**,7*S**. Consequently, **9** was characterized as (2*S**,7*S**)-(−)-octane-1,2,7,8-tetrol.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. FAB-MS were recorded with a JEOL HX-110 spectrometer using glycerol as matrix. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL A-500 spectrometer with tetramethylsilane as an internal standard, and chemical shifts were recorded in δ value. ^{1}H–^{13}C COSY, HMBC and NOESY spectra were obtained with standard JEOL software. Column chromatography (C. C.) was carried out under TLC monitoring using Kieselgel 60 (70—230 mesh, Merck), Sephadex LH-20 (25—100 μm, Pharmacia), Lobar RP-8 column (Merck) and Amberlite XAD-II (Organo). TLC was performed on silica gel (Merck 5721) and spots were detected with *p*-anisaldehyde-H_2SO_4 reagent. HPLC separation was carried out with Symmetryprep C_{18} 7 μm [Waters; column size, 7.8×300 mm; ODS], carbohydrate analysis [Waters; column size, 3.9×300 mm; CHA] and Wakobeads T-100-S [Wako; column size, 6.0×150 mm].

Extraction and Separation Commercial amomum seed (the seed of *Amomum xanthioides* WALL.; purchased from Uchida Wakanyaku, Ltd., Lot 252808; 2.0 kg) was extracted with 70% methanol (8 l×3), and the extract (177.6 g) was partitioned into ether–water and ethyl acetate–water, respectively. The aqueous portion (123.4 g) was chromatographed over Amberlite XAD-II (H_2O→MeOH) to give water eluate (103.3 g) and methanol eluate (20.1 g) fractions.

The methanol eluate fraction was subjected to Sephadex LH-20 (MeOH) to give five fractions (frs. A—E). Fraction B (8.35 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (4 : 1 : 0.1→7 : 3 : 0.5→6 : 4 : 1)→MeOH] to give eleven fractions (frs. B_1—B_{11}). Fraction B_2 (0.12 g) was subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)→MeOH] to give seven fractions (frs. $B_{2\text{-}1}$—$B_{2\text{-}7}$), and fr. $B_{2\text{-}1}$ was subjected to Sephadex LH-20 (MeOH) to give **9** (2 mg). Fraction B_3 (0.79 g) was subjected to Lobar RP-8 column [MeCN–H_2O (3 : 17)→MeOH] to give twelve fractions (frs. $B_{3\text{-}1}$—$B_{3\text{-}12}$), and fr. $B_{3\text{-}6}$ was subjected to HPLC [ODS, MeOH–H_2O (2 : 3)] to give **8** (3 mg). Fraction $B_{3\text{-}9}$ was subjected to HPLC [ODS, MeOH–H_2O (2 : 3) and CHA, MeCN–H_2O (97 : 3)] to give **6** (18 mg). Fraction B_4 (1.65 g) was subjected to Lobar RP-8 column [MeCN–H_2O (3 : 17)→MeOH] to give nine fractions (frs. $B_{4\text{-}1}$—$B_{4\text{-}9}$), and fr. $B_{4\text{-}3}$ was subjected to HPLC [ODS, MeCN–H_2O (1 : 19)] to give **7** (63 mg). Fraction $B_{4\text{-}4}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **1** (205 mg), and fr. $B_{4\text{-}6}$ was subjected to HPLC [ODS, MeCN–H_2O (3 : 17)] to give **2** (245 mg). Fraction $B_{4\text{-}8}$ was subjected to HPLC [ODS, MeOH–H_2O (2 : 3)] to give **5** (5 mg), and fr. $B_{4\text{-}8\text{-}2}$ was subjected to HPLC [Wakobeads T-100-S, MeCN–H_2O (19 : 1)] to give **3** (2 mg) and **4** (20 mg). Fraction C (1.87 g) was chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5→6 : 4 : 1)→MeOH] to give seven fractions (frs. C_1—C_7). Fraction C_2 (112 mg) was subjected to a Lobar RP-8 column [MeCN–H_2O (3 : 17)] to give **10** (46 mg).

The following compounds were identified by comparison with authentic compounds or published physical and spectral data or results of spectral analysis. (1*R*,2*S*,4*S*,5*R*)-angelicoidenol 2-*O*-*β*-D-glucopyranoside {**2**, an amorphous powder, $[\alpha]_D^{23}$+7° (*c*=2.0, MeOH)}, (1*R*,2*R*,4*S*,6*R*)-bornane-2,6-diol 2-*O*-*β*-D-glucopyranoside {**3**, an amorphous powder, $[\alpha]_D^{23}$−45° (*c*=0.1, MeOH), positive FAB-MS *m/z*: 355.1739 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$; 355.1733), 333.1913 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$; 333.1913)}, (1*R*,4*S*,6*S*)-6-hydroxycamphor *β*-D-glucopyranoside {**5**, colorless needles (MeOH), mp 123—125 °C, $[\alpha]_D^{23}$−66° (*c*=0.4, MeOH), positive FAB-MS *m/z*: 353.1565 $[M+Na]^+$ (Calcd for $C_{16}H_{26}NaO_7$; 353.1577), 331.1741 $[M+H]^+$ (Calcd for $C_{16}H_{27}O_7$; 331.1757)}, (1*S*,4*R*,6*S*)-6-hydroxycamphor *β*-D-glucopyranoside {**6**, Colorless needles (MeOH), mp 93—96 °C, $[\alpha]_D^{23}$+37° (*c*=1.4, MeOH), positive FAB-MS *m/z*: 353.1583 $[M+Na]^+$ (Calcd for $C_{16}H_{26}NaO_7$; 353.1577), 331.1748 $[M+H]^+$ (Calcd for $C_{16}H_{27}O_7$; 331.1757)}, vanillic acid *β*-D-glucopyranosyl ester {**7**, An amorphous powder, $[\alpha]_D^{23}$−12° (*c*=1.3, MeOH), positive FAB-MS *m/z*: 331.1031 $[M+H]^+$ (Calcd for $C_{14}H_{19}O_9$; 331.1029)}, benzyl *β*-D-glucopyranoside {**8**, Colorless needles (MeOH), mp 120—121 °C, $[\alpha]_D^{21}$−53° (*c*=0.2, MeOH)} and adenosine {**10**, Colorless needles (MeOH), mp 233—235 °C, $[\alpha]_D^{21}$−62° (*c*=1.0, H_2O)}.

(1*R*,2*S*,4*R*,7*S*)-Vicodiol 9-*O*-*β*-D-Glucopyranoside (1) Colorless needles (MeOH), mp 173—174 °C, $[\alpha]_D^{23}$−16° (*c*=4.4, MeOH). Positive FAB-MS *m/z*: 665 $[2M+H]^+$, 369 $[M+K]^+$, 355.1716 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$; 355.1732), 333.1912 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$; 333.1913), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC Correlations: H-2_{exo}/C-3, C-4, C-6, C-7, C-10; H-3_{endo}/C-1, C-2, C-4, C-5; H-3_{exo}/C-1, C-2, C-4, C-5, C-7; H-4/C-1, C-2, C-3, C-5, C-6, C-7, C-8; H-5_{endo}/C-1, C-3, C-4, C-6, C-7; H-5_{exo}/C-3, C-4, C-6, C-7; H-6_{endo}/C-1, C-2, C-4, C-5, C-7; H-6_{exo}/C-2, C-5, C-7; H_3-8/C-1, C-4, C-7, C-9; H-9a/C-1, C-4, C-7, C-8, Glc C-1; H-9b/C-1, C-4, C-7, C-8, Glc C-1; H_3-10/C-1, C-2, C-6, C-7; Glc H-1/C-9.

Enzymatic Hydrolysis of 1 A mixture of **1** (16 mg) and *β*-glucosidase (5 mg, Toyobo Co. Inc., Lot 32275) in water (5 ml) was shaken in a water bath at 37 °C for 20 d. The mixture was concentrated *in vacuo* to dryness and the residue was chromatographed over silica gel [$CHCl_3$–MeOH (19 : 1, 6 : 4)] to afford **1a** (8 mg) and a sugar fraction. The sugar fraction was passed through Sephadex LH-20 (MeOH) to give a syrup, and HPLC [carbohydrate analysis (Waters), detector; JASCO RI-930 detector and JASCO OR-990 chiral detector, solv.; MeCN–H_2O (17 : 3), 2 ml/min; t_R 4.50 min (same location as that of D-glucose)] showed the presence of D-glucose.

(1*R*,2*S*,4*R*,7*S*)-Vicodiol (1a) An amorphous powder, $[\alpha]_D^{23}$+16° (*c*=0.6, MeOH; lit.[6] −17°, *c*=1, $CHCl_3$). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2.

(1*S*,2*S*,4*R*,6*S*)-Bornane-2,6-diol 2-*O*-*β*-D-Glucopyranoside (4) Colorless needles (MeOH), mp 114—116 °C, $[\alpha]_D^{23}$+9° (*c*=0.8, MeOH). Positive FAB-MS *m/z*: 655 $[2M+H]^+$, 355.1751 $[M+Na]^+$ (Calcd for $C_{16}H_{28}NaO_7$; 355.1732), 333.1924 $[M+H]^+$ (Calcd for $C_{16}H_{29}O_7$; 333.1913), 315 $[M-H_2O+H]^+$, 153 $[M-C_6H_{12}O_6+H]^+$ (base). ^{1}H-NMR (pyridine-d_5,

500 MHz) δ: Table 1. ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: Table 2. HMBC Correlations: H-2$_{exo}$/C-1, C-3, C-4, C-6; H-3$_{endo}$/C-1, C-2, C-4, C-5, C-7; H-3$_{exo}$/C-1, C-2, C-4, C-5; H-4/C-1, C-2, C-3, C-6, C-7, C-8, C-9; H-5$_{endo}$/C-1, C-3, C-4, C-6, C-7; H-5$_{exo}$/C-3, C-4, C-6; H-6$_{endo}$/C-2, C-7; H$_3$-8/C-1, C-4, C-7, C-9; H$_3$-9/C-1, C-4, C-7, C-8; H$_3$-10/C-1, C-2, C-6, C-7; Glc H-1/C-2.

(2*S,7*S**)-(−)-Octane-1,2,7,8-tetrol (9)** An amorphous powder, $[\alpha]_D^{23}$ −10° (c=0.1, MeOH). Positive FAB-MS m/z: 201 $[M+Na]^+$ (base), 179.1285 $[M+H]^+$ (Calcd for $C_8H_{19}O_4$; 179.1285). ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 3.79 (2H, dd, J=4.0, 12.0 Hz, H-1,8a), 4.01 (2H, dd, J=3.0, 12.0 Hz, H-1,8b), 4.67 (2H, dddd, J=3.0, 4.0, 6.5, 10.0 Hz, H-2,7), 2.14 (4H, m, H$_2$-3,6), 2.49 (2H, ddd, J=7.0, 10.5, 17.5 Hz, H-4,5a), 2.67 (2H, ddd, J=6.5, 10.5, 17.5 Hz, H-4,5b). ^{13}C-NMR (pyridine-d_5, 125 MHz) δ: 63.95 (C-1,8), 81.49 (C-2,7), 23.87 (C-3,6), 29.00 (C-4,5). HMBC Correlations: H-1a/C-2, C-3; H-1b/C-2, C-3; H-3/C-1, C-2, C-4; H-4a/C-2, C-3; H-4b/C-2, C-3.

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