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CYCLITOLS AND THEIR GLYCOSIDES FROM LEAVES OF *MARSDENIA TOMENTOSA*

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Key Word Index—*Marsdenia tomentosa*; Asclepiadaceae; leaves; cyclitols; kijolanitol; conduritol A α-D-galactoside.

Abstract—Four cyclitol glycosides and a new tetrol and pentol, were obtained, along with five known cyclitols from the fresh leaves of *Marsdenia tomentosa*. The locations of the glycosidic linkage in the cyclitols were determined by spectral and chemical methods. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Marsdenia tomentosa, belonging to the same genus as condurango, is the only species indigenous to the mainland of Japan and many studies on its pregnane constituents have been reported [1]. This species is also a food plant for *Parantica sita*, one of the danaid butterflies in Japan. Since oviposition-stimulating activities appeared to be evoked by the polar fraction of the leaf extract, our first investigation focused on identification of the constituents. This paper deals with cyclitols and their glycosides, along with their component sugars, in the polar fraction.

RESULTS AND DISCUSSION

When the polar fraction of the methanol extract was further treated on a charcoal column and then analysed by preparative HPLC, seven cyclitols (**1**–**7**) and four glycosides (**8**–**11**) were isolated along with glucose, fructose, sucrose, D-hamamelose and 1-kestose. Among these, the major cyclitol was identified as conduritol A (**1**) and **2**–**5** were (−)-conduritol F, (−)-viburnitol, (−)-bornesitol and myoinositol, respectively [2], based on their physical constants and NMR and mass spectrometry considerations.

Compound **6** was obtained as prisms and afforded a $[M+Na]^+$ peak at *m/z* 171.0634, suggesting it to be a cyclohexanetetrol. Based on the ^1H and ^{13}C NMR spectra, the structure was suggested to be dihydroconduritol A and confirmed by direct comparison with an authentic sample, prepared by catalytic reduction of **1**.

Compound **7** (kijolanitol) afforded a $[M+1]^+$ peak at *m/z* 165.0764, suggesting the molecular formula $C_6H_{12}O_5$. The acetate was obtained as prisms and its FAB mass spectrum confirmed it to be a cyclohexanepentol. In the ^{13}C NMR spectrum, only four carbon signals were observed at δ 34.5, 73.0, 76.8 and 73.4, the corresponding ^1H signals were observed at δ 1.76 and 2.15 (*dt* each, $J = 16$, 4 Hz), 4.08 (*q*, $J = 4$ Hz), 3.53 (*dd*, $J = 9.4$ Hz) and 3.91 (*t*, $J = 9$ Hz). Compound **7** was also optically inactive, as were **1** and **6** and its structure was assigned as 1D-1,2,4,5/3-cyclohexanepentol.

In its ^1H NMR spectrum, compound **8** showed olefinic protons at δ 5.89 (*dd*, $J = 10$, 2 Hz) and 5.94 (*dd*, $J = 10$, 3 Hz). Since 12 signals were observed in the ^{13}C NMR spectrum and one doublet signal at δ 5.17 (*d*, $J = 3$ Hz) was assignable to an anomeric proton of an α-linked hexose, **8** was considered to be a glycoside of **1** or **2**. In the ^1H NMR spectrum of **8**-heptaacetate, the component sugar was assignable to galactose; it was cleaved to **1** and galactose by acid hydrolysis. Based on its optical rotation value ($[\alpha]_D$ +48.8°) and GC analysis of the thiazolidine derivative of the sugar [3] after hydrolysis of **8**, galactose was confirmed to be of the D-series. Dihydro-**8** (**8a**), obtained by catalytic reduction of **8**, showed a glycosylation shift (+5.9 ppm) on the carbon (C-1 or C-4) next to the methylene carbon (C-5 or C-6), suggesting the presence of the galactosyl linkage at C-1 (*S*) or C-4 (*R*). In comparison with the ^{13}C NMR spectra of **8a** and **6**, one of the methylene carbons possibly assignable to C-6, appeared at higher field by −3.5 ppm, suggesting the proximity of the C-2′

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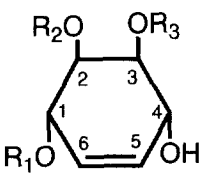
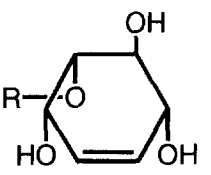
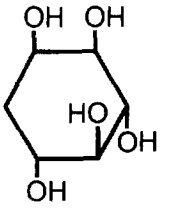


1 : R_1=R_2=R_3=H
6 : R_1=R_2=R_3=H
5,6-Dihydro
8 : R_1=α-D-Galactose
R_2=R_3=H
11 : R_1=H,
R_2, R_3=β-D-Glucose, H



2 : R=H
10 : R=β-D-Glucose



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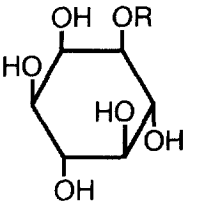
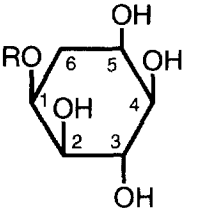
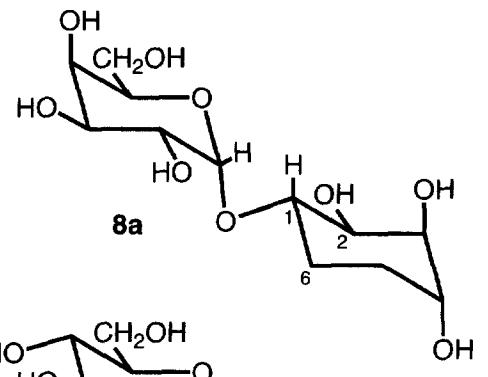


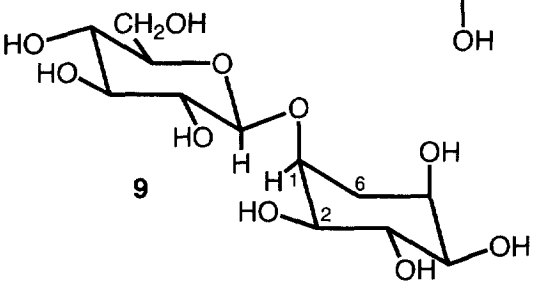
4 : R=CH_3
5 : R=H



7 : R=H
9 : R=β-D-Glucose



8a

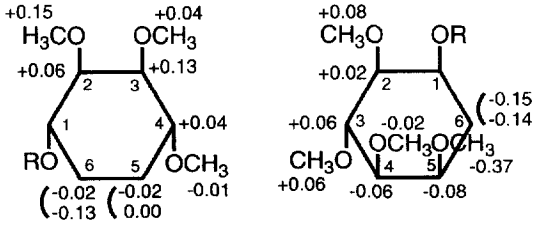


9

hydroxyl group in the galactose moiety to the methylene group when the anomeric proton and H-1 retained a *syn*-relationship [4, 5]. Therefore, the galactose linkage to conduritol A was considered to be at the C-1 hydroxyl. The possibility of its linkage to the C-4 hydroxyl group will be excluded unless the conformation of **6** retained $^4C_1$ form. In order to confirm the linkage of the galactose moiety at C-1, the modified Mosher's procedure [6] was applied.

After methylation of **8a** (**8b**) [7], followed by methanolysis, the aglycone of **8b** was transformed into (−)-(*S*)- and (+)-(*R*)-α-methoxy-α-(trifluoromethyl) phenylacetates (MTPA esters, **8c** and **8d**, respectively). The differences of the ^{1}H chemical shifts in the cyclitol moieties of the (−)-(*S*)-MTPA and (+)-(*R*)-MTPA esters ($\Delta\delta$ value (δS-δR) showed positive e values in H-2, H-3 and 2-, 3-OCH_3, while negative in H-5 and H-6 (Fig. 1). Consequently the free carbinol group to which the α-D-galactose was linked in **8** was determined to be C-1 with the *S* configuration.

The molecular formula of **9** was suggested to be $C_{12}H_{22}O_{10}$ based on its FAB mass spectrum. Acid hydrolysis of **9** afforded **7** and glucose; the sugar was confirmed to be D-glucose based on GC analysis of the corresponding thiazolidine derivative [3]. In NOE measurements, the irradiation of the anomeric proton signal at δ 4.61 (*d*, J = 8 Hz) showed a response with the signal at δ 4.23 (*q*, J = 4 Hz), which was adjacent



8c : R=(-)-(*S*)-MTPA
8d : R=(+)-(*R*)-MTPA

9b : R=(-)-(*S*)-MTPA
9c : R=(+)-(*R*)-MTPA

Fig. 1. Difference of chemical shifts (δS-δR in ppm) between corresponding protons in MTPA esters of partially methylated cyclitols.

to a methylene group. In comparison with the ^{13}C NMR spectra of **7** and **9**, the methylene carbon signal showed a small glycosylation shift (−0.4 ppm), suggesting that the 2′-OH of D-glucose is close to the C-2-OH [4, 5]. In order to determine the location of the sugar, **9** was subjected to the same procedure as described for **8**. Tetramethyl-**7** derived from octamethyl-**9** (**9a**) was transformed into MTPA esters (**9b** and **9c**). The $\Delta\delta$ value (δS-δR) was positive for H-2 and H-3 but negative for H4, 5 and 6, indicating that the free carbinol group retained the *S*-configuration (Fig. 1). Therefore, the location of glucose was assigned to the C-1 hydroxyl group.

Based on FAB mass spectrometry, **10** and **11** were suggested to have the same molecular formula, $C_{12}H_{20}O_9$. On acid hydrolysis, **2** and **1** were obtained from **10** and **11**, respectively, along with glucose. Since C-2 showed the same glycosylation shift in the ^{13}C NMR spectrum as **10**, the location of the glucosyl linkage was considered to be at the C-2 hydroxyl group. Compound **10** was therefore assigned as the 2-*O*-β-D-glucoside of conduritol F. In **11**, the location of glucose could either being at C-2 or C-3, but was not determined.

Among the constituents of condurango, the bark of *Marsdenia condurango*, nine cyclitols have been isolated from the water-soluble fraction [2], while many pregnane glycosides have been reported from the less polar fraction [8, 9]. The five cyclitols described in the present work are already known from condurango. The other two, dihydroconduritol A and kijolanitol, are new natural products. It should be noted that **8**, one of the major glycosides, was revealed to be an α-linked D-galactoside, although the other glucosides had a β-glycosidic linkage.

EXPERIMENTAL

General

^1H NMR (400 or 500 MHz) and ^{13}C NMR (100 MHz) with TMS as int. standard in D_2O, unless otherwise mentioned. For TLC and silica gel CC (normal phase), the following solvent systems were used. 1: $CHCl_3$–MeOH–H_2O (20:10:1–20:10:2), 2: EtOAc–MeOH–H_2O (8:2:1). Spray reagent for TLC: 1: dil. H_2SO_4, 2: ninhydrin reagent. HPLC: RI; C_{18}-column using H_2O; NH-column using 75% Me CN. GC: FID; column, Shimadzu DB-1 (0.25 mm × 30 m); column temp. 250°, inj. temp. 300°, detector temp. 300°; carrier gas, He 30 cm s^{-1}, make-up gas He 50 ml s^{-1}, split ratio 1:30.

Plant material

Marsdenia tomentosa Morren et Decaisne was collected in Hiroshima Prefecture in August 1995. The plant is now cultivated in the gardens of Fukuoka University. Voucher No. of the dried plant sample: FUK-950801A.

Extraction and isolation

Leaves (1 kg) were homogenized in MeOH and filtered. The MeOH soln was concd *in vacuo* and H_2O added. The mixt. was partitioned with $CHCl_3$. The aq. layer was passed through a MCI-gel HP-20 column and the first eluate with H_2O (30.1 g) was then rechromatographed on a charcoal column. Eluates with H_2O–20% MeOH were further chromatographed on a silica gel column with solvents 1 and 2. Finally, all cyclitols were purified by HPLC. **1** (conduritol A): 0.6 g, **2** ((−)-conduritol F): 21 mg, **3** ((−)-viburnitol): 22 mg, **4** ((−)-bornesitol): 132 mg, **5** (myoinositol): 35 mg, **6**: 35 mg, **7**: 26 mg, **8** 185 mg, **9**: 150 mg, **10**: 25 mg, **11**: 9 mg. Sugars: glucose and fructose: not weighed, sucrose: 530 mg, D-hamamelose: 30 mg, 1-kestose: 10 mg.

Dihydroconduritol A (**6**). Prisms from MeOH, mp 202–204°. FABMS *m/z*: 171.0634, $C_6H_{12}O_4$+Na requires 171.0633. NMR: Tables 1 and 2. Tetraacetyl-**6** (Ac_2O+pyridine, solid), *m/z*: 339.1052,

Table 1. ^{13}C NMR spectral data for cyclitols **6**–**10** and **11** [δ in D_2O (100 MHz)]

C	6	7	8	9	10*	11†
1	72.4	73.0	78.2	82.3	65.5	70.1 (71.5)
2	75.7	76.8	73.5	76.1	79.9	83.7 (74.4)
3	75.7	73.4	75.0	73.3	71.9	74.4 (83.7)
4	72.4	76.8	71.5	76.6	73.5	71.5 (70.1)
5	28.5	73.0	133.6	72.1	133.8	131.7 (132.2)
6	28.5	34.5	128.7	34.1	126.9	132.2 (131.7)
1′			100.7	106.6	102.2	105.5
2′			71.0	76.3	74.3	76.0
3′			72.2	78.4	77.0	78.5
4′			72.1	72.3	70.8	72.4
5′			74.1	78.8	77.4	78.7
6′			64.0	63.4	61.9	63.6

* Dissolved in D_2O–CD_3OD.

† For 2-*O*-glucoside. Chemical shifts for 3-*O*-glucoside in parentheses.

Table 2. ^{1}H NMR spectral data for cyclitols **6**–**10** and **11** [δ in D_2O (400 MHz)]

H	**6**	**7**	**8**	**9**	**10***	**11**†
1	3.86 (*m*)	4.08 (*q*, 4)	4.23 (*dd*, 5, 3)	4.23 (*q*, 4)	4.43 (*dd*, 5, 3)	4.38 (*dd*, 6, 1) [4.23 (*dd*, 5, 1)]
2	3.79 (*d*, 8)	3.53 (*dd*, 9, 4)	4.08 (*dd*, 5, 2)	3.63 (*dd*, 9, 4)	3.76–3.79	3.98 (*ddd*, 10, 6, 2) [4.06 (*ddd*, 10, 5, 2)]
3	3.79 (*d*, 8)	3.91 (*t*, 9)	3.88 (*dd*, 5, 2)	3.94 (*t*, 9)	3.76–3.79	4.06 (*ddd*, 10, 5, 2) [3.98 (*ddd*, 10, 6, 2)]
4	3.86 (*m*)	3.53 (*dd*, 9, 4)	4.24 (*dd*, 5, 2)	3.53 (*dd*, 9, 3)	4.10 (*dt*, 7, 2)	4.23 (*dd*, 5, 1) [4.38 (*dd*, 6, 1)]
5	1.63 (*m*)	4.08 (*q*, 4)	5.89 (*dd*, 10, 2)	4.05 (*q*, 4)	5.81 (*dd*, 10, 2)	5.84 (*br d*, 10) [5.82 (*br d*, 10)]
	1.82 (*m*)					
6	1.63 (*m*)	1.76 (*dt*, 16, 4)	5.94 (*dd*, 10, 3)	1.83 (*dt*, 16, 4)	5.88 (*ddd*, 10, 5, 1)	5.82 (*br d*, 10) [5.84 (*br d*, 10)]
	1.82 (*m*)	2.15 (*dt*, 16, 4)		2.38 (*dt*, 16, 4)		
1′			5.17 (*d*, 3)	4.61 (*d*, 8)	4.56 (*d*, 8)	4.65 (*d*, 8)
2′			3.84 (*dd*, 10, 3)	3.36 (*t*, 9)	3.39 (*dd*, 8, 9)	3.34 (*dd*, 8, 9)
3′			3.87 (*dd*, 10, 3)	3.51 (*t*, 9)	3.49 (*t*, 9)	3.52 (*t*, 9)
4′			4.01 (*dd*, 3, 1)	3.45 (*t*, 9)	3.40 (*t*, 9)	3.44 (*t*, 9)
5′			4.05–4.10	3.47 (*m*)	3.42 (*m*)	3.48 (*m*)
6′			3.77 (2H, *d*, 6)	3.75 (*dd*, 12, 5)	3.72 (*dd*, 12, 6)	3.75 (*dd*, 12, 6)
				3.92 (*dd*, 12, 2)	3.90 (*dd*, 12, 1)	3.92 (*dd*, 12, 2)

Coupling constants (J in Hz) in parentheses.

* Dissolved in D_2O–CD_3OD.

† For 2-*O*-glucoside. Chemical shifts for 3-*O*-glucoside in parentheses.

$C_{14}H_{20}O_8$ + Na requires 339.1056. ^{1}H NMR ($CDCl_3$): δ 1.78, 1.96 (2H each, *m*, H-5,6), 2.06, 2.07 (6H each *s*, OAc), 5.05 (2H, *m*, H-1,4), 5.27 (2H, *br d*, J = 6 Hz, H-2,3). Analytical data for **6** were in good agreement with dihydroconduritol A (mp 205–209°) prepd from conduritol A by catalytic reduction (H_2/PdO).

Kijolanitol (1D-1,2,4,5/3-*cyclohexanepentol*) (**7**). Solid. FABMS *m/z*: 165.0764, $C_6H_{12}O_5$ + H requires 165.0763. NMR: Tables 1 and 2. The pentaacetate (Ac_2O-pyridine) was recrystallized from MeOH, mp 170–172 . FABMS *m/z*: 397.1112, $C_{16}H_{22}O_{10}$ + Na requires 397.1111. ^{1}H NMR ($CDCl_3$): δ 2.02, 2.09 (6H each, *s*, OAc), 2.04 (3H, *s*, OAc), 1.89, 2.33 (1H each, *dt*, J = 16, 4 Hz, H-6), 5.00 (2H, *dd*, J = 9, 4 Hz, H-2,4), 5.35 (2H, *q*, J = 4 Hz, H-1,5), 5.65 (1H, *t*, J = 9 Hz, H-3).

Conduritol A 1-O-α-D-*galactopyranoside* (**8**). Solid $[\alpha]_D^{24}$ +106.5° (MeOH, *c* 0.83), FABMS *m/z*: 331.1006, $C_{12}H_{20}O_9$ + Na requires 331.1005. NMR: Tables 1 and 2. Heptaacetyl-**8** (Ac_2O-pyridine) was obtained as a solid. FABMS *m/z*: 625.1746, $C_{26}H_{34}O_{16}$ + Na requires 625.1744. ^{1}H NMR ($CDCl_3$): δ 1.99, 2.03, 2.06, 2.07, 2.08, 2.10, 2.13 (3H each, *s*, OAc), 4.09, 4.14 (1H each, *dd*, J = 11, 7 Hz, H-6′), 4.23 (1H, *dd*, J = 5, 3 Hz, H-1), 4.39 (1H, *td*, J = 7, 1 Hz, H-5′), 5.09 (1H, *dd*, J = 11, 4 Hz, H-2′), 5.34 (1H, *d*, J = 4 Hz, H-1′), 5.41 (1H, *dd*, J = 4, 2 Hz, H-4), 5.48 (1H, *dd*, J = 3, 1 Hz, H-4′), 5.81 (1H, *dd*, J = 10, 3 Hz, H-6), 5.85 (1H, *dd*, J = 10, 3 Hz, H-5). **8** was heated with 1N HCl for 2 h and deacidified with IR-410. The mixt. was subjected to HPLC (C_{18} column using H_2O) to isolate conduritol A and D-galactose $[\alpha]_D^{25}$ +48.8° (H_2O, *c* 0.16, 24 h). Galactose was converted into its thiazolidine derivative with L-cysteine methyl ester hydrochloride [3] and the derivative then examined by GC after trimethylsilylation (*R*, 30.1; D-Galactose, 30.1; L-Galactose, 31.6).

Dihydro-**8** (**8a**) was prep as a solid by catalytic reduction (H_2/PdO). FABMS *m/z*: 333.1169, $C_{12}H_{22}O_9$ + Na requires 333.1162. ^{1}H NMR: δ 1.65 (1H, *m*, H-5a), 1.70–1.85 (3H, *m*, H-5b, H-6), 3.75 (2H, *d*, J = 6 Hz, H-6′), 3.77 (1H, *dd*, J = 8, 3 Hz, H-3), 3.82 (1H, *dd*, J = 10, 4 Hz, H-2′), 3.88 (1H, *td*, J = 9, 4 Hz, H-1), 3.90 (1H, *dd*, J = 10, 4 Hz, H-3′), 4.00 (1H, *br s*, H-4′), 4.03 (1H, *t*, J = 6 Hz, H-5′), 5.08 (1H, *d*, J = 4 Hz, H-1′). ^{13}C NMR δ: 25.0 (C-6), 28.8 (C-5), 64.0 (C-6′), 71.1 (C-4), 72.2 (×2), 72.3 (C-2′,3′4′), 74.0 (C-5′), 74.4 (C-2), 75.9 (C-3), 78.3 (C-1), 99.3 (C-1′). **8a** was methylated by Hakomori's procedure with MeI, NaH and DMSO [7] to give heptamethyl-**8** (**8b**). FABMS *m/z*: 431.2256, $C_{19}H_{36}O_9$ + Na requires 431.2257. ^{1}H NMR: δ 1.60–1.80 (4H, *m*, H-5,6), 3.38, 3.39, 3.45, 3.47, 3.51, 3.57 (3H each, *s*, OMe), 4.06 (1H, *t*, H-5′), 5.07 (1H, J = 4 Hz, H-1′). **8b** was refluxed with 1N HCl in MeOH, deacidified with Ag_2CO_3 and the solvent evapd. The residue containing trimethyl dihydroconduritol A was treated with (−)-(*S*)-MTPA and (+)-(*R*)-MTPA, respectively, in the presence of DCC and DMAP, to afford the MTPA esters of the trimethyl-cyclohexanetetrol (**8c** and **8d**). **8c** ((−)-(S)-*MTPA ester*). FABMS *m/z*: 429.1493, $C_{19}H_{25}O_6F_3$ + Na requires 429.1501. ^{1}H NMR: δ 1.57, 1.89 (1H each, *m*, H-6), 1.70, 1.75 (1H each, *m*, H-5), 3.34 (3H, *s*, 4-OMe), 3.41 (3H, *s*, 2-OMe), 3.47 (3H, *s*, 3-OMe), 3.50 (1H, *dd*, J = 9, 3 Hz, H-2), 3.57 (1H, *br s*, H-4), 3.64 (1H, *br s*, H-3), 5.27 (1H, *td*, J = 9, 5 Hz, H-1). **8d** ((+)-(R)-*MTPA ester*). FABMS *m/z*: 429.1504, $C_{19}H_{25}O_6F_3$ + Na requires 429.1501. ^{1}H NMR: δ 1.70, 1.91 (1H each, *m*, H-6), 1.70, 1.77 (1H each, *m*, H-5), 3.26 (3H, *s*, 2-OMe), 3.35 (3H, *s*, 4-OMe), 3.42 (3H, *s*, 3-OMe), 3.44 (1H, *dd*, J = 9, 3 Hz, H-2), 3.51 (1H, *br s*, H-3), 3.53 (1H, *br s*, H-4), 5.31 (1H, *td*, J = 9, 5 Hz, H-1).

Kijolanitol 1-O-β-D-*glucopyranoside* (**9**). Prisms, mp 229–231°. $[\alpha]_D^{24}$ −2.4° (MeOH), *c* 0.95). FABMS *m/z*: 349.1125, $C_{12}H_{22}O_{10}$+Na requires 349.1110. NMR: Tables 1 and 2. NOE measurement: H-1′ (δ 4.61, *d*, *J* = 8 Hz)/H-1 (4.23, *q*, *J* = 4 Hz). **9** was heated with 1N HCl to give **7** and glucose, which was converted into its thiazolidine derivative, as described for and examined by GC (R_t 28.8; D-Glucose, 28.8; L-Glucose, 29.8). **9**-*octamethylate* (**9a**, *Hakomori's method*). FABMS *m/z* 461.2359, $C_{20}H_{38}O_{10}$+Na requires *m/z* 461.2362. ^{1}H NMR ($CDCl_3$): δ 1.46, 2.41 (1H each, *m*, H-6), 3.36, 3.40, 3.47, 3.48, 3.52, 3.54, 3.61, 3.62 (3H, *s*, OMe), 4.08 (1H, *q*, *J* = 4 Hz, H-1), 4.44 (1H, *d*, *J* = 8 Hz, H-1′). MTPA esters of tetramethyl-**7** (**9b** and **9c**) were prepd from **9a** using the same procedure as described for **8b**. **9b** ((−)-(S)-*MTPA ester*). FABMS *m/z*: 459.1605, $C_{20}H_{27}O_7F_3$+Na requires 459.1606. ^{1}H NMR ($CDCl_3$): δ 1.46, 2.25 (1H each, *m*, H-6), 2.94 (3H, *s*, 5-OMe), 3.13 (1H, *dd*, *J* = 9, 4 Hz, H-4), 3.22 (1H, *dd*, *J* = 9, 4 Hz, H-2), 3.45 (3H, *s*, 2-OMe), 3.47 (3H, *s*, 4-OMe), 3.57 (3H, *s*, 3-OMe), 3.60 (1H, *q*, *J* = 4 Hz, H-5), 3.65 (1H, *t*, *J* = 9 Hz, H-3), 5.55 (1H, *q*, *J* = 4 Hz, H-1). **9c** ((+)-(R)-*MTPA ester*). *FABMS m/z*: 459.1607, $C_{20}H_{27}O_7F_3$+Na requires 459.1606. ^{1}H NMR ($CDCl_3$): δ 1.60, 2.40 (1H each, *m*, H-6), 3.19, 3.20 (1H each *dd*, *J* = 9, 4 Hz, H-4,2), 3.31 (3H, *s*, 5-OMe), 3.37 (3H, *s*, 2-OMe), 3.49 (3H, *s*, 4-OMe), 3.51 (3H, *s*, 3-OMe), 3.59 (1H, *t*, *J* = 9 Hz, H-3), 3.68 (1H, *q*, *J* = 4 Hz, H-5), 5.53 (1H, *q*, *J* = 4 Hz, H-1).

(−)-*Conduritol F* 2-O-β-D-*glucopyranoside* (**10**). Solid. $[\alpha]_D^{25}$ −22.5° (H_2O, *c* 1.25). FABMS *m/z*: 331.1002, $C_{12}H_{20}O_9$+Na requires 331.1005. NMR: Tables 1 and 2. **10** was heated with 1N HCl for 1 h to afford **2** and glucose.

Conduritol A β-D-*glucopyranoside* (**11**). Solid. $[\alpha]_D^{26}$ +21.3° (H_2O, *c* 0.47). FABMS *m/z*: 331.1003, $C_{12}H_{20}O_9$+Na requires 331.1005 NMR: Tables 1 and 2. On heating of **11** with 1N HCl, **1** and glucose were obtained.

D-*Hamamelose*. Solid $[\alpha]_D^{23}$ −15.6°C (H_2O, 24 h). Two acetates were obtained (Ac_2O, pyridine). *Acetate-1*. FABMS *m/z*: 413.1063, $C_{16}H_{22}O_{11}$+Na requires 413.1060. ^{1}H NMR ($CDCl_3$): δ 2.01, 2.08, 2.09, 2.10, 2.13 (3H each, *s*, OAc), 4.15 (1H, *dd*, *J* = 12, 6 Hz, H-5a), 4.28 (1H, *dd*, *J* = 12, 4 Hz, H-5b), 4.36 (1H, *m*, H-4), 4.70, 4.86 (1H each, *d*, *J* = 13 Hz, H-2′), 5.42 (1H, *d*, *J* = 8 Hz, H-3), 6.43 (1H, *s*, H-1). *Acetate-2*. FABMS *m/z*: 413.1058, $C_{16}H_{22}O_{11}$+Na requires 413.1060. ^{1}H NMR ($CDCl_3$): δ 2.05, 2.09, 2.10, 2.11, 2.13 (3H each, *s*, OAc), 4.30 (1H, *dd*, *J* = 13, 4 Hz, H-5a), 4.31 (1H, *m*, H-4), 4.39 (1H, *dd*, *J* = 13, 4 Hz, H-5b), 4.48, 4.67 (1H each, *d*, *J* = 13 Hz, H-2′), 5.28 (1H, *d*, *J* = 4 Hz, H-3), 6.51 (1H, *s*, H-1).

1-*Kestose* (O-β-D-*fructofuranosyl*-(2 → 1)-β-D-*fructofuranosyl* α-D-*glucopyranoside*). Solid. $[\alpha]_D^{26}$ +67.1° (H_2O, *c* 0.35). FABMS *m/z*: 527.1589, $C_{18}H_{32}O_{16}$+Na requires 527.1588.

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REFERENCES

1. Sasaki, T., Hayashi, K. and Mitsuhashi, H., *Chem. Pharm. Bull*, 1972, **20**, 628.
2. Kindl, H. and Hoffmann-Ostenhof, O., *Phytochemistry*, 1966, **5**, 1091.
3. Hara, S., Okabe, H. and Mihashi, K., *Chem. Pharm. Bull.*, 1987, **35**, 501.
4. Kasai, R., Suzuo, M., Asakawa, J. and Tanaka, O., *Tetrahedron Letters*, 1977, 175.
5. Tori, K., Seo, S., Yoshimura, Y., Arita, H. and Tomita, Y., *Tetrahedron Letters*, 1977, 179.
6. Ohtani, I., Kusumi, T., Kashman, Y. and Kakisawa, H., *J. Am. Chem. Soc.*, 1991, **113**, 4092.
7. Hakomori, S., *J. Biochem.*, 1964, **55**, 205.
8. Tschesche, R., *Tetrahedron*, 1968, **24**, 4359.
9. Hayashi, K., Wada, H., Mitsuhashi, H., Aiba, T., Narita, T. and Mizuno, D., *Chem. Pharm. Bull.*, 1981, **29**, 2725.