Antisweet Natural Products. VIII.[1] Structures of Hodulosides VI—X from *Hovenia dulcis* THUNB. var. *tomentella* MAKINO

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From the Fresh leaves of *Hovenia dulcis* THUNB. var. *tomentella* MAKINO, five new dammarane glycosides named hodulosides VI—X (1—5) were isolated. Their structures were determined on the basis of chemical and spectral evidence. Hodulosides VII—X showed antisweet activities.

Keywords *Hovenia dulcis* var. *tomentella*; Rhamnaceae; hoduloside; antisweet substance; 30-hydroxydammarane; 3β,20(*S*),25,30-tetrahydroxy-16-oxodammar-23-ene

In the previous paper,[1] we have reported several antisweet principles, named hodulosides I—V, from the leaves of *Hovenia dulcis* THUNB. (Rhamnaceae), known to contain antisweet substances.[2] Hodulosides I and II were glycosides of hovenolactone, while hodulosides III—V were glycosides of jujubogenin. The leaves of *Hovenia dulcis* THUNB. var. *tomentella* MAKINO also showed a sweetness-reducing activity. So, we have initiated a chemical study of the title plant.

The EtOH extract obtained from the fresh leaves of *H. dulcis* var. *tomentella* (9.5 kg) was subjected to Amberlite XAD-2 column chromatography to give a saponin fraction (100 g). Repeated separation of the saponin fraction by medium-pressure liquid chromatography (MPLC) and HPLC using reversed phase packing (octadecyl silica (ODS)) furnished five new compounds named hodulosides VI (**1**, 0.00047% from the crude drug), VII (**2**, 0.00074%), VIII (**3**, 0.00063%), IX (**4**, 0.00021%) and X (**5**, 0.00026%).

Hoduloside VII (**2**), the major component, was obtained as an amorphous powder and deduced to have the molecular formula $C_{47}H_{78}O_{18}$ from the deprotonated molecular ion peak at *m/z*: 929 in the negative FAB-MS and based on elemental analysis. Acid hydrolysis of **2** afforded L-arabinose, L-rhamnose and D-glucose in a molar ratio of 1 : 1 : 1.[3] The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one α-arabinopyranosyl unit [H-1: δ 4.88 (d, J = 5.6 Hz), C-1: δ 105.0], one β-glucopyranosyl unit [H-1: δ 4.93 (d, J = 7.8 Hz), C-1: δ 105.2] and one α-rhamnopyranosyl unit [H-1: δ 6.15, s, C-1: δ 101.8].

The molecular formula, $C_{47}H_{78}O_{18}$ implied nine degrees of unsaturation. Five can be assigned to one carbonyl group (δ 220.5; IR 1730 cm^{-1}), one olefinic bond (δ 142.7, 123.2), and three hemiacetal linkages of the sugar parts. The remaining four are due to the tetracyclic triterpene ring system indicated by the positive Salkowsky reaction. ^{1}H–^{1}H correlation spectroscopy (^{1}H–^{1}H COSY), ^{1}H–^{13}C COSY and ^{1}H-detected multiple-bond heteronuclear multiple quantum coherence (HMBC) experiments enabled us to construct the aglycone skeleton. The ^{1}H–^{1}H connectivity from the COSY spectrum of **2** suggested the isolated spin systems (subunits **a**—**d**, chart 1). With information obtained from the HMBC experiment and with reference to the data of saponin C_2 (**6**),[4] subunits **a**—**c** could be assembled into the A–D rings, while subunit **d** extended to the side chain carrying tetiary hydroxyls on C-20 and C-25, and a double bond on C-23, with reference to the data of compound **3**.[5] The chemical shift value (δ 88.3) of the C-3 carbon of the aglycone, glycosylated with α-L-arabinose whose C-1

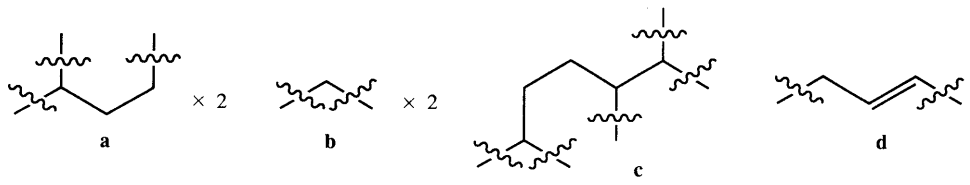


Chart 1

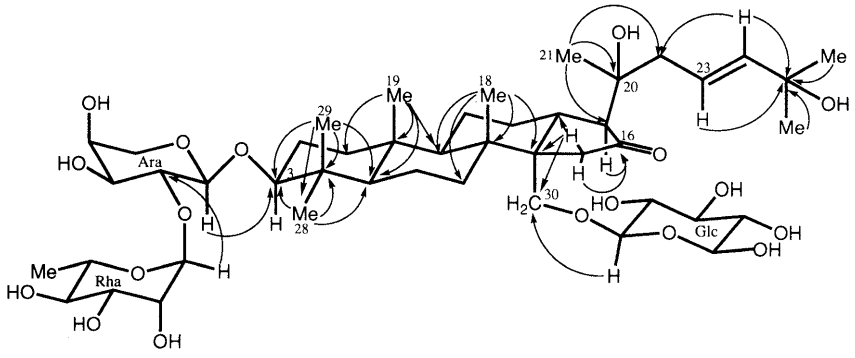


Fig. 1. The HMBC Correlations for Hoduloside VII (**2**)

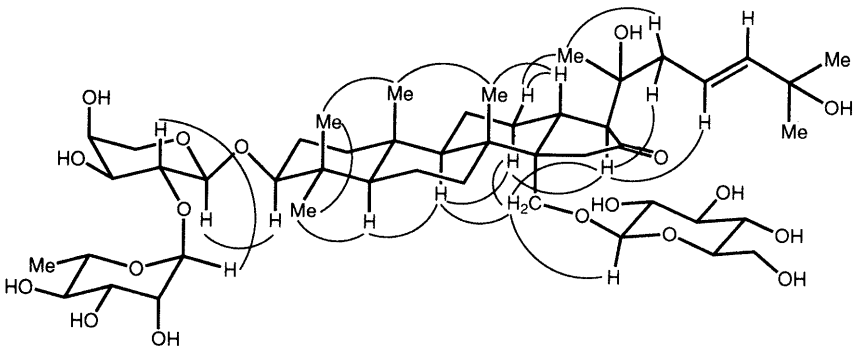


Fig. 2. The Main NOE Correlations for Hoduloside VII (**2**)

configuration was *R*, showed the C_3 to have *S* configuration,[6] suggesting that **2** is a dammarene 3-*O*-glycoside. The stereochemistry of the aglycone was established by a rotating frame Overhauser enhancement spectroscopy (ROESY) experiment (Fig. 2). This experiment clearly defined the usual chair conformation of rings A, B and C. The nuclear Overhauser effect (NOE) was detected between C_{17}-H and C_{12}-Hα, and C_{17}-H and C_{30}-H_2, but not between C_{17}-H and C_{13}-H, confirming the C_{17}-*S* configuration. The NOE detected among C_{12}-Hβ–C_{21}-H_3, C_{17}-H, and among C_{17}-H–C_{22}-H, C_{23}-H indicated the C_{20} *S* configuration. Accordingly, the aglycone of **2** can be represented as 3β,20(*S*),25,30-tetrahydroxy-16-oxodammar-23-ene. We attempted to obtain the aglycone, a new compound, by enzymatic hydrolysis, but without success.

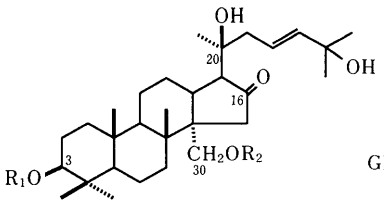
The sugar sequence was determined as follows. The electron impact-MS (EI-MS) of **2** acetate showed fragment ion peaks due to a terminal deoxyhexosyl (*m/z* 273) and a hexosyl (*m/z* 331), and a deoxyhexosylpentosyl (*m/z* 489), disclosing the sugar units to be –Glc and –Ara–Rha. In the HMBC spectrum of **2**, long-range correlations were seen between the carbinol carbon (δ 88.3) and anomeric proton (δ 4.88) of arabinose, the carbinol carbon (δ 76.0) of arabinose and anomeric proton (δ 6.15) of rhamnose, and the carbinol carbon (δ 71.5) and anomeric proton (δ 4.93) of glucose, indicating that the *O*-3 of aglycone should be glycosylated with α-arabinose bearing an α-rhamnosyl unit on *O*-2, and the glucosyl unit should be linked to C_{30}-OH. Further, the NOE was also observed between C_3-H (δ 3.12) of the aglycone and C_1-H (δ 4.88) of arabinose, C_2-H (δ 4.55) of arabinose and C_1-H (δ 6.15) of rhamnose, and C_1-H (δ 4.93) of glucose and C_{30}-H_2 (δ *ca.* 4.30, 4.71) of aglycone, respectively, in the ROESY experiment. Hence, the structure of hoduloside VII was established as 3β,20(*S*),25,30-tetrahydroxy-16-oxodammar-23-ene-3-*O*-α-L-rhamnopyranosyl (1→2)-α-L-arabinopyranoside-30-*O*-β-D-glucopyranoside.

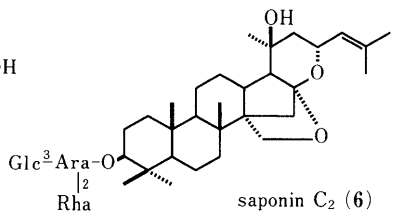
Comparison of the ^{13}C-NMR spectra of **1**, **3**—**5** with that of **2** showed that **1** and **3**—**5** were also glycosides of the same aglycone framework that varied structurally from **2** only in their saccharide moieties, and that these sugar units were also affixed to the C-3 and C-30 positions.

Hoduloside VI (**1**) had the molecular formula, $C_{41}H_{68}O_{14}$ [FAB-MS, *m/z*: 783 $(M-H)^-$] and gave L-arabinose and D-glucose in the ratio of 1 : 1 on acid hydrolysis. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one α-arabinopyranosyl unit [H-1: δ 4.86 (d, J=7.7 Hz), C-1: δ 107.6] and one β-glucopyranosyl unit [H-1: δ 5.03 (d, J=7.7 Hz), C-1: δ 105.2]. The NOE was observed between C_3-H (δ 3.34) of the aglycone and C_1-H (δ 4.86) of arabinose, indicating that the *O*-3 of aglycone should be glycosylated with α-arabinose. The NOE between C_{30}-H and C_1-H of glucose indicated the *O*-30 of aglycone to be glycosylated with β-glucose. Hence, the structure of hoduloside VI was established as 3β,20(*S*),25,30-tetrahydroxy-16-oxodammar-23-ene-3-*O*-α-L-arabinopyranoside-30-*O*-β-D-glucopyranoside.

Hoduloside VIII (**3**) had the molecular formula, $C_{46}H_{76}O_{18}$ [FAB-MS, *m/z* 915 $(M-H)^-$], *i.e.*, 132 mass units more than that of **1**. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one α-arabinopyranosyl unit [H-1: δ 4.86 (d, J=7.7 Hz), C-1: δ 107.3], one β-glucopyranosyl unit [H-1: δ 4.89 (d, J=7.3 Hz), C-1: δ 105.2] and one β-xylopyranosyl unit [H-1: δ 4.83 (d, J=7.8 Hz), C-1: δ 105.8]. On acid hydrolysis, **3** furnished L-arabinose, L-rhamnose and D-xylose in a molar ratio of 1 : 1 : 1 indicating **3** to have one additional xylopyranosyl unit compared to **2**. The EI-MS of **3** acetate showed the fragment ion peaks due to a terminal pentosyl (*m/z* 259) and a pentosylhexosyl (*m/z* 547). A ^{13}C-NMR spectral comparison of **3** with **1** showed a glycosylation shift of +7.1 ppm at the C-6 position of the glucose moiety in **3**, indicating the site of glycosylation. Hence, the structure of hoduloside VIII was established as 3β,20(*S*),25,30-tetrahydroxy-16-oxodammar-23-ene-3-*O*-α-L-arabinopyranoside-30-*O*-β-D-xylopyranosyl (1→6)-β-D-glucopyranoside.

Hoduloside IX (**4**) had the molecular formula $C_{52}H_{86}O_{22}$ based on the quasi-molecular ion peak at *m/z* 1061 $[M-H]^-$ and also showed peaks at *m/z* 929 $[M-H-Xyl]^-$, 915 $[M-H-Rha]^-$ in the FAB-MS. Acid hydrolysis of **4** provided D-glucose, D-xylose, L-arabinose and L-rhamnose in the ratio of 1 : 1 : 1 : 1. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one α-arabinopyranosyl unit [H-1: δ 4.98 (d, J=5.4 Hz), C-1: δ 104.8], one β-glucopyranosyl unit [H-1: δ 4.93 (d, J=7.3 Hz), C-1: δ 105.2], one β-xylopyranosyl unit [H-1: δ 4.85 (d, J=7.8 Hz), C-1: δ 105.8] and one α-rhamnopyranosyl unit [H-1: δ 6.15, s, C-1: δ 101.7]. The EI-MS of **4** acetate showed characteristic fragment ion peaks due to a terminal pentosyl (*m/z* 259), terminal deoxyhexosyl (*m/z* 273), pentosyldeoxyhexosyl (*m/z* 487) and pentosylhexosyl (*m/z* 547). In the ^{13}C-NMR data of **4**, the sugar signals at C-3 were superimposable on those of **1**, while the sugar signals at C-30 were in good agreement with those of **3**. Consequently, hoduloside IX was characterized as 3β,20(*S*),25,30-tetrahydroxy-16-oxodammar-23-ene-3-*O*-α-





saponin C_2 (**6**)

hoduloside	R_1	R_2
VI (**1**)	-Ara	-Glc
VII (**2**)	-Ara-2-Rha	-Glc
VIII (**3**)	-Ara	-Glc-6-Xyl
IX (**4**)	-Ara-2-Rha	-Glc-6-Xyl
X (**5**)	-Ara-2-Rha (3-Glc)	-Glc

Ara : α-L-arabinopyranosyl
Rha : α-L-rhamnopyranosyl
Glc : β-D-glucopyranosyl
Xyl : β-D-xylopyranosyl

Chart 2

TABLE I. ^{13}C-NMR Spectral Data for Compounds **1**—**6** (50 MHz, Pyridine-d_5, δ-Values)

C no.	**1**	**2**[a]	**3**	**4**	**5**	**6**
1	38.9	38.8	39.0	38.9	38.8	39.0
2	26.6	26.9	26.9	26.8	26.8	26.8
3	88.5	88.3	88.6	88.4	87.7	88.1
4	39.7	39.7	39.9	39.7	39.7	39.6
5	56.1	56.0	56.1	56.1	56.1	56.3
6	18.6	18.5	18.7	18.6	18.5	18.4
7	36.2	36.1	36.5	36.3	36.1	36.1
8	40.7	40.7	40.9	40.7	40.6	37.6
9	51.7	51.6	51.8	51.6	51.5	53.0
10	37.4	37.4	37.5	37.4	37.3	37.3
11	21.8	21.9	21.9	21.8	21.7	21.8
12	27.4	27.4	27.4	27.3	27.2	28.5
13	41.8	41.8	41.9	41.8	41.7	37.2
14	49.2	49.1	49.4	49.2	49.0	53.8
15	45.4	45.3	45.2	45.4	45.2	36.9
16	220.6	220.5	220.8	220.6	220.3	110.6
17	58.0	57.9	58.2	58.0	57.8	54.0
18	17.1	17.1	17.2	17.0	17.0	18.9
19	16.7	16.6	16.8	16.7	16.6	16.4
20	75.0	75.0	75.1	75.0	74.9	68.5
21	26.9	26.9	26.9	26.8	26.7	30.1
22	44.1	44.1	44.0	44.0	44.1	45.5
23	123.2	123.2	123.2	123.2	123.2	68.7
24	142.6	142.7	142.8	142.7	142.6	127.1
25	70.2	70.1	70.3	70.1	69.9	134.2
26	30.7	30.7	30.7	30.8	30.6	25.6
27	30.7	30.7	30.7	30.8	30.6	18.4
28	27.9	28.1	28.3	28.0	27.8	28.1
29	16.9	16.7	16.9	16.9	16.8	16.8
30	71.5	71.5	71.5	71.4	71.4	65.9

a) 150 MHz.

TABLE II. ^{13}C-NMR Spectral Data for Compounds **1**—**6** (50 MHz Pyridine-d_5, δ-Values)

Compd. No.	**1**	**2**[a]	**3**	**4**	**5**	**6**
3-*O*-Ara						
1	107.6	105.0	107.3	104.8	104.8	104.9
2	73.0	76.0	73.1	76.0	74.6	74.8
3	74.7	74.1	74.7	73.9	82.4	82.4
4	69.6	68.9	69.6	68.8	68.4	68.3
5	66.9	64.9	66.7	64.8	65.0	65.0
Rha (1→2)						
1		101.8		101.7	102.0	101.9
2		72.5		72.4	72.5	72.5
3		72.6		72.6	72.5	72.5
4		74.1		74.1	73.9	73.9
5		70.0		69.9	70.0	70.0
6		18.7		18.6	18.6	18.6
Glc (1→3)						
1					104.8	104.8
2					75.0	75.0
3					78.2	78.3
4					71.4	71.5
5					78.6	78.6
6					62.5	62.6
30-*O*-Glc						
1	105.2	105.2	105.2	105.2	105.2	
2	75.1	75.1	75.1	75.0	75.0	
3	78.9	78.9	78.7	78.7	78.9	
4	71.6	71.5	71.2	71.5	71.4	
5	78.6	78.5	77.1	77.1	78.6	
6	62.8	62.8	69.9	69.9	62.7	
Xyl (1→6)						
1			105.8	105.8		
2			74.9	74.7		
3			78.1	78.0		
4			71.2	71.3		
5			67.0	67.0		

a) 150 MHz.

L-rhamnopyranosyl (1→2)-α-L-arabinopyranoside-30-*O*-β-D-xylopyranosyl (1→6)-β-D-glucopyranoside.

Hoduloside X (**5**) had the molecular formula, $C_{53}H_{88}O_{23}$ [FAB-MS, *m/z* 1091 $(M-H)^-$], *i.e.*, 162 mass units more than that of **2**. Acid hydrolysis of **5** afforded D-glucose, D-xylose and L-arabinose in the ratio of 2 : 1 : 1. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one α-arabinopyranosyl unit [H-1: δ 4.84 (d, J=5.7 Hz), C-1: δ 104.8], two β-glucopyranosyl units [H-1: δ 4.98 (d, J=7.5 Hz), 5.14 (d, J=7.5 Hz), C-1: δ 104.8, 105.2] and one α-rhamnopyranosyl unit [H-1: δ 6.22, s, C-1: δ 102.0]. The EI-MS of **5** acetate showed fragment ion peaks due to terminal deoxyhexosyl (*m/z* 273) and hexosyl (*m/z* 331), pentosyldeoxyhexosylhexosyl (*m/z* 777). The C-3 signal of the 3-*O*-arabinosyl unit in **5** was shifted to lower field by +8.3 ppm from **2** because of the glycosylation shift, disclosing a β-glucopyranosyl group to be located at C-3 of arabinose. Further, the chemical shifts of the 3-*O*-sugar

units in **5** were in good agreement with those of **6**, confirming a glucosyl unit to be connected to C-30-OH. Hence, hoduloside X was characterized as 3β,20(*S*),25,30-tetrahydroxy-16-oxodammar-23-ene-3-*O*-{β-D-glucopyranosyl (1→3)-[α-L-rhamnopyranosyl (1→2)]-α-L-arabinopyranoside}-30-*O*-β-D-glucopyranoside.

Position 30 of the aglycone in hodulosides VI—X from *H. dulcis* var. *tomentella* is glucosylated, while the same position in hodulosides I—V from *H. dulcis* is etherified by acetalization at position 16, implying that the aglycone of hodulosides VI—X is a precursor of that of hodulosides I—V and that *H. dulcis* var. *tomentella* is a more primitive species.

A 1 mM solution of each of hoduloside VII—IX completely suppressed the sensation of sweetness induced by 0.2 M sucrose. This activity was the same as that of hoduloside I.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were taken on a JASCO DIP-140 digital polarimeter, IR spectra on a Hitachi IR-27G, and NMR spectra on Varian UNITY 200 and 600 spectrometers in C_5D_5N solution using tetramethylsilane (TMS) as an internal standard. NMR experiments included ^{1}H–^{1}H-COSY, ^{13}C–^{1}H-COSY, distortionless enhancement by polarization transfer (DEPT), HMBC (512 × 1024 data matrix size, 128 scans, recycle delay = 1.16 s) and ROESY. Coupling constants (J values) are given in hertz (Hz). The FAB-MS (Xe gun, 10 kV, *m*-nitrobenzyl alcohol as the matrix) were measured on a JEOL JMS-PX303 mass spectrometer. For column chromatography, Kiesel gel 60 (230—400 mesh, Merck), and for TLC, Silica gel 60F-254 (Merck) were used. HPLC was carried out with a Waters ALC/GPC 244 instrument.

Isolation of Saponins Fresh leaves (9.5 kg) of *H. dulcis* THUNB. var. *tomentella* MAKINO collected in Tokushima prefecture, in October 1991, were extracted with absolute EtOH at room temperature for 2 weeks. The EtOH extract obtained after evaporation of the solvent *in vacuo* was applied to an Amberlite XAD-2 column. The column was washed with water, then the adsorbed materials were eluted with 100% MeOH. The MeOH eluate (100 g) was chromatographed on Bondpack C_{18} with 40—80% MeOH to give four fractions (frs. 1—4). Fraction 3 was subjected to MPLC on ODS (Develosil Lop ODS, 20% CH_3CN) to give four fractions. (frs. 3-1—4). Frs. 3-2 and 3-3 were purified by preparative HPLC (YMC, ODS S-5, 15—20% CH_3CN) to afford hoduloside IX (**4**, 0.00021%) from fr. 3-2 and hodulosides VI (**1**, 0.00047% from the crude drug), VII (**2**, 0.00074%), VIII (**3**, 0.00063%) and X (**5**, 0.00026%) from fr. 3-3.

Hoduloside VI (**1**): An amorphous white powder, $[\alpha]_D$ −38.6° (c = 2.5, MeOH). IR (KBr) cm^{-1}: 3400, 1730. Negative FAB-MS m/z: 783 $[M(C_{41}H_{68}O_{14})-H]^-$, 651 $[M-H-Ara]^-$, 621 $[M-H-Glc]^-$. *Anal.* Calcd for $C_{41}H_{68}O_{14}\cdot H_2O$: C, 61.33; H, 8.79. Found: C, 61.21; H, 8.91. ^{1}H-NMR (200 MHz, C_5D_5N) δ: 0.79, 0.91, 1.04, 1.17, 1.50, 1.50, 1.53 (3H each, s, *tert*-CH_3 × 7), 2.52, 2.78 (each 1H, d, J = 16.3 Hz, H-15), *ca.* 2.90 (H-22), 3.02 (1H, dd, J = 13.5, 7.8 Hz, H-22), 3.30 (1H, d, J = 11.4 Hz, H-17), *ca.* 3.34 (H-3), 4.71 (1H, d, J = 10.3 Hz, H-30), 6.10 (1H, d, J = 15.6 Hz, H-24), 6.47 (1H, ddd, J = 15.6, 7.8, 7.8 Hz, H-23), 4.86 (1H, d, J = 7.2 Hz, H-1 of Ara), 5.03 (1H, d, J = 7.7 Hz, H-1 of Glc). ^{13}C-NMR: Tables I and II.

Hoduloside VII (**2**): An amorphous white powder, $[\alpha]_D$ −52.1° (c = 5.2, MeOH). IR (KBr) cm^{-1}: 3400, 1730. Negative FAB-MS m/z: 929 $[M(C_{47}H_{78}O_{18})-H]^-$, 783 $[M-H-Rha]^-$, 767 $[M-H-Glc]^-$. *Anal.* Calcd for $C_{47}H_{78}O_{18}\cdot H_2O$: C, 59.48; H, 8.50. Found: C, 59.75; H, 8.14. ^{1}H-NMR (600 MHz, C_5D_5N) δ: 0.79 (3H, s, H_3-19), 1.04 (each 3H, s, H_3-18, -29), 1.08 (3H, s, H_3-28), 1.51 (each 3H, s, H_3-26, -27), 1.53 (3H, s, H_3-21), 1.63 (3H, d, J = 6.3 Hz, H-6 of Rha), 2.43, 2.64 (each 1H, d, J = 16.1 Hz, H-15), *ca.* 2.77 (1H, m, H-22), 2.91 (1H, dd, J = 13.5, 7.8 Hz, H-22), 3.12 (1H, dd, J = 12.0, 5.5 Hz, H-3), 3.21 (1H, d, J = 11.4 Hz, H-17), 6.01 (1H, d, J = 15.6 Hz, H-24), *ca.* 4.30, 4.71 (1H, d, J = 10.3 Hz, H-30), 6.01 (1H, d, J = 15.6 Hz, H-24), 6.35 (1H, ddd, J = 15.6, 7.8, 7.8 Hz, H-23), 4.88 (1H, d, J = 5.6 Hz, H-1 of Ara), 4.93 (1H, d, J = 7.8 Hz, H-1 of Glc), 6.15 (1H, s, H-1 of Rha). ^{13}C-NMR: Tables I and II.

Hoduloside VIII (**3**): An amorphous white powder, $[\alpha]_D$ −34.4° (c = 4.6, MeOH). IR (KBr) cm^{-1}: 3400, 1730. Negative FAB-MS m/z: 915 $[M(C_{46}H_{76}O_{18})-H]^-$, 783 $[M-H-Xyl]^-$. *Anal.* Calcd for $C_{46}H_{76}O_{18}\cdot 3/2H_2O$: C, 58.42; H, 8.43. Found: C, 58.64; H, 8.45. ^{1}H-NMR (200 MHz, C_5D_5N) δ: 0.80, 0.93, 1.06, 1.25, 1.52, 1.52, 1.54 (3H each, s, *tert*-CH_3 × 7), 2.43 (each 1H, d, J = 16.3 Hz, H-15), *ca.* 2.80 (H-15), *ca.* 2.83 (H-22), 3.06 (1H, d, J = 11.4 Hz, H-17), 3.26 (1H, m, H-3), 4.76 (1H, d, J = 10.5 Hz, H-30), 6.00 (1H, d, J = 15.6 Hz, H-24), 6.31 (1H, ddd, J = 15.6, 7.8, 7.8 Hz, H-23), 4.83 (1H, d, J = 7.8 Hz, H-1 of Xyl), 4.86 (1H, d, J = 7.7 Hz, H-1 of Ara), 4.89 (1H, d, J = 7.3 Hz, H-1 of Glc). ^{13}C-NMR: Tables I and II.

Hoduloside IX (**4**): An amorphous white powder, $[\alpha]_D$ −37.6° (c = 1.8, MeOH). IR (KBr) cm^{-1}: 3400, 1730. Negative FAB-MS m/z: 1061 $[M(C_{52}H_{86}O_{22})-H]^-$, 929 $[M-H-Xyl]^-$, 915 $[M-H-Rha]^-$. *Anal.* Calcd for $C_{52}H_{86}O_{22}\cdot H_2O$: C, 57.76; H, 8.20. Found: C, 57.59; H, 7.99. ^{1}H-NMR (200 MHz, C_5D_5N) δ: 0.79, 1.04, 1.05, 1.17, 1.51, 1.51, 1.53 (3H each, s, *tert*-CH_3 × 7), 2.43, 2.78 (each 1H, d, J = 15.9 Hz, H-15), *ca.* 2.75 (H-15), 2.95 (1H, dd, J = 13.5, 7.8 Hz, H-22), 3.11 (1H, d, J = 11.2 Hz, H-17), *ca.* 3.26 (1H, m, H-3), 4.81 (1H, d, J = 10.5 Hz, H-30), 6.01 (1H, d, J = 15.6 Hz, H-24), 6.33 (1H, ddd, J = 15.6, 7.8, 7.8, H-23), 4.81 (1H, d, J = 10.5 Hz, H-30), 4.85 (1H, d, J = 7.8 Hz, H-1 of Xyl), 4.93 (1H, d, J = 7.3 Hz, H-1 of Glc), 4.98 (1H, d, J = 5.4 Hz, H-1 of Ara), 6.15 (1H, s, H-1 of Rha). ^{13}C-NMR: Tables I and II.

Hoduloside X (**5**): An amorphous white powder, $[\alpha]_D$ −35.0° (c = 1.8, MeOH). IR (KBr) cm^{-1}: 3400, 1730. Negative FAB-MS m/z: 1091 $[M(C_{53}H_{88}O_{23})-H]^-$, 945 $[M-H-Rha]^-$, 929 $[M-H-Glc]^-$. *Anal.* Calcd for $C_{53}H_{88}O_{23}\cdot 5/2H_2O$: C, 55.92; H, 8.23. Found: C, 55.96; H, 7.86. ^{1}H-NMR (200 MHz, C_5D_5N) δ: 0.76, 1.01, 1.09, 1.10, 1.51, 1.51, 1.52 (3H each, s, *tert*-CH_3 × 7), 1.64 (3H, d, J = 5.5 Hz, H-6 of Rha), 2.42, 2.68 (each 1H, d, J = 15.9 Hz, H-15), *ca.* 2.78 (H-15), 2.96 (1H, dd, J = 13.5, 7.8 Hz, H-22), *ca.* 2.78 (H-22), *ca.* 3.18 (1H, m, H-3), 3.27 (1H, dd, J = 11.5 Hz, H-17), 4.71 (1H, d, J = 10.3 Hz, H-30), 6.00 (1H, d, J = 15.6 Hz, H-24), 6.39 (1H, ddd, J = 15.6, 7.8, 7.8, H-23), 4.84 (1H, d, J = 5.7 Hz, H-1 of Ara), 4.98 (1H, d, J = 7.5 Hz, H-1 of C-30-Glc), 5.14 (1H, d, J = 7.5 Hz, H-1 of C-3-Glc), 6.22 (1H, s, H-1 of Rha). ^{13}C-NMR: Tables I and II.

Identification of Component Sugars of 1—5 A solution of each compound (each 2—3 mg) in 5% H_2SO_4 in 50% EtOH was heated at 100 °C for 3 h. The reaction mixture was diluted with water, neutralized with Amberlite IR-45 and concentrated *in vacuo* to dryness. The mole ratio and configuration of each sugar were determined by using refractive index (RI) detection (Waters 410) and chiral detection (Shodex OR-1), respectively, in HPLC (Shodex RSpak DC-613, 75% CH_3CN, 1 m/min, 70 °C) by comparison with authentic sugars (10 mmol each of L-Rha, D-Xyl, L-Ara and D-Glc). These sugars gave the following peaks: L-(−)-Rha; 4.80 min, D-(+)-Xyl; 5.75 min, L-(+)-Ara; 6.20 min, D-(+)-Glc; 7.38 min.

Acetylation of 1, 3—5 Each compound, **1** and **3—5** (2 mg), was acetylated with Ac_2O–pyridine (each 0.1 ml) at room temperature overnight. Work-up as usual gave a colorless oil in each case. **1**-Ac: Negative FAB-MS m/z: 1077 $[M(C_{55}H_{82}O_{21})-H]^-$. **2**-Ac: Negative FAB-MS m/z: 1307 $[M(C_{65}H_{96}O_{27})-H]^-$. **3**-Ac: Negative FAB-MS m/z: 1293 $[M(C_{64}H_{94}O_{27})-H]^-$. **4**-Ac: Negative FAB-MS m/z: 1523 $[M(C_{74}H_{101}O_{33})-H]^-$. **5**-Ac: Negative FAB-MS m/z: 1595 $[M(C_{77}H_{112}O_{35})-H]^-$. **1—5**-Ac: IR ($CCl_4$) cm^{-1}: 3550—3540, 1760—1750, 1230—1220, 1035—1030.

Bioassay of Antisweet Activity The antisweet activity of a 1 mM solution of each of **1—5** was tested on three volunteers. Each participant held the test solutions in the mouth for 3 min, spat, rinsed with distilled water and tasted a sucrose solution (0.1 or 0.2 M).

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