Antisweet Natural Products. VII.[1] Hodulosides I, II, III, IV, and V from the Leaves of *Hovenia dulcis* THUNB.

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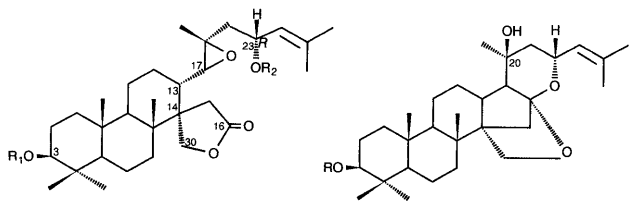
From the fresh leaves of *Hovenia dulcis* THUNB., five new dammarane glycosides named hodulosides I—V (1—5) were isolated besides the known saponins hovenoside I (6), saponins C_2, (7), E (8) and H (9) and jujuboside B (10). Their structures were determined on the basis of chemical and spectral evidence. Further nuclear magnetic resonance spectral analysis of neohesperidosyl moieties of 1 led to the conclusion that the reported shifts of C_2 and C_3 of the glucosyl part in neohesperidose should be revised. All of the compounds (1—10) showed antisweet activities.

Keywords *Hovenia dulcis*; Rhamnaceae; hoduloside; hodulcin; hovenolactone; jujubogenin; antisweet substance; abnormal glycosylation shift

As a part of our studies on naturally occurring antisweet substances, we have reported the antisweet principles of *Ziziphus jujuba* (Rhamnaceae).[1,2] The leaves of *Hovenia dulcis* (Rhamnaceae) were also suggested to have the ability temporarily to destroy a sweet taste. But the chemical structure of the active component, hodulcin (main saponin), named by Kennedy *et al.*, has not yet been elucidated.[3] Therefore, we have initiated a chemical study of the title plant.

The EtOH extract obtained from the fresh leaves of *H. dulcis* (5 kg) was partitioned among EtOAc, BuOH and H_2O. The antisweet active BuOH soluble portion was purified by column chromatography on octadecyl silica gel (ODS) followed by systematic high-performance liquid chromatography (HPLC) (ODS, 20—25% CH_3CN) to provide five new dammarane saponins, hodulosides I (**1**, 70 mg), II (**2**, 120 mg), III (**3**, 2 g), IV (**4**, 100 mg) and V (**5**, 50 mg), together with hovenoside I (**6**, 130 mg),[4] saponins C_2 (**7**, 1.8 g),[5] E (**8**, 5 g)[5] and H (**9**, 150 mg),[5] and jujuboside B (**10**, 50 mg).[1]

On enzymatic hydrolysis, **1** and **2** yielded **8** as a prosapogenin. A comparison of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectral data due to the aglycone moieties with those of **8** revealed that **1** was a 3, 23-bisdesmoside of hovenolactone[5] and **2** was a 3-monodesmoside (Tables I and II). A detailed proton spin decoupling experiment, ^{1}H–^{1}H correlation spectroscopy (^{1}H–^{1}H COSY), ^{1}H–^{13}C COSY, homonuclear Hartman–Hahn (HOHAHA), heteronuclear multiple-bond correlation (HMBC) and two dimensional nuclear Overhauser effect spectroscopy (NOESY) experiments led to determination of the complete structures of **1**—**5**, inclusive of the sequence of the sugar moieties and the position of attachment of the sugar chains to the aglycone (Tables III and IV).



	R_1	R_2
1	-glc^{2}rha	-glc
2	-glc^{2}rha	-H
	|3	
	glc	
8	-glc^{2}rha	-H
9	-glc	

	R
3	-ara^{2}qui
	|3
	glc
4	-ara^{2}glc
	|3
	glc
5	-glc^{2}rha
	|3
	glc

	R
6	-ara^{2}xyl
	|3
	glc
7	-ara^{2}rha
	|3
	glc
10	-ara^{2}rha
	|3
	glc^{2}xyl

Chart 1

Hoduloside I (**1**) was obtained as an amorphous powder and had the molecular formula $C_{48}H_{78}O_{19}$ as deduced from the quasi-molecular ion peak at *m/z* 957 in the negative fast atom bombardment spectrum (FAB-MS) and carbon counts in the ^{13}C-NMR spectrum. Acid hydrolysis of **1** afforded D-glucose and L-rhamnose in the molar ratio of 2:1 (HPLC) as component sugars. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of two β-glucopyranosyl units [H-1: δ 4.94 (d, J=7.0 Hz), C-1: δ 105.4 and H-1: δ 4.92 (d, J=8.0 Hz), C-1: δ 103.2] and one α-rhamnopyranosyl unit [H-1: δ 6.60 (s), C-1: δ 101.5]. The electron impact mass spectrum (EI-MS) for the peracetate of **1** showed the characteristic fragment ion peaks due to terminal deoxyhexosyl (*m/z* 273) and hexosyl (*m/z* 331), and deoxyhexosylhexosyl (*m/z* 561) groups. Comparison of the ^{13}C-NMR spectrum of **1** with that of **8** showed a glycosylation shift[6] for the C-23 signal (+8.5 ppm, from δ 65.5 to 74.0), demonstrating the C-*O*-23 to be glycosylated. Further, in the HMBC and NOESY spectra, correlations were observed between C-23 (δ 74.0) and H-1 (23-glc, δ 4.92), and between H-23 (δ 4.88) and H-1 (23-glc), respectively (Table IV). Hence, **1** was characterized as 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl-23-*O*-β-D-glucopyranosyl hovenolactone.

During the structure elucidation of **1** by using NMR data, we found abnormal glycosylation shifts in the glucosyl unit of the neohesperidosyl moiety. In the ^{13}C-NMR spectra of glycosides having a neohesperidosyl unit,[5,7,8] the C-2 and C-3 carbons of the glucosyl part have generally been assigned to a lower field signal (δ 79—81) and a higher field one (δ 76—78), respectively, on the basis of the glycosylation shift rule.[6] But, in the ^{13}C–^{1}H COSY spectrum of **1**, cross peaks were observed between the former (δ 79.8) and H-3 of glucose (δ 4.27), and between the latter (δ 77.4) and H-2 of glucose (δ 4.30), indicating that the signal appearing at lower field (δ 79—81) and that at higher field (δ 76—78) should be as-

signed to be the C-3 and C-2 carbons of the glucosyl unit of neohesperidoside, respectively (Figs. 1 and 2). Those assignment errors seem to have been the cause of the apparent abnormal glycosylation shifts on formation of the neohesperidosyl linkage. For example, comparison of the ^{13}C-NMR spectrum of **8** with that of **9** showed glycosylation shifts for the C-1 signal (−1.5 ppm), C-2 signal (+1.9 ppm), and C-3 signal (+1.5 ppm) of the glucopyranosyl moiety. Similar examples were also observed in the galactosyl unit of glycosides having the -*O*-gal^2-rha sequence.[1)]

Table I. ^{13}C-NMR Spectral Data for the Aglycone Moieties of Compounds **1**—**8** (in Pyridine-d_5, 150 MHz)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
C-1	38.6	38.9	38.2	38.7	39.0	38.7	38.9	38.9
C-2	26.6	26.7	26.8	26.8	26.8	26.8	26.8	26.9
C-3	88.4	88.5	89.1	88.9	88.6	89.0	88.9	88.6
C-4	39.4	39.5	39.9	39.9	39.7	39.9	39.6	39.6
C-5	55.3	55.5	56.2	56.2	56.3	56.2	56.3	55.5
C-6	18.2	18.1	18.3	18.4	18.4	18.3	18.3	18.1
C-7	33.7	33.9	36.1	36.1	36.0	36.1	36.0	34.0
C-8	39.9	40.2	37.5	37.6	37.5	37.5	37.5	40.2
C-9	52.3	52.4	53.0	53.1	53.0	53.0	53.0	52.5
C-10	36.6	36.8	37.3	37.3	37.2	37.1	37.3	36.9
C-11	19.5	19.8	21.8	21.8	21.8	21.8	21.7	19.9
C-12	25.1	25.4	28.5	28.6	28.6	28.5	28.5	25.4
C-13	39.7	39.8	37.1	37.2	37.2	37.0	37.1	39.8
C-14	51.3	51.5	53.7	53.8	53.8	53.5	53.8	51.5
C-15	34.1	34.3	36.8	36.9	36.8	36.9	36.9	34.3
C-16	177.0	177.1	110.5	110.6	110.6	110.6	110.6	177.2
C-17	63.5	63.8	54.0	54.0	54.0	54.0	54.0	63.9
C-18	17.7	18.0	18.9	18.9	18.9	18.9	18.9	18.2
C-19	15.9	16.1	16.3	16.3	16.4	16.3	16.4	16.2
C-20	57.0	57.8	68.5	68.6	68.5	68.5	68.5	57.8
C-21	17.7	17.8	30.1	30.1	30.1	30.1	30.1	17.9
C-22	44.9	47.6	45.5	45.6	45.5	45.4	45.5	47.7
C-23	74.0	65.4	68.6	68.8	68.6	68.6	68.6	65.5
C-24	127.3	130.4	127.1	127.1	127.1	127.1	127.1	130.4
C-25	134.3	132.4	134.1	134.2	134.2	134.1	134.2	133.0
C-26	25.7	25.8	25.5	25.6	25.6	25.6	25.6	25.9
C-27	18.2	18.1	18.3	18.4	18.4	18.4	18.3	18.0
C-28	27.8	27.8	27.9	28.0	27.9	27.7	27.9	28.0
C-29	16.7	16.9	16.5	16.6	16.9	16.3	16.6	17.0
C-30	69.5	69.6	65.8	65.9	65.9	65.8	65.7	69.6

Table II. ^{13}C-NMR Spectral Data for the Sugar Moieties of Compounds **1**—**5**, **8** and **9** (in Pyridine-d_5, 150 MHz)

	1	**2**	**3**	**4**	**5**	**8**	**9**
3-*O*-Ara or glc							
C-1′	105.4	105.0	105.7	105.5	105.0	105.5	107.0
C-2′	77.4	76.8	77.2	77.5	76.9	77.7	75.8
C-3′	79.8	89.6	83.7	83.3	89.6	79.9	78.4
C-4′	72.0	69.9	68.9	68.9	69.9	72.3	71.9
C-5′	78.2	78.0	66.1	66.1	78.0	78.3	78.8
C-6′	62.8	62.8			62.7	63.0	63.2
Glc or qui or rha (1→2)							
C-1″	101.5	101.7	104.1	104.4	101.7	101.7	
C-2″	72.4	72.5	76.3	76.2	72.4	72.6	
C-3″	72.4	72.5	78.5	78.7	72.5	72.5	
C-4″	74.0	73.9	77.0	72.4	73.9	74.1	
C-5″	69.5	69.8	72.8	77.5	69.9	69,6	
C-6″	18.6	18.7	18.6	63.2	18.7	18.7	
Glc (1→3)							
C-1‴		104.0	105.1	105.0	104.0		
C-2‴		75.1	75.3	75.3	75.2		
C-3‴		78.5	78.3	78.3	78.4		
C-4‴		71.5	71.5	71.5	71.4		
C-5‴		78.7	78.5	78.5	78.7		
C-6‴		62.3	62.5	62.5	62.3		
23-*O*-Glc							
C-1	103.2						
C-2	75.3						
C-3	78.7						
C-4	71.6						
C-5	78.2						
C-6	62.7						

Table III. ^{1}H-NMR Spectral Data for the Sugar Moieties of Compounds **1**—**5** (in Pyridine-d_5, 600 MHz)

	1	**2**	**3**	**4**	**5**
3-*O*-Glc or ara					
1′	4.94 (d, 7.0)	4.87 (d, 7.7)	4.71 (d, 7.0)	4.78 (d, 7.0)	4.86 (d, 7.8)
2′	4.30 (dd, 8.8, 7.0)	4.31 (d, 9.0, 7.7)	4.67 (dd, 9.0, 7.0)	4.74 (dd, 8.8, 7.0)	4.31 (dd, 9.0, 7.8)
3′	4.27 (dd, 9.0, 8.8)	4.24 (d, 9.0, 9.0)	4.26 (dd, 9.0, 3.5)	4.32 (dd, 8.8, 3.5)	4.25 (dd, 9.0, 9.0)
4′	4.12 (dd, 9.0, 8.7)	4.10 (dd, 9.5, 9.0)	4.49 (dd, 3.5, 2.0)	4.50 (dd, 3.5, 2.5)	4.10 (dd, 9.5, 9.0)
5′	3.94 (ddd, 8.7, 5.5, 2.5)	3.91 (ddd, 9.5, 5.5, 2.5)	4.13 (dd, 11.0, 2.0)	4.15 (dd, 11.0, 2.5)	3.92 (ddd, 9.5, 5.0, 2.5)
6′	4.35 (dd, 11.5, 5.5)	4.29 (dd, 11.2, 5.5)	3.62 (d, 11.0)	3.65 (d, 11.0)	4.28 (dd, 11.0, 5.0)
	4.56 (dd, 11.5, 2.5)	4.52 (dd, 11.2, 2.5)			4.51 (dd, 11.0, 2.5)
Rha or qui or glc (1→2)					
1″	6.60 s	6.54 s	5.41 (d, 8.0)	5.51 (d, 7.8)	6.53 s
2″	4.85 (d, 3.0)	4.86 (d, 3.0)	4.01 (dd, 9.0, 8.0)	4.06 (dd, 8.8, 7.8)	4.86 (d, 3.0)
3″	4.68 (dd, 9.5, 3.0)	4.64 (dd, 9.5, 3.0)	4.09 (dd, 9.0, 9.0)	4.20 (dd, 8.8, 7.6)	4.64 (dd, 9.5, 3.0)
4″	4.33 (dd, 9.5, 9.5)	4.34 (dd, 9.5, 9.5)	3.68 (dd, 9.0, 9.0)	4.19 (dd, 7.8, 7.6)	4.35 (dd, 9.5, 9.5)
5″	4.80 (dt, 9.5, 6.0)	4.80 (dt, 9.5, 6.0)	3.48 (dt, 9.0, 6.0)	3.70 (ddd, 7.8, 6.0, 3.0)	4.81 (dt, 9.5, 6.0)
6″	1.70 (d, 6.0)	1.71 (d, 6.0)	1.54 (d, 6.0)	4.29 (dd, 12.0, 6.0)	1.70 (d, 6.0)
				4.36 (dd, 12.0, 3.0)	
Glc (1→3) or 23-*O*-glc					
1‴	4.92 (d, 8.0)	5.17 (d, 8.0)	5.31 (d, 8.0)	5.32 (d, 7.8)	5.16 (d, 8.0)
2‴	3.98 (dd, 9.0, 8.0)	4.05 (dd, 8.7, 8.0)	3.99 (dd, 8.0, 8.0)	4.00 (dd, 8.8, 7.8)	4.04 (dd, 9.0, 8.0)
3‴	4.23 (dd, 9.2, 9.0)	4.21 (dd, 9.0, 8.7)	4.22 (dd, 9.0, 8.0)	4.22 (dd, 8.8, 7.6)	4.21 (dd, 9.5, 9.0)
4‴	4.21 (dd, 9.5, 9.2)	4.13 (dd, 9.5, 9.0)	4.19 (dd, 9.5, 9.0)	4.20 (dd, 7.8, 7.6)	4.12 (dd, 9.5, 9.0)
5‴	3.84 (ddd, 9.5, 5.0, 2.5)	4.06 (ddd, 9.5, 5.5, 2.5)	3.93 (ddd, 9.5, 5.0, 2.5)	3.94 (ddd, 7.8, 5.0, 2.0)	4.06 (ddd, 9.0, 5.0, 2.5)
6‴	4.31 (dd, 11.5, 5.0)	4.29 (dd, 11.2, 5.5)	4.32 (dd, 12.5, 5.0)	4.34 (dd, 12.0, 5.0)	4.28 (dd, 12.0, 5.0)
	4.43 (dd, 11.5, 2.5)	4.58 (dd, 11.2, 2.5)	4.47 (dd, 12.5, 2.5)	4.48 (dd, 12.0, 2.0)	4.58 (dd, 12.0, 2.5)

Hoduloside II (**2**) had the same molecular formula, $C_{48}H_{78}O_{19}$ [FAB-MS, *m/z* 957 $(M-H)^-$], as **1**. On acid hydrolysis, **2** afforded D-glucose and L-rhamnose in the ratio of 2 : 1. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of two β-glucopyranosyl units [H-1: δ 4.87 (d, $J=7.7$ Hz), C-1: δ 105.0 and H-1: δ 5.17 (d, $J=8.0$ Hz), C-1: δ 104.0] and one α-rhamnopyranosyl unit [H-1: δ 6.54 (s), C-1: δ 101.7]. The EI-MS of the peracetate of **2** showed the fragment ion peaks of a terminal deoxyhexosyl group (*m/z* 273), an hexosyl group (*m/z* 331), and a deoxyhexosyl(hexosyl)hexosyl (*m/z* 849) group. In the same way as for **1**, a glycosylation shift (**2** *vs.* **8**) of +9.7 ppm was observed for the C-3 of inner glucose (from δ 79.9 to 89.6), indicating the site of glycosylation. Therefore, **2** was characterized as 3-*O*-α-L-rhamnopyransoyl(1→2)-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranosyl hovenolactone.

TABLE IV. Selected Cross-Peaks from the HMBC and NOESY Experiments for Compounds **1**—**5** (in Pyridine-d_5, 600 MHz)

	HMBC	NOESY
1	C-3–H-1′(3-glc) C-2′(3-glc)–H-1″(rha) C-23–H-1‴(23-glc)	H-3–H-1′(3-glc) H-2′(3-glc)–H-1″(rha) H-23–H-1‴(23-glc)
2	C-3–H-1′(glc) C-2′(glc)–H-1″(rha)	H-3–H-1′(glc) H-2′(glc)–H-1″(rha) H-3′(glc)–H-1‴(glc)
3	C-3–H-1′(ara) C-2′(ara)–H-1″(qui) C-3′(ara)–H-1‴(glc)	H-3–H-1′(ara) H-2′(ara)–H-1″(qui) H-3′(ara)–H-1‴(glc)
4	C-3–H-1′(ara) C-2′(ara)–H-1″(glc) C-3′(ara)–H-1‴(glc)	H-3–H-1′(ara) H-2′(ara)–H-1″(glc) H-3′(ara)–H-1‴(glc)
5	C-3–H-1′(glc) C-2′(glc)–H-1″(rha)	H-3–H-1′(glc) H-2′(glc)–H-1″(rha) H-3′(glc)–H-1‴(glc)

The ^{13}C-NMR signals of compounds **3**—**5** were analogous with those of **6** and **7** except for those of sugar moieties, revealing **3**—**5** to be jujubogenin 3-*O*-glycosides.

Hoduloside III (**3**), was obtained as colorless needles. The FAB-MS of **3** showed ion peaks at *m/z* 911 $[M-H]^-$ and 745 $[M-\text{hexosyl}-H]^-$, suggesting the molecular formula, $C_{47}H_{76}O_{17}$. Acid hydrolysis of **3** provided L-arabinose, D-glucose and D-quinovose in the ratio of 1 : 1 : 1. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one α-arabinopyranosyl group [H-1: δ 4.71 (d, $J=7.0$ Hz), C-1: δ 105.7], one β-glucopyranosyl group [H-1: δ 5.31 (d, $J=8.0$ Hz), C-1: δ 105.1] and one β-quinovopyranosyl group [H-1: δ 5.41 (d, $J=8.0$ Hz), C-1: δ 104.1]. The EI-MS of the acetate of **3** showed fragment ion peaks due to terminal deoxyhexosyl (*m/z* 273) and hexosyl (*m/z* 331), deoxyhexosyl(hexosyl)pentosyl (*m/z* 777). The anomeric protons at δ 4.71 (arabinose), 5.31 (glucose) and 5.41 (quinovose) showed long-range correlations with the ^{13}C signals at δ 89.1 (C-3), 83.7 (C-3 of ara) and 77.2 (C-2 of ara), respectively in the HMBC spectrum (Table IV). Consequently, **3** was characterized as 3-*O*-β-D-quinovopyranosyl(1→2)-[β-D-glucopyranosyl(1→3)]-α-L-arabinopyranosyl jujubogenin.

Hoduloside IV (**4**) had the molcular formula, $C_{47}H_{76}O_{18}$

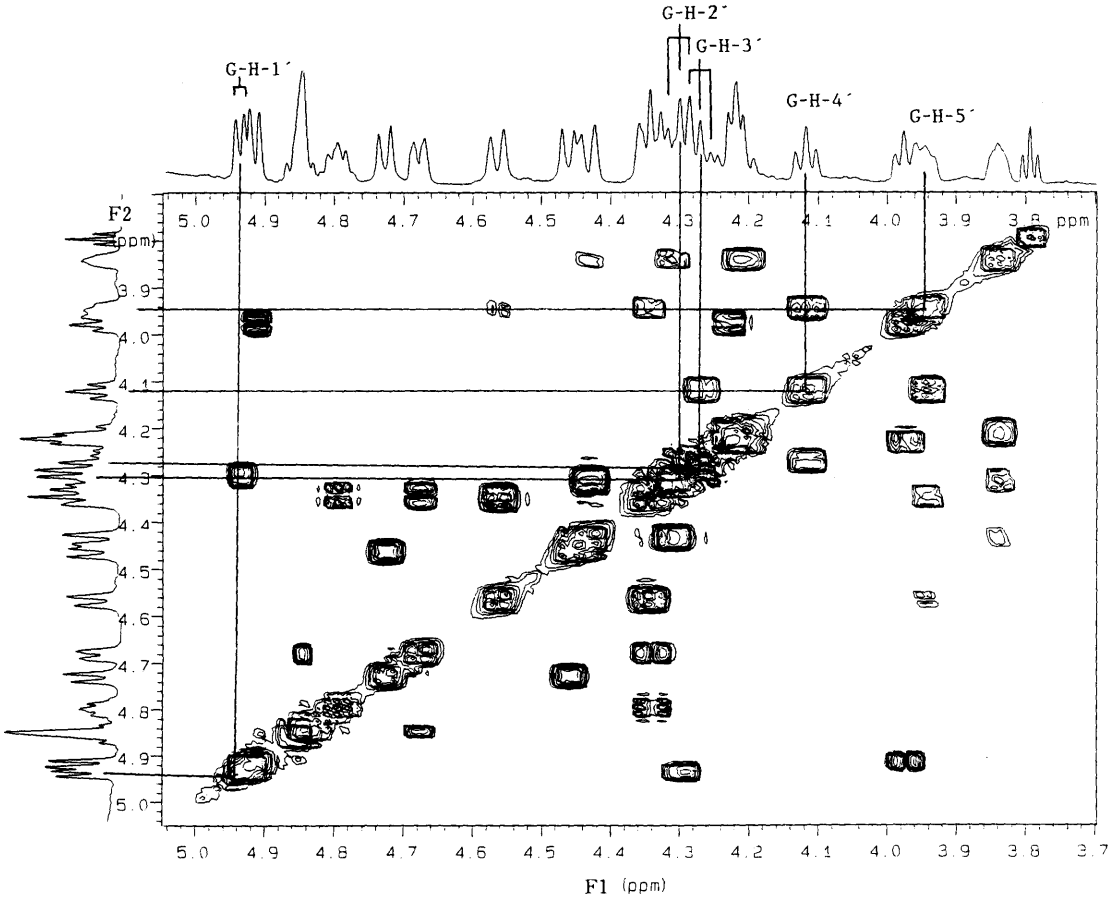


Fig. 1. ^{1}H–^{1}H Correlation 2D Spectrum of **1** in Pyridine-d_5 (600 MHz)

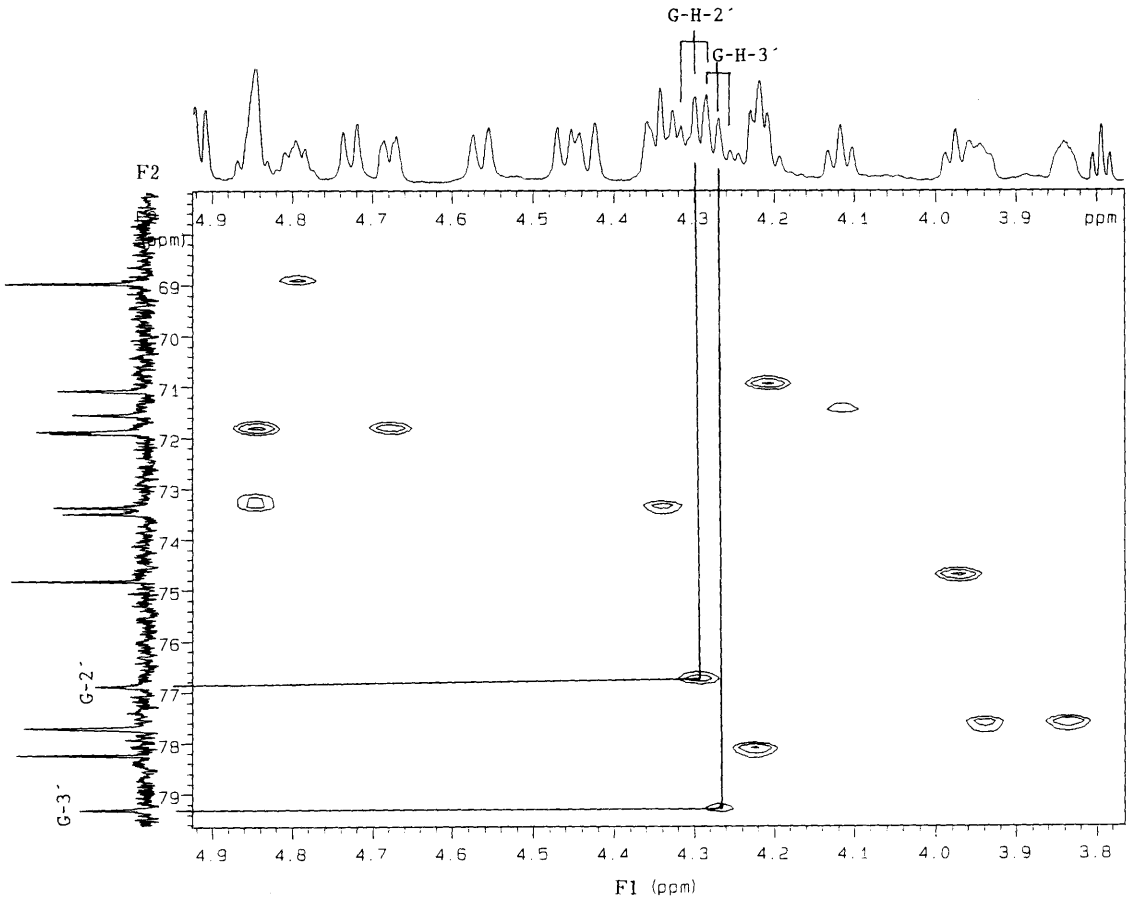


Fig. 2. ^{13}C–^{1}H Correlation 2D Spectrum of **1** in Pyridine-d_5 (600 MHz)

[FAB-MS, *m/z* 927 $(M-H)^-$]. On acid hydrolysis, **4** afforded L-arabinose and D-glucose in the ratio of 1 : 2. The ^1H- and ^{13}C-NMR spectra indicated the presence of one α-arabinopyranosyl unit [H-1: δ 4.78 (d, $J=7.0$ Hz), C-1: δ 105.5] and two β-glucopyranosyl units [H-1: δ 5.32 (d, $J=7.8$ Hz), C-1: δ 105.0 and H-1: δ 5.51 (d, $J=7.8$ Hz), C-1: δ 104.4]. The EI-MS of acetate of **4** exhibited the fragment ion peaks at *m/z* 331 (hexosyl) and *m/z* 835 [hexosyl(hexosyl)pentosyl]. The chemical shifts of the arabinosyl unit in **4** were in good agreement with those of **3**, suggesting that C-*O*-2 and C-*O*-3 of the arabinosyl unit should be glycosylated with β-glucopyranosyl. Hence, **4** was characterized as 3-*O*-β-D-glucopyranosyl(1→2)-[β-D-glucopyranosyl(1→3)]-α-L-arabinopyranosyl jujubogenin.

Hoduloside V (**5**), $C_{48}H_{78}O_{18}$ [FAB-MS *m/z* 941 $(M-H)^-$], afforded D-glucose and L-rhamnose (2 : 1) on acid hydrolysis. The EI-MS of the acetate of **5** showed the fragment ion peaks at *m/z* 273 (deoxyhexosyl), *m/z* 331 (hexosyl) and *m/z* 849 [deoxyhexosyl(hexosyl)hexosyl]. The carbon signals due to the sugar moieties of **5** were superimposable on those of **2**, indicating the presence of the same sugar linkages. Therefore, **5** was characterized as 3-*O*-α-L-rhamnopyranosyl(1→2)-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranosyl jujubogenin.

A 1 mmol solution of each of hodulosides II—V and hovenoside I and saponins C_2 and E and a 2 mmol solution of saponin H completely suppressed the sweet taste of 0.1 mol of sucrose. A 1 mmol solution of hoduloside I or jujuboside B completely suppressed the sweet taste of 0.2 mol of sucrose.

Kennedy *et al.* reported the isolation of hodulcin, a dammarane saponin containing of arabinose: glucose (1 : 3) as sugar components, as an antisweet principle from the dried leaves of *H. dulcis*.[3] However, in the present study, we could not find such a compound.

Experimental

All instruments used were as cited in the previous paper.[1] Medium performance liquid chromatography (MPLC) and HPLC were carried out with Develosil Lop ODS (30 μm, 1.5 cm i.d. × 25 cm, Nomura Kagaku) and Develosil ODS-T-7 (7 μm, 2.0 cm i.d. × 25 cm, Nomura Kagaku), respectively.

Isolation of Saponins The fresh leaves (5 kg) of *H. dulcis* were extracted with 60% EtOH at room temperature for 2 weeks. The extract (330 g) obtained after evaporation of the solvent *in vacuo* was suspended in water and extracted successively with *n*-hexane–EtOAc (1 : 1), EtOAc, and 1-BuOH saturated with H_2O. Yields of the extracts were as follows: *n*-hexane–EtOAc extract 30 g, EtOAc extract 80 g, 1-BuOH extract 80 g and residue from the aqueous layer 100 g. The 1-BuOH fraction was chromtographed on ODS (37—55 μm) with 40—80% MeOH to give four fractions (frs. 1—4). Fraction 2 was subjected to MPLC on ODS (Develosil Lop ODS, 25% CH_3CN) to give four fractions (fr. 2-1—fr. 2-4). Further purification by preparative HPLC (Nomura ODS T-7, 19—20% CH_3CN) afforded hoduloside I (**1**, 120 mg) from fr. 2-2 and hoduloside II (**2**, 120 mg), saponin E (**8**, 5 g) and saponin H (**9**, 150 mg) from fr. 2-3. The precipitate of fr. 3 (10 g) was purified by preparative HPLC (Nomura ODS T-7, 25% CH_3CN) to afford hoduloside III (**3**, 3 g), hovenoside I (**6**, 130 mg), and saponin C_2 (**7**, 2.8 g). The filtrate of fr. 3 was subjected to MPLC on ODS (Develosil Lop ODS, 28% CH_3CN) to give three fractions (fr. 3-1—3-3). Fraction 3-2 and fr. 3-3 were purified by perparative HPLC (Nomura ODS T-7, 22—25% CH_3CN) to afford hoduloside IV (**4**, 100 mg), hoduloside V (**5**, 50 mg) and jujuboside B (**10**, 50 mg)

from fr. 3-2 and hoduloside III (**3**, 300 mg) from fr. 3-3.

Hoduloside I (1) An amorphous powder, mp 184—186 °C, $[\alpha]_D^{22}$ −19.5° (c=4.9, MeOH). Negative FAB-MS m/z: 905 $[M-H]^-$, 811 $[M-rha-H]^-$, 795 $[M-glc-H]^-$, 649 $[M-glc-rha-H]^-$, 487 $[genin-H]^-$. *Anal.* Calcd for $C_{48}H_{78}O_{19}\cdot 41/2H_2O$: C, 55.43: H, 8.43. Found: C, 55.22; H, 8.13. ^{1}H-NMR δ: 0.66 (C_{19}-H), 0.76 (C_{18}-H), 1.15 (C_{29}-H), 1.22 (C_{28}-H), 1.38 (C_{21}-H), 1.66 (C_{26}-H), 1.70 (C_{27}-H), 3.28 (1H, dd, J=11.4, 4.0 Hz, H-3), 2.65, 2.96 (each 1H, d, J=18.4 Hz, H-15), 3.05 (1H, d, J=9.0 Hz, H-17), 1.70 (1H, d, J=13.8 Hz, H-22), 2.43 (1H, dd, J=13.8, 6.0 Hz, H-22), 4.88 (1H, dd, J=9.5, 6.0 Hz, H-23), 5.42 (1H, d, J=9.5 Hz, H-24), 4.46, 4.73 (each 1H, d, J=10.3 Hz, H-30). For other NMR data, see Tables I, II, III and IV.

Hoduloside II (2) An amorphous powder, mp 188—190 °C, $[\alpha]_D^{22}$ −14.6° (c=1.9, MeOH). Negative FAB-MS m/z: 957 $[M-H]^-$, 811 $[M-rha-H]^-$, 795 $[M-glc-H]^-$, 649 $[M-glc-rha-H]^-$, 487 $[genin-H]^-$. *Anal.* Calcd for $C_{48}H_{78}O_{19}\cdot 7/2H_2O$: C, 56.82; H, 8.22. Found: C, 57.10; H, 8.41. ^{1}H-NMR δ: 0.73 (C_{19}-H), 0.82 (C_{18}-H), 1.17 (C_{29}-H), 1.26 (C_{28}-H), 1.49 (C_{21}-H), 1.67 (C_{27}-H), 1.72 (C_{26}-H), 3.38 (1H, dd, J=12.0, 5.0 Hz, H-3), 2.72, 3.04 (each 1H, d, J=18.2 Hz, H-15), 3.02 (1H, d, J=9.0 Hz, H-17), 1.77 (1H, d, J=13.2 Hz, H-22), 2.43 (1H, dd, J=13.2, 7.0 Hz, H-22), 4.83 (1H, dd, J=9.0, 7.0 Hz, H-23), 5.47 (1H, d, J=9.0 Hz, H-24), 4.57, 4.64 (each 1H, d, J=10.3 Hz, H-30). For other NMR data, see Tables I, II, III and IV.

Hoduloside III (3) Colorless needles from MeOH, mp 297—299 °C, $[\alpha]_D^{22}$ −36.9° (c=1.0, pyridine). Negative FAB-MS m/z: 911 $[M-H]^-$, 749 $[M-glc-H]^-$. *Anal.* Calcd for $C_{47}H_{76}O_{17}\cdot 4H_2O$: C, 57.30; H, 8.60. Found: C, 57.37; H, 8.33. ^{1}H-NMR δ: 0.70 (C_{19}-H), 1.04 (C_{18}-H), 1.07 (C_{29}-H), 1.24 (C_{28}-H), 1.34 (C_{21}-H), 1.62 (C_{26}-H), 1.64 (C_{27}-H), 3.18 (1H, dd, J=12.0, 5.5 Hz, H-3), *ca.* 1.50, 2.44 (each 1H, d, J=8.5 Hz, H-15), 1.62 (1H, dd, J=12.0, 10.0 Hz, H-22), 1.71 (1H, d, J=12.0 Hz, H-22), 5.17 (dd, J=10.0, 8.0 Hz, H-23), 5.50 (1H, d, J=8.0 Hz, H-24), 4.13, 4.23 (each, d, J=8.5 Hz, H-30). For other NMR data, see Tables I, II, III and IV.

Hoduloside IV (4) Colorless needles from MeOH, mp 246—248 °C, $[\alpha]_D^{22}$ −12.9° (c=3.5, MeOH). Negative FAB-MS m/z: 927 $[M-H]^-$, 765 $[M-glc-H]^-$. *Anal.* Calcd for $C_{47}H_{76}O_{18}\cdot 3H_2O$: C, 57.42; H, 8.41. Found: C, 57.61; H, 8.63. ^{1}H-NMR δ: 0.70 (C_{19}-H), 1.05 (C_{18}-H), 1.07 (C_{29}-H), 1.24 (C_{28}-H), 1.36 (C_{21}-H), 1.66 (C_{26}-H), 1.68 (C_{27}-H), 3.21 (1H, dd, J=12.0, 5.5 Hz, H-3), *ca.* 1.50, 2.46 (each 1H, d, J=8.3 Hz, H-15), 1.64 (1H, dd, J=12.0, 10.0 Hz, H-22), 1.74 (1H, d, J=12.0 Hz, H-22), 5.18 (1H, dd, J=10.0, 8.0 Hz, H-23), 5.52 (1H, d, J=8.0 Hz, H-24), 4.16, 4.25 (each, d, J=8.5 Hz, H-30). For other NMR data, see Tables I, II, III and IV.

Hoduloside V (5) Colorless needles from MeOH, mp 215—217 °C, $[\alpha]_D^{22}$ −31.4° (c=4.3, MeOH). Negative FAB-MS m/z: 941 $[M-H]^-$, 795 $[M-rha-H]^-$. *Anal.* Calcd for $C_{48}H_{78}O_{18}\cdot 3H_2O$: C, 57.82; H, 8.49. Fond: C, 57.88; H, 8.28. ^{1}H-NMR δ: 0.70 (C_{19}-H), 1.04 (C_{18}-H), 1.14 (C_{29}-H), 1.21 (C_{28}-H), 1.38 (C_{21}-H), 1.66 (C_{26}-H), 1.68 (C_{27}-H), 3.33 (1H, dd, J=12.0, 5.5 Hz, H-3), *ca.* 1.50, 2.44 (each 1H, d, J=8.5 Hz, H-15), 1.62 (1H, dd, J=12.0, 10.0 Hz, H-22), 1.71 (1H, d, J=12.0 Hz, H-22), 5.20 (1H, dd, J=10.0, 8.0 Hz, H-23), 5.52 (1H, d, J=8.0 Hz, H-24), 4.13, 4.23 (each, d, J=8.5 Hz, H-30). For other NMR data, see Tables I, II, III and IV.

Hovenoside I (6) Colorless needles from MeOH, mp 278—280 °C, $[\alpha]_D^{22}$ −12.1° (c=1.2, MeOH). Negative FAB-MS m/z: 897 $[M-H]^-$. For NMR data, see Table I.

Saponin C_2 (7) Colorless needles from MeOH, mp 288—290 °C, $[\alpha]_D^{22}$ +0° (c=5.8, pyridine). Negative FAB-MS m/z: 911 $[M-H]^-$. For NMR data, see Table I.

Saponin E (8) An amorphous powder, mp 180—182 °C, $[\alpha]_D^{22}$ −23.4° (c=5.3, MeOH). Negative FAB-MS m/z: 795 $[M-H]^-$, 649 $[M-rha-H]^-$. For NMR data, see Tables I and II.

Saponin H (9) An amorphous powder, mp 160—162 °C, $[\alpha]_D^{22}$ −9.6° (c=2.9, MeOH). Negative FAB-MS m/z: 649 $[M-H]^-$, 487 $[genin-H]^-$. For NMR data, see Table II.

Jujuboside B (10) Colorless needles from MeOH, mp 223—225 °C, $[\alpha]_D^{22}$ −32.5° (c=4.3, MeOH). Negative FAB-MS m/z: 1043 $[M-H]^-$.

Identification of Component Sugars A solution of one of **1**—**5** (3—4 mg) in 5% H_2SO_4 in 50% EtOH (2 ml) was heated at 100 °C for 3 h. The reaction mixture was diluted with H_2O, neutralized with Amberlite IR-45 and evaporated *in vacuo* to dryness. The residue was checked by HPLC (Shodex RSpak DC-613 (Na^+ form), 4.8 mm i.d. × 15 cm, 85% CH_3CN, 0.6 ml/min, 70 °C using refraction index detection (Waters 410) and chiral detection (Shodex OR-1) with authentic sugars (0.05 mg/5 μl of each of D, L-ara, L-rha, D, L-glc, D-qui) as standards. These sugars gave the following peaks. t_R: L(−)-rhamnose; 11.0 min (8×10^{-3} deg), D(+)-quinovose; 11.4 min (4×10^{-2} deg), L(+)-arabinose, 17.4 min (3.5×10^{-2} deg), D(+)-glucose, 25.8 min (2.5×10^{-2} deg). **1**: L-rha, D-glc; **2**: L-rha, D-glc; **3**: D-qui, L-ara, D-glc; **4**: L-ara, D-glc; **5**: L-rha, D-glc.

Acetylation of Compounds 1—5 Compounds **1**—**5** (each 3 mg) were each acetylated with Ac_2O–pyridine (each 0.5 ml) at room temperature overnight and worked up as usual to give a colorless oil. The acetates of **1**—**5** each showed a single spot on TLC (CH_2Cl_2: MeOH = 40 : 1). Peracetates of **1** and **2**: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770, 1760—1750, 1230—1220, 1030—1025. Acetate of **3**—**5**: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550—3540, 1760—1750, 1230—1220, 1035—1030.

Enzymatic Hydrolysis of Compounds 1 and 2 Compound **1** (35 mg) was dissolved in EtOH–H_2O (1 : 9) and 0.01 M NaH_2PO_4 buffer (pH 4.0), 2 ml each, and incubated with glycosidases (30 mg, mixture from *Turbo cornutus*; Seikagaku Corp.) for 48 h at 37°C, then worked up as usual. The crude sapogenins were subjected to HPLC (ODS, 20% CH_3CN) to give **8** (20 mg). The same treatment (2 weeks) of **2** (35 mg) gave **8** (5 mg).

Bioassay of Antisweet Activity The activity of a 1 mmol solution of each of **1**—**10** was tested on three volunteers. Each participant held the test solutions in the mouth for 3 min, spat, rinsed with distilled water and then tasted sucrose solutions (0.1 and 0.2 M).

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