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STEROIDAL GLYCOSIDES FROM ROOTS OF *CYNANCHUM CAUDATUM*

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Key Word Index—*Cynanchum caudatum*; Asclepiadaceae; roots; esterified pregnane glycoside; 2,6-dideoxy-3-*O*-methylhexopyranose; glucopyranose.

Abstract—Roots of *Cynanchum caudataum* afforded 15 pregnane glycosides which had cynanchogenin, caudatin and gagaminin as the aglycone moiety and 2,6-dideoxy-3-*O*-methylhexopyranoses and glucopyranose as component sugars. The structures of these compounds were elucidated by spectroscopic methods and from chemical evidence. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

In connection with a study on the constituents of some species of the Asclepiadaceae, we investigated *Cynanchum caudatum*. The isolation and structures of pregnane glycosides from roots of this species have been reported previously [1–5]. In the present work, we undertook the structural elucidation of 13 new glycosides.

RESULTS AND DISCUSSION

The methanol extract of roots of *C. caudatum* afforded the new natural compounds **2**–**14** and **15** in addition to a known compound, cynanchoside D_2 (**1**) [6].

Compound **2** was suggested to have the molecular formula $C_{55}H_{88}O_{21}$, based on its FAB mass spectrum. Comparing the ^1H and ^{13}C NMR spectral data of **2** with those of cynanchoside D_2 showed that **2** had the same sugar sequence, β-D-glucopyranosyl-(1 → 4)-β-D-oleandropyranosyl-(1 → 4)-β-D-cymaropyranosyl-(1 → 4)-β-D-cymaropyranoside, as that of cynanchoside D_2. Moreover, the aglycone moiety was identified as caudatin on the basis of the NMR spectral data. The observation of a glycosylation shift around C-3 of the aglycone moiety showed that the sugar sequence was linked to the C-3 position of caudatin. Thus, the structure of **2** was determined to be caudatin 3-*O*-β-D-glucopyranosyl-(1 → 4)-β-D-oleandropyranosyl-(1 → 4)-β-D-cymaropyranosyl-(1 → 4)-β-D-cymaropyranoside, which has been reported as the artificial compound hydrolysed with β-glucosidase [7].

Compound **3** was considered to be cynanchogenin 3-*O*-pentaglycoside because five anomeric proton and carbon signals were observed at δ 4.69 (*dd*, *J* = 9.5, 1.5 Hz), 4.89 (*dd*, *J* = 9.5, 1.5 Hz), 5.11 (*d*, *J* = 8.0 Hz), 5.12 (*dd*, *J* = 9.5, 1.5 Hz), 5.27 (*dd*, *J* = 9.5, 1.5 Hz) and δ 96.5, 100.0, 100.5, 101.9, 104.5 in the ^1H and ^{13}C NMR spectra, in addition to the signals due to cynanchogenin. Enzymic hydrolysis with cellulase produced a previously reported compound, **3′** [3], which was confirmed by comparison of ^1H NMR spectral data and HPLC analysis with those of an authentic sample. In addition, glucitol acetate was detected by GC analysis after 10% H_2SO_4 hydrolysis followed by $NaBH_4$ reduction and acetylation (see Experimental). In the NOE difference spectrum of **3**, irradiation at the anomeric proton signal at δ 5.11 (*d*, *J* = 8.0 Hz) caused enhancement of the signal intensity at δ 3.73 (*t*, *J* = 8.5 Hz) (H-4 of β-D-oleandropyranose). Accordingly, this glucopyranose was linked to the C-4 position of the second β-D-oleandropyranose as the terminal sugar. Based on this evidence, the structure of **3** was determined as shown in the formula.

As the ^1H and ^{13}C NMR spectra of the sugar moieties in compound **4** and **5** were consistent with those from **3**, the sugar sequence of these compounds was also considered to be the same. Compounds **4′** [3] and **5′** [5] were acquired by enzymic hydrolysis of **4** and **5**, respectively. Thus, the structures of **4** and **5** were as indicated in the formulae. Compounds **6** and **7** were also considered to be pentaglycosides which had cynanchogenin and caudatin as the aglycone moiety, respectively. Since acid hydrolysis followed by $NaBH_4$ reduction and acetylation of **6** and **7** gave glucitol

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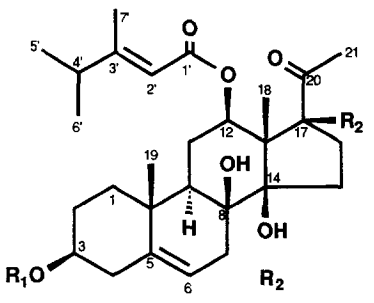
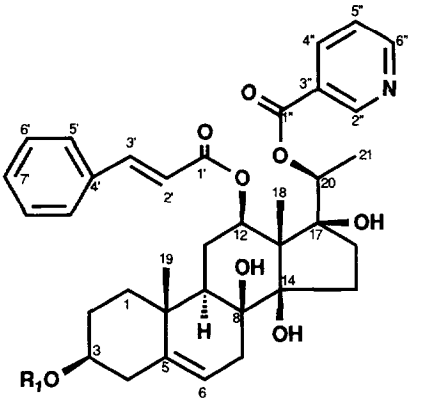


I: H (cynanchogenin)
II: OH (caudatin)

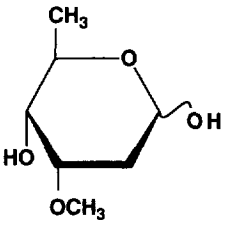
R_1



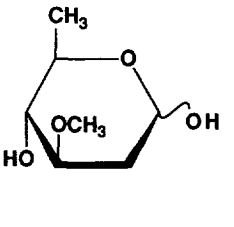
III : (gagaminin)

a: β-D-cym. – β-D-cym. – β-D-ole. – β-D-glc.
b: β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole. – β-D-glc.
b': β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole.
c: β-D-cym. – β-D-cym. – β-D-ole. – β-D-cym. – β-D-glc.
c': β-D-cym. – β-D-cym. – β-D-ole. – β-D-cym.
d: β-D-cym. – β-D-cym. – β-D-ole. – α-L-cym. – β-D-glc.
d': β-D-cym. – β-D-cym. – β-D-ole. – α-L-cym.
e: β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole. – β-D-cym. – β-D-glc.
e': β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole. – β-D-cym.
f: β-D-cym. – β-D-cym. – β-D-ole. – β-D-cym. – β-D-ole. – β-D-glc.
f': β-D-cym. – β-D-cym. – β-D-ole. – β-D-cym. – β-D-ole.
g: β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole. – β-D-ole. – β-D-glc.
g': β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole. – β-D-ole.
h: β-D-cym. – β-D-cym. – β-D-ole. – β-D-cym. – α-L-ole – β-D-glc.
h': β-D-cym. – β-D-cym. – β-D-ole. – β-D-cym. – α-L-ole
i: β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole. – β-D-cym. – β-D-cym. – β-D-glc.
i': β-D-cym. – β-D-cym. – β-D-ole. – β-D-ole. – β-D-cym. – β-D-cym.

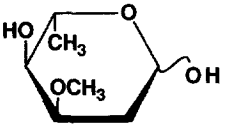
1: I - a **9**: II - e
2: II - a **9'**: II - e'
3: I - b **10**: I - f
3': I - b' **10'**: I - f'
4: II - b **11**: II - f
4': II - b' **11'**: II - f'
5: III - b **12**: II - g
5': III - b' **12'**: II - g'
6: I - c **13**: I - h
6': I - c' **13'**: I - h'
7: II - d **14**: II - h
7': II - d' **14'**: II - h'
8: I - e **15**: I - i
8': I - e' **15'**: I - i'



D-cymaropyranose



D-oleandropyranose



L-cymaropyranose

acetate, both compounds contained glucose as the sugar moiety. Secondly, enzymic hydrolysis with cellulase of **6** and **7** produced cynanchogenin 3-*O*-*β*-D-cymaropyranosyl-(1 → 4)-*β*-D-oleandropyranosyl-(1 → 4)-*β*-D-cymaropyranosyl-(1 → 4)-*β*-D-cymaropyranoside (**6'**) [3] and caudatin 3-*O*-α-L-cymaropyranosyl-(1 → 4)-*β*-D-oleandropyranosyl-(1 → 4)-*β*-D-cymaropyranosyl-(1 → 4)-*β*-D-cymaropyranoside (**7'**) [4], respectively, which were identified on the basis comparison of their ^{1}H NMR with those of authentic samples. Moreover, the position of attachment of glucose was indicated by a NOE difference spectrum irradiating at the anomeric proton signal of glucose (*δ* 4.93 (*d*, *J* = 8.0 Hz) in **6** and *δ* 5.01 (*d*, *J* = 8.0 Hz) in **7**). Accordingly, the structures of **5** and **6** were elucidated as shown in the formulae.

Compounds **8**–**14** consisted of cynanchogenin or caudatin as the aglycone moiety and six monosaccharides, respectively. The component sugars in **8** and **9** were determined to be three *β*-D-cymaropyranoses, two *β*-D-oleandropyranoses and one *β*-D-glucopyranose by enzymic hydrolysis which yielded **8'** [3] and **9'** [3] and acid hydrolysis. The attached position of glucose was shown by the difference NOE spectrum obtained by irradiating at the anomeric proton signal of glucose. Similarly, the component sugars of **10**–**14** were identified as three *β*-D-cymaropyranoses, two *β*-D-oleandropyranoses and one *β*-

D-glucopyranose in **10** and **11**, two β-D-cymaropyranoses, three β-D-oleandropyranoses and one β-D-glucopyranose in **12**, and two β-D-cymaropyranoses, one α-L-cymaropyranose, two β-D-oleandropyranose and one β-D-glucopyranose in **13** and **14**.

Compound **15** was considered to be cynanchogenin 3-*O*-heptaglycoside and enzymic hydrolysis with cellulase produced cynanchogenin 3-*O*-β-D-cymaropyranosyl-(1 → 4)-β-D-cymaropyranosyl-(1 → 4)-β-D-oleandropyranosyl-(1 → 4)-β-D-oleandropyranosyl-(1 → 4)-β-D-cymaropyranosyl-(1 → 4)-β-D-cymaropyranoside (**15′**) [5]. Because GC analysis after acid hydrolysis followed by $NaBH_4$ reduction and acetylation detected glucitol acetate, the remaining monosaccaride was glucose. The attached position of this glucose was decided from the NOE spectrum to be C-4 of the terminal β-D-cymaropyranose in **15′**. Thus, the structure of **15** was elucidated as shown in the formula.

EXPERIMENTAL

^1H and ^{13}C NMR were recorded at 400 and 100 MHz, respectively. TMS was used as int. standard.

Plant material. Cynanchum caudatum M. was collected in Shizuoka prefecture, Japan, in August 1993, and identified by Prof. T. Noro (University of Shizuoka).

Extraction and isolation. Procedures for extracting and isolating pregnane glycosides are described elsewhere [3]. The pregnane glycoside fr. isolated afforded compounds **1** (18 mg), **2** (7 mg), **3** (17 mg), **4** (6 mg), **5** (9 mg), **6** (7 mg), **7** (5 mg), **8** (12 mg), **9** (4 mg), **10** (8 mg), **11** (8 mg), **12** (4 mg), **13** (6 mg), **14** (5 mg) and **15** (7 mg).

Compound **2**. Amorphous powder. $[\alpha]_D^{24}$ +5.1°. (MeOH: *c* 0.77). FAB-MS *m/z*: 1107 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **3**. Amorphous powder. $[\alpha]_D^{24}$ −16.2°. (MeOH: *c* 1.4). FAB-MS *m/z*: 1235 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **4**. Amorphous powder. $[\alpha]_D^{24}$ ≃0°. (MeOH: *c* 0.63). FAB-MS *m/z*: 1251 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **5**. Amorphous powder. $[\alpha]_D^{24}$ +91.8°. (MeOH: *c* 0.73). UV λ_{max}^{MeOH} nm (log ε): 218 (4.42), 222 (sh), 281 (4.38). FAB-MS *m/z*: 1356 $[M+H]^+$, 1378 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **6**. Amorphous powder. $[\alpha]_D^{24}$ −1.4°. (MeOH: *c* 0.66). FAB-MS *m/z*: 1235 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **7**. Amorphous powder. $[\alpha]_D^{24}$ −36.8°. (MeOH: *c* 0.50). FAB-MS *m/z*: 1251 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **8**. Amorphous powder. $[\alpha]_D^{24}$ −5.2°. (MeOH: *c* 1.1). FAB-MS *m/z*: 1379 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **9**. Amorphous powder. $[\alpha]_D^{24}$ +8.9°. (MeOH: *c* 0.40). FAB-MS *m/z*: 1395 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Table 1. ^{13}C NMR spectra data of aglycone moieties (measured in C_5D_5N solution at 35°

C	I	II	III
Aglycone moiety			
1	39.0	39.0	39.3
2	29.9	29.9	29.9
3	77.8*	77.7*	77.7*
4	39.3	39.3	38.8
5	139.5	139.5	139.4
6	119.2	119.1	119.3
7	34.2	34.8	34.1†
8	74.6	74.4	74.3
9	44.9	44.6	44.1
10	37.6	37.4	37.3
11	25.1	25.1	25.7
12	72.4	72.6	74.6
13	55.8	58.1	57.2
14	87.6	89.5	88.9
15	35.2	33.9	34.9†
16	21.9	33.0	33.7†
17	60.7	92.4	87.5
18	15.9	10.7	11.5
19	18.2	18.2	18.0
20	209.1	209.3	76.4
21	32.1	27.5	15.4
Ester moiety			
1′	166.1	166.0	166.7
2′	114.3	114.2	120.3
3′	165.2	165.3	144.0
4′	38.1	38.2	134.9
5′	20.8†	20.8†	128.5
6′	20.9†	20.9†	129.2
7′	16.5	16.5	130.5
1″	—	—	164.7
2″	—	—	153.8
3″	—	—	127.0
4″	—	—	137.3
5″	—	—	123.0
6″	—	—	151.6

† Interchangeable in each column.
* Interchangeable between Tables 1 and 2.

Compound **10**. Amorphous powder. $[\alpha]_D^{24}$ −5.5°. (MeOH: *c* 0.81). FAB-MS *m/z*: 1379 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **11**. Amorphous powder. $[\alpha]_D^{24}$ +5.5°. (MeOH: *c* 0.98). FAB-MS *m/z*: 1395 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **12**. Amorphous powder. $[\alpha]_D^{24}$ −5.3°. (MeOH: *c* 0.40). FAB-MS *m/z*: 1395 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **13**. Amorphous powder. $[\alpha]_D^{26}$ −55.6°. (MeOH: *c* 0.58). FAB-MS *m/z*: 1379 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **14**. Amorphous powder. $[\alpha]_D^{26}$ −40.8°. (MeOH: *c* 0.49). FAB-MS *m/z*: 1395 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Compound **15**. Amorphous powder. $[\alpha]_D^{24}$ +0.6°. (MeOH: *c* 0.69). FAB-MS *m/z*: 1523 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1–3.

Table 2. ^{13}C NMR spectral data of sugar moieties (measured in C_5D_5N at 35°)

C	a	b	c	d	e	f	g	h	i
	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.
1	96.5	96.5	96.5	96.4	96.5	96.5	96.4	96.5	96.5
2	37.3[a]	37.2[a]	37.3[a]	37.3[a]	37.0[a]	37.3[a]	37.1[a]	37.3[a]	37.3[a]
3	78.1*[b]	78.1*[b]	78.0*[b]	78.0*[b]	78.0*[b]	78.0*[b]	78.0*[b]	78.1*[b]	78.0*[b]
4	83.4[c]	83.5[c]	83.4[c]	83.4[c]	83.4[c]	83.4[c]	83.5[c]	83.4[c]	83.4[c]
5	68.9[d]	69.1[d]	69.1[d]	69.1[d]	68.9[d]	69.1[d]	69.0[d]	69.1[d]	69.1[d]
	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.
1	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5
2	37.1[a]	37.6[a]	37.1[a]	37.2[a]	37.3[a]	37.1[a]	37.3[a]	37.3[a]	37.2[a]
3	77.8*[b]	77.8*[b]	77.8*[b]	77.7*[b]	77.7*[b]	77.7*[b]	77.8*[b]	77.8*[b]	77.8*[b]
4	83.3[c]	83.2	83.2[c]	83.1[c]	83.2[c]	83.2[c]	83.2[c]	83.2[c]	83.2[c]
5	69.1[d]	68.9[d]	68.9[d]	68.6[d]	69.0[d]	68.9[d]	68.9[d]	68.9[d]	68.9[d]
	D-ole.	D-ole.	D-ole.	D-ole.	D-ole.	D-ole.	D-ole.	D-ole.	D-ole.
1	101.9	101.9	102.0	101.9	101.9	101.9	101.9	101.9	101.9
2	37.5[a]	37.7[a]	37.8[a]	37.1[a]	37.7[a]	37.7[a]	37.5[a]	37.0[a]	37.9[a]
3	79.4	79.0	78.8	79.2[e]	79.0[e]	78.9	79.0[e]	79.0[e]	79.0[e]
4	83.2[c]	82.7	82.6	81.6	82.8[f]	82.6	82.8[f]	82.7[e]	82.8[f]
5	72.1	71.7	71.8[e]	72.2[f]	71.9[g]	71.8	71.7	71.7[f]	71.7[g]
	D-glc.	D-ole.	D-cym.	L-cym.	D-ole.	D-cym.	D-ole.	D-ole.	D-ole.
1	104.5	100.0	98.3	97.3	100.1	98.4	100.1	100.0	100.1
2	75.7	37.0[a]	36.8	32.3	37.9[a]	37.1[a]	37.6[a]	37.6[a]	37.7[a]
3	78.7	79.6	78.2	73.7	79.1[e]	78.1*[b]	79.3[e]	79.2[e]	79.2[e]
4	72.1	83.4[c]	83.3[c]	79.3[e]	82.9[f]	83.3[c]	82.9[f]	81.8	82.9[f]
5	78.0	72.1[e]	69.7	64.9	71.7[g]	69.2[d]	72.7	72.2[f]	71.9[g]
6	63.2	—	—	—	—	—	—	—	—
		D-glc.	D-glc.	D-glc.	D-cym.	D-ole.	D-ole.	L-cym.	D-cym.
1	—	104.5	106.6	102.4	98.4	101.9	100.1	97.4	98.5
2	—	75.7	75.4	75.4	36.7	37.5[a]	37.8[a]	32.3	37.1[a]
3	—	78.7	78.4	78.7	78.2	79.3	79.6	73.7	78.0*[b]
4	—	72.2[e]	71.9[e]	71.9[f]	83.2[c]	83.3[c]	83.5	79.3[e]	83.2[c]
5	—	78.1	78.4	78.5	69.7	72.1	72.1	64.8	69.3[d]
6	—	63.2	63.2	63.0	—	—	—	—	—
					D-glc.	D-glc.	D-glc.	D-glc.	D-cym.
1	—	—	—	—	106.6	104.5	104.5	102.3	100.4
2	—	—	—	—	75.4	75.7	75.7	75.4	36.8[a]
3	—	—	—	—	78.4	78.7	78.7	78.6	78.1*[b]
4	—	—	—	—	71.9[g]	72.1	72.1	71.9[f]	83.1[c]
5	—	—	—	—	78.4	78.1*[b]	78.0	78.5	69.4[d]
6	—	—	—	—	63.2	63.3	63.2	63.0	—
									D-glc.
1	—	—	—	—	—	—	—	—	106.6
2	—	—	—	—	—	—	—	—	75.4
3	—	—	—	—	—	—	—	—	78.4
4	—	—	—	—	—	—	—	—	71.9[g]
5	—	—	—	—	—	—	—	—	78.4
6	—	—	—	—	—	—	—	—	63.1
6s	18.5	18.5	18.5	18.4	18.5	18.5×2	18.5	18.4	18.4
	18.6	18.6	18.6	18.5	18.6	18.6	18.6	18.5	18.5
	18.9	18.7	18.7×2	18.6×2	18.7×3	18.7	18.7×2	18.6	18.6×2
		18.9				18.9	18.9	18.7×2	18.7×2
OMes	57.2	57.2	57.4	56.4	57.4	57.2	57.2	56.4	57.4
	58.9	57.3	58.7	57.0	57.5	57.4	57.3	57.0	57.5
	59.0	58.9×2	58.9×2	58.8	58.6	58.9×3	57.4	57.3	58.7
				59.0	58.8		58.8	58.8	58.8
					58.9		58.9	58.9	58.9×2

[a-g] Interchangeable in each column.

* Assignments may be interchangeable between Tables 1 and 2.

Table 3. ^{1}H NMR spectral data of sugar moieties (measured in C_5D_5N at 35°C)

H	a	b	c	d	e	f	g	h	i
	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.
1	5.27 1H, *dd* (9.5, 1.5)	5.27 1H, *dd*, (9.5, 1.5)	5.27 1H, *brd* (9.5)	5.28 1H, *dd* (9.5, 1.5)	5.27 1H, *dd* (9.5, 1.5)	5.28 1H, *brd* (9.5)	5.27 1H, *brd* (9.5)	5.28 1H, *dd* (9.5, 2.0)	5.27 1H, *brd* (9.5)
3	4.08 1H, *q* (3.0)	4.09 1H, *q* (3.0)	4.08 1H, *q* (3.0)	4.09 1H, *q* (3.0)	4.09 1H, *q* (3.0)	4.09 1H, *q* (3.0)	4.09 1H, *q* (3.0)	4.09 1H, *q* (3.0)	4.09 1H, *q* (3.0)
4	3.51 1H, *dd* (9.5, 3.0)	3.53 —*	3.51 —*	3.51 1H, *dd* (9.5, 3.0)	3.51 —*	3.51 —*	3.53 —*	3.51 *	3.51 —*
5	4.22 1H, *dq* (9.5, 6.0)	4.22 1H, *dq* (9.5, 6.0)	4.22 —*	4.22 —*	4.22 —*	4.22 —*	4.22 1H, *dq* (9.5, 6.5)	4.23 —*	4.22 —*
6	1.39 3H, *d* (6.0)	1.39 3H, *d* (6.0)	1.39 3H, *d* (6.5)	1.39 3H, *d* (6.5)	1.39 3H, *d* (6.0)	1.39 3H, *d* (6.5)	1.40 3H, *d* (6.5)	1.40 3H, *d* (6.5)	1.40 3H, *d* (6.5)
	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.	D-cym.
1	5.11 1H, *dd* (9.5, 1.5)	5.12 1H, *dd* (9.5, 1.5)	5.11 1H, *dd* (9.5, 2.0)	5.12 1H, *dd* (9.5, 1.5)	5.12 1H, *dd* (9.5, 1.5)	5.12 1H, *brd* (9.5)	5.13 1H, *dd* (9.5, 1.5)	5.13 1H, *dd* (9.5, 2.0)	5.12 1H, *dd* (9.5, 2.0)
3	4.01 —*	4.02 1H, *q* (3.0)	4.01 *	4.01 —*	4.02 1H, *q* (3.0)	4.04 1H, *q* (3.0)	4.03 1H, *q* (3.0)	4.03 1H, *q* (3.0)	4.03 —*
4	3.43 1H, *dd* (9.5, 3.0)	3.45 1H, *dd* (9.5, 3.0)	3.44 1H, *dd* (9.5, 3.0)	3.45 1H, *dd* (9.5, 3.0)	3.45 1H, *dd* (9.5, 3.0)	3.45 1H, *dd* (9.5, 3.0)	3.46 1H, *dd* (9.5, 3.0)	3.46 1H, *dd* (9.5, 3.0)	3.46 1H, *dd* (9.5, 3.0)
5	4.16 1H, *dq* (9.5, 6.0)	4.17 1H, *dq* (9.6, 6.0)	4.17 —*	4.16 1H, *dq* (9.5, 6.5)	4.16 —*	4.17 1H, *dq* (9.5, 6.5)	4.18 —*	4.18 1H, *dq* (9.5, 6.5)	4.17 —*
6	1.37 3H, *d* (6.0)	1.38 3H, *d* (6.0)	1.38 3H, *d* (6.5)	1.38 3H, *d* (6.5)	1.38 3H, *d* (6.0)	1.38 3H *d* (6.5)	1.39 3H, *d* (6.5)	1.39 3H, *d* (6.5)	1.39 3H, *d* (6.5)
	D-ole.	D-olc.	D-ole.	D-ole.	D-ole.	D-ole.	D-ole.	D-ole.	D-olc.
1	4.69 1H, *dd* (9.5, 1.5)	4.69 1H, *dd* (9.5, 1.5)	4.67 1H, *dd* (9.5, 1.5)	4.67 1H, *dd* (9.5, 1.5)	4.69 1H, *dd* (9.5, 1.5)	4.69 1H, *brd* (9.5)	4.70 1H, *dd* (9.5, 1.5)	4.70 1H, *dd* (9.5, 1.5)	4.69 1H, *dd* (9.5, 1.5)
3	3.63 —*	3.53 —*	3.53 —*	3.46 *	3.51 —*	3.53 —*	3.53 —*	3.52 —*	3.52 —*
4	3.72 1H, *t* (8.5)	3.48 —*	3.53 —*	3.37 1H, *t* (9.0)	3.51 —*	3.52 *	3.53 —*	3.52 —*	3.52 *
5	3.66 *	3.52 —*	3.48 —*	3.46 —*	3.51 —*	3.50 —*	3.53 —*	3.53 *	3.50 —*
6	1.71 3H, *d* (6.0)	1.43 3H, *d* (6.0)	1.41 3H, *d* (6.5)	1.38 3H, *d* (6.5)	1.43 3H, *d* (6.0)	1.44 3H, *d* (6.5)	1.73 3H, *d* (6.5)	1.44 3H, *d* (6.5)	1.43 3H, *d* (6.5)
	D-glc.	D-olc.	D-cym.	L-cym.	D-ole.	D-cym.	D-ole.	D-ole.	D-olc.
1	5.10 1H, *d* (8.0)	4.89 1H, *dd* (9.5, 1.5)	5.27 1H, *brd* (9.5)	5.08 1H, *dd* (4.5, 1.5)	4.88 1H, *dd* (9.5, 1.5)	4.69 1H, *brd* (9.5)	4.89 1H, *brd* (9.5)	4.87 1H, *dd* (9.5, 1.5)	4.88 1H, *dd* (9.5, 1.5)
2	3.99 1H, *t* (8.0)								
3	4.19 —*	3.64 —*	4.14 1H, *q* (3.0)	3.96 —*	3.51 —*	4.03 *	3.53 —*	3.46 —*	3.52 —*
4	4.19 *	3.73 1H, *t*, (8.5)	3.67 1H, *dd* (9.5, 3.0)	3.97 1H, *dd* (8.0, 3.0)	3.51 *	3.45 1H, *dd* (9.5, 3.0)	3.53 1H, *t* (8.5)	3.38 1H, *t* (9.0)	3.52 —*
5	3.94 1H, *m*	3.64 —*	4.28 1H, *da* (9.5, 6.5)	4.78 1H, *dq* (8.0, 6.5)	3.51 —*	4.22 —*	3.53 —*	3.46 —*	3.50 —*
6	4.33 1H, *dd* (11.5, 5.5)	1.73 3H, *d* (6.0)	1.63 3H, *d* (6.5)	1.51 3H, *d* (6.5)	1.43 3H, *d* (6.0)	1.39 3H, *d* (6.5)	1.45 3H, *d* (6.5)	1.40 3H, *d* (6.5)	1.43 3H, *d* (6.5)
	4.51 1H, *dd* (11.5, 2.5)	—	—	—	—	—	—	—	—

Table 3.—*Continued.*

H	a	b	c	d	e	f	g	h	i
		D-glc.	D-glc.	D-glc.	D-cym.	D-ole.	D-ole.	L-cym.	D-cym.
1	—	5.11 1H, *d* (8.0)	4.93 1H, *d* (8.0)	5.01 1H, *d* (8.0)	5.27 1H, *dd* (9.5, 1.5)	5.28 1H, *brd* (9.5)	4.89 1H, *brd* (9.5)	5.08 1H, *dd* (4.5, 2.0)	5.27 1H, *brd* (9.5)
2	—	3.99 1H, *t* (8.0)	3.99 —*	3.99 —*					
3	—	4.19 —*	4.22 —*	4.23 *	4.14 —*	3.64 —*	3.64 —*	3.97 *	4.05 1H, *q* (3.0)
4	—	4.19 *	4.17 —*	4.21 —*	3.67 1H, *dd* (9.5, 3.0)	3.71 1H, *t* (8.5)	3.73 1H, *t* (8.5)	3.97 —*	3.43 1H, *dd* (9.5, 3.0)
5		3.93 1H, *m*	3.97 —*	3.98 —*	4.27 1H, *dq* (9.5, 6.0)	3.64 —*	3.64 —*	4.77 —*	4.17 *
6	—	4.33 1H, *dd* (11.5, 5.5)	4.38 1H, *dd* (11.5, 5.5)	4.38 1H, *dd* (11.5, 5.5)	1.62 2H, *d* (6.0)	1.72 3H, *d* 96.5)	1.45 3H, *d* (6.5)	1.52 3H, *d* (6.5)	1.34 3H, *d* (6.5)
		4.50 1H, *dd* (11.5, 2.5)	4.57 1H, *brd* (11.5)	4.55 1H, *dd* (11.5, 2.5)	—	—	—	—	—
					D-glc.	D-glc.	D-glc.	D-glc.	D-cym.
1	—	—	—	—	4.93 1H, *d* (8.0)	5.11 1H, *d* (8.0)	5.12 1H, *t* (8.0)	5.02 1H, *d* (8.0)	5.08 1H, *dd* (9.5, 1.5)
2	—	—		—	3.98 1H, *t* (8.0)	3.99 1H, *t* (8.0)	3.99 1H, *t* (8.0)	3.98 1H, *t* (8.0)	–
3		—	—	—	4.22 1H, *t* (8.0)	4.19 —*	4.19 —*	4.23 —*	4.11 1H, *q* (3.0)
4	—	—	—	—	4.16 1H, *t* (8.0)	4.19 —*	4.19 —*	4.21 *	3.66 1H, *dd* (9.5, 3.0)
5	—		—	—	3.97 1H, *m*	3.94 1H, *m*	3.93 1H, *m*	3.98 —*	4.25 1H, *dq* (9.5, 6.5)
6	—	—	—	—	4.38 1H, *dd* (11.5, 5.0)	4.34 1H, *dd* (11.5, 5.5)	4.33 1H, *dd* (11.5, 5.5)	4.38 1H, *brd* (11.5)	1.61 3H, *d* (6.5)
	—	—		—	4.56 1H, *brd* (11.5)	4.51 1H, *brd* (11.5)	4.51 1H, *brd* (11.5)	4.55 1H, *brd* (11.5)	—
									D-glc.
1	—		—	—	—		—	—	4.93 1H, *d* (8.0)
2	—	—	—		—	—	—		4.00 1H, *t* (8.0)
3	—		—	—	—	—		—	4.23 —*
4		—	—	—		—	—	—	4.17 1H, *t* (8.0)
5	—	—		—	—	—		—	3.97 —*
6	—	—	—	—	—		—	—	4.38 1H, *dd* (11.5, 5.5)
	—	—	—		—	—	—		4.56 1H, *dd* (11.5, 2.5)
OMes	3.53 3H, *s*	3.49 3H, *s*	3.51 3H, *s*	3.35 3H, *s*	3.49 3H, *s*	3.52 3H, *s*	3.51 3H, *s* × 2	3.36 3H, *s*	3.50 3H, *s*
	3.57 3H, *s*	3.55 3H, *s*	3.54 3H, *s*	3.50 3H, *s*	3.53 3H, *s* × 2	3.53 3H, *s*	3.55 3H, *s*	3.50 3H, *s* × 2	3.53 3H, *s*
	3.62 3H, *s*	3.58 3H, *s*	3.57 3H, *s*	3.57 3H, *s*	3.58 3H, *s*	3.57 3H, *s* × 2	3.59 3H, *s*	3.58 3H, *s*	3.55 3H, *s*
		3.62 3H, *s*	3.62 3H, *s*	3.62 3H, *s*	3.62 3H, *s*	3.62 3H, *s*	3.63 3H, *s*	3.62 3H, *s*	3.58 3H, *s*
									3.60 3H, *s*
									3.62 3H, *s*

* Overlapping with other signals

Enzymic hydrolysis of compounds **3**–**14** *and* **15**. Compounds **3**–**15** (**3** (8 mg), **4** (6 mg), **5** (7 mg), **6** (7 mg), **7** (5 mg), **8** (11 mg), **9** (4 mg), **10** (7 mg), **11** (10 mg), **12** (4 mg), **13** (4 mg), **14** (3 mg) and **15** (4 mg)) were dissolved in H_2O (*ca* 3 ml) and cellulase (Sigma) (*ca* 30–50 mg) was added. The mixt. was stirred at 40° for 5 days. After hydrolysis, the reaction mixt. was dild with H_2O and extracted with EtOAc. The EtOAc extract of each compound contained **3′**–**14′** and **15′** (**3′** (0.8 mg), **4′** (0.7 mg), **5′** (0.1 mg), **6′** (1.3 mg), **7′** (1.3 mg), **8′** (1.4 mg), **9′** (1.3 mg), **10′** (0.6 mg), **11′** (0.2 mg), **12′** (0.1 mg), **13′** (0.8 mg), **14′** (0.6 mg) and **15′** (0.1 mg)), whose structures were confirmed by comparison of their ^{1}H NMR and HPLC analysis with those of authentic samples.

Acid hydrolysis of compounds **2**–**14** *and* **15**. Compounds **2**–**15** (*ca* 0.2 mg) dissolved in dioxane and 10% H_2SO_4 (1:1) were heated at 100° for 1 hr. After hydrolysis, reaction mixt. were passed through an Amberlite IRA-60E column and the eluates obtained concd to dryness. The residue was reduced with $NaBH_4$ (*ca* 1 mg) for 1 hr at room temp. The reaction mixt. was passed through an Amberlite IR-120B column and the eluate concd to dryness. Boric acid was removed by codistillation with MeOH and the residue acetylated with Ac_2O and pyridine (1 drop each) at room temp. overnight. The reagents were then evapd off *in vacuo*. From each glycoside, glucitol acetate was detected by GC. Conditions: Supelco SP-2380 capillary column, 0.25 mm × 0.30 m; temp. 250°; carrier gas, N_2; R_t (min), glucitol acetate 14.7.

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REFERENCES

1. Wada, K., Hayashi, K., Mitsuhashi, H. and Bando, H., *Chemical and Pharmaceutical Bulletin*, 1979, **27**, 2252.
2. Wada, K., Hayashi, K., Mitsuhashi, H. and Bando, H., *Chemical and Pharmaceutical Bulletin*, 1982, **30**, 3500.
3. Warashina, T. and Noro, T., *Chemical and Pharmaceutical Bulletin*, 1995, **43**, 977.
4. Warashina, T. and Noro, T., *Chemical and Pharmaceutical Bulletin*, 1995, **43**, 1734.
5. Warashina, T. and Noro, T., *Chemical and Pharmaceutical Bulletin*, 1996, **44**, 358.
6. Mitsuhashi, H. and Hayashi, K., *Shouyakugaku Zasshi*, 1985, **39**, 1.
7. Zhang, Z. and Zhou, J., *Acta Chimica Sinica*, 1983, **41**, 1058.