Acacia concinna Saponins. I. Structures of Prosapogenols, Concinnosides A—F, Isolated from the Alkaline Hydrolysate of the Highly Polar Saponin Fraction[1)]

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A highly polar saponin mixture from pods of *Acacia concinna* (Leguminosae) was hydrolyzed with alkali to yield five new triterpenoidal prosapogenols named concinnosides A (6), B (3), C (7), D (4), and E (8), together with four known glycosides, acaciaside (2), julibroside A_1 (10), julibroside A_3 (9), albiziasaponin C (5), and their aglycone, acacic acid lactone (1). The structures of these new prosapogenols were elucidated based on spectroscopic means. A less polar saponin fraction from the pods gave spinasteryl glucoside and its dihydro derivative.

Key words *Acacia concinna*; prosapogenol; concinnoside; alkaline hydrolysis; acacic acid lactone; spinasteryl glucoside

Acacia concinna D.C. (Leguminosae), commonly known as shika-kai in Hindi, grows widely in tropical jungles of South India. The pods of this plant are rich in saponins and are used for washing hair, promoting hair growth and also as an expectorant, emetic and purgative.[2)] Recently, we found that a saponin fraction of the pods showed a strong cytotoxic activity against KB cells,[3)] and this prompted a structural investigation. Although earlier researchers had reported the presence of acacic acid and acacic acid lactone derivatives in the acid hydrolysate of the saponin fraction,[4)] the isolation of pure saponins was very difficult and efforts have so far been fruitless. Since a preliminary investigation revealed that the saponin fraction is a complex mixture of saponins bearing ester linkage(s), we decided to carry out alkaline hydrolysis and to determine the structures of the components separately, and then, taking advantage of this knowledge, to investigate the structures of the genuine saponins.

On alkaline hydrolysis, the saponin mixture gave prosapogenols and monoterpene-glycosides. In this paper, we deal with the structures of the prosapogenols. The structures of the monoterpene-glycosides will be discussed in a forthcoming paper.

Results and Discussion

Isolation of Prosapogenols Treatment of the MeOH extract of pods of *A. concinna* with ethyl acetate gave soluble and insoluble fractions. The ethyl acetate-soluble fraction gave a mixture of phytosterol glucosides, from which spinasteryl glucoside and its dihydro derivative (stigmast-7-en-3β-yl glucoside) were identified.

The ethyl acetate-insoluble fraction was a mixture of highly polar saponins, which was hydrolyzed with 0.5 N NaOH in aqueous MeOH at room temperature. After acidification with HCl, the hydrolysate was successively extracted with ethyl acetate and BuOH. The EtOAc extract gave monoterpene-glycosides. The BuOH extract was fractionated by means of a combination of octadecyl silica gel (ODS) and silica gel column chromatographies followed by purification by recycling HPLC on an ODS column, yielding eleven compounds (see Experimental), in the following approximate yields: **1** (0.1%), **2** (0.74%), **3** (0.3%), **4** (0.08%), **5** (0.11%), **6** (0.11%), **7** (0.05%), **8** (0.18%), **9** (0.07%), **10** (0.29%), and **11** (0.04%). Among them, compound **1** was identical with acacic acid lactone (**1**)[5,6)] in melting point and spectral data. Compound **11** was revealed to be a monoterpenoid, whose structure will be discussed in a forthcoming paper.

Separate extraction of seeds similarly gave spinasteryl glucoside and stigmast-7-en-3β-yl glucoside from the low-polarity fraction and the following prosapogenols from the highly polar saponin fraction: compounds **2** (0.11%), **3** (0.04%), **4** (0.24%), **5** (0.07%), and **10** (0.04%). The results indicate that compounds **2** and **4** are the major constituents in pods and seeds, respectively, and compounds **6**, **7**, **8**, **9** are characteristic of the pods.

Structure of Prosapogenols Compounds **2**—**10** were considered to be monodesmosides of acacic acid lactone (**1**) because the ^{13}C-NMR data of the aglycone moiety were almost identical with those of **1**[5)] except for C-3, where the sugar moiety is attached. This was supported by an IR absorption (1752—1773 cm^{-1}) indicative of a γ-lactone and seven singlet *C*-Me signals (δ 0.77—1.42) in the ^{1}H-NMR spectra. Compounds **2**, **9**, and **10** were identified as acaciaside (**2**),[5b)] julibroside A_3 (**9**),[7)] and julibroside A_1 (**10**),[7)] respectively, by comparisons of their ^{13}C- and ^{1}H-NMR data with those reported in the literature. The others appeared to be new compounds, and were named concinnosides A (**6**), B (**3**), C (**7**), D (**4**), E (**8**), and F (**5**).[8)]

Concinnoside A (compound **6**) was obtained as colorless needles, mp 192—194 °C. The molecular formula $C_{41}H_{64}O_{13}$ was suggested from the positive fast atom bombardment (FAB)-mass spectral (MS) peak at *m/z* 787 $[M+Na]^+$. The ^{1}H-NMR spectrum showed, in addition to signals due to the aglycone moiety, two anomeric proton signals at δ 4.32 (d, J=7.8 Hz) and 4.33 (d, J=6.3 Hz), which corresponded to the ^{13}C signals at δ 107.0 and 105.4 (from the ^{1}H–^{13}C COSY spectrum in pyridine-d_5), indicating the presence of two sugar moieties. Detailed analysis of the ^{1}H–^{1}H correlation spectroscopy (COSY) spectrum revealed that they are β-glucoside and α-arabinoside. The arabinosyl moiety must be at a terminus, since its ^{13}C-NMR data are in good agreement with those of Me α-L-arabinopyranoside.[9)] The glucosyl moiety is substituted at C-6′, since, in the ^{13}C-NMR spectrum, its

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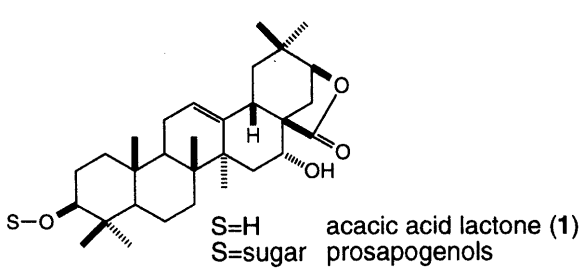
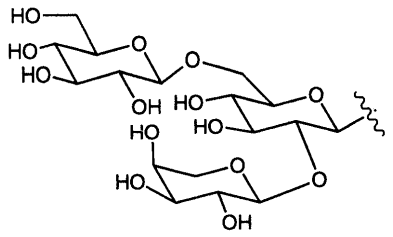
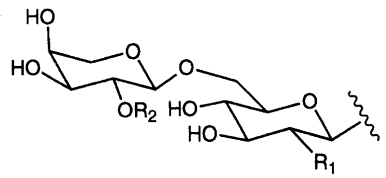




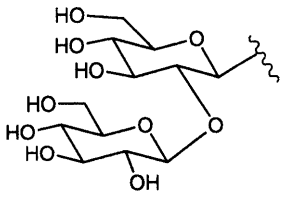


3: R_1=NHAc, R_2= H
(concinnoside B)

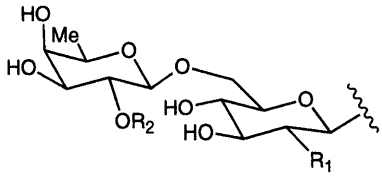
4: R_1=NHAc, R_2=α-L-Ara
(concinnoside D)

5: R_1=O-β-D-Glc, R_2=β-D-Xyl
(albiziasaponin C=concinnoside F)

6: R_1=OH, R_2=H
(concinnoside A)



7 (concinnoside C)



8: R_1=O-β-D-Glc, R_2=H
(concinnoside E)

9: R_1=NHAc, R_2=β-D-Xyl
(julibroside A_3)

10: R_1=O-β-D-Glc, R_2=β-D-Xyl
(julibroside A_1)

Chart 1. Prosapogenols Isolated from Pods and Seeds of *A. concinna*

Table 1. ^{13}C-NMR Data (in Pyridine-d_5) for Compounds **1**—**10** (Aglycone Moiety)

Carbon	1	2	3	4	5	6	7	8	9	10
1	38.1	38.6	38.5	38.6	38.7	38.7	38.7	38.6	38.6	38.7
2	27.2	26.7	26.4	26.6	26.8	26.7	26.2	26.7	26.7	26.8
3	78.0	89.1	89.3	88.7	88.6	88.9	88.9	89.0	88.1	88.1
4	39.4	39.5	39.2	39.3	39.6	39.5	39.5	39.5	39.4	39.7
5	56.0	55.9	55.8	55.9	56.0	55.9	56.0	55.9	55.9	56.0
6	18.7	18.4	18.4	18.5	18.4	18.4	18.4	18.4	18.4	18.5
7	32.6	32.5	32.5	32.6	32.5	32.5	32.6	32.5	32.6	32.6
8	40.4	40.3	40.3	40.4	40.3	40.3	40.3	40.3	40.4	40.4
9	47.4	47.2	47.2	47.3	47.3	47.2	47.2	47.2	47.3	47.3
10	37.3	36.8	36.8	37.0	37.0	36.9	36.9	36.9	37.0	37.0
11	23.8	23.7	23.7	23.8	23.8	23.7	23.7	23.7	23.8	23.8
12	124.6	124.6	124.6	124.6	124.5	124.6	124.5	124.6	124.6	124.6
13	140.3	140.1	140.0	140.1	140.1	140.1	140.3	140.1	140.1	140.2
14	43.4	43.3	43.3	43.3	43.3	43.3	43.3	43.3	43.3	43.3
15	38.2	38.2	38.0	38.2	38.1	38.2	38.1	38.2	38.2	38.2
16	66.7	66.7	66.6	66.7	66.7	66.7	66.6	66.7	66.7	66.7
17	50.0	50.0	49.9	50.0	49.9	50.0	50.0	50.0	50.0	50.0
18	41.8	41.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7	41.7
19	43.4	43.0	43.0	42.9	42.9	43.0	42.9	43.0	42.8	42.8
20	34.2	34.1	34.1	34.1	34.1	34.2	34.2	34.2	34.1	34.1
21	83.4	83.4	83.5	83.4	83.4	83.5	83.4	83.4	83.4	83.4
22	28.1	27.2	27.2	27.2	27.1	27.2	27.2	27.2	27.1	27.2
23	28.7	28.6	28.6	28.6	28.6	28.6	28.6	28.6	28.6	28.5
24	15.7	15.7	15.5	15.7	15.7	15.7	15.6	15.7	15.7	15.8
25	16.2	16.2	16.2	16.2	16.2	16.2	16.3	16.2	16.3	16.2
26	16.5	16.8	17.0	17.0	16.8	17.0	16.8	16.8	17.0	16.8
27	28.1	28.1	28.0	28.1	28.0	28.1	28.1	28.1	28.1	28.0
28	181.2	181.2	181.4	181.2	181.2	181.3	181.1	181.2	181.3	181.3
29	28.8	28.7	28.7	28.9	28.9	28.8	28.8	28.7	29.0	28.9
30	23.8	24.3	24.3	24.3	24.2	24.3	24.2	24.3	24.2	24.2

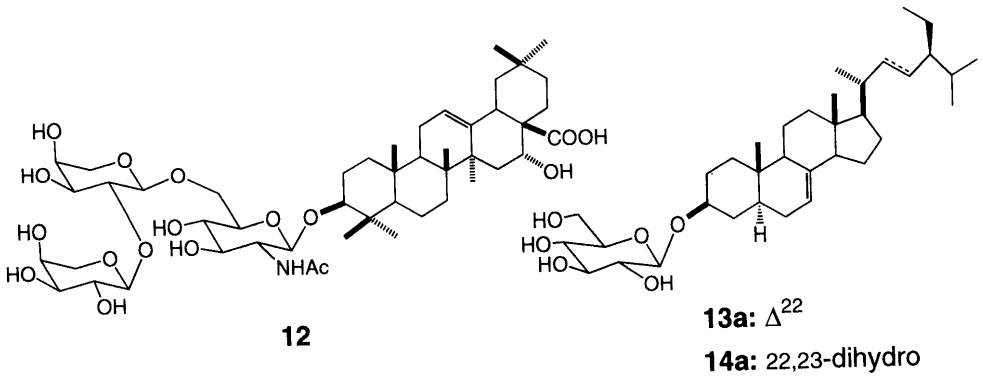
C-6′ signal (δ 69.9) is shifted down-field by 7.2 ppm and the C-5′ signal (δ 76.7) up-field by 1.4 ppm compared to those of Me β-D-glucopyranoside.[9] Thus, concinnoside A was determined to be acacic acid lactone-3-*O*-α-L-arabinopyranosyl(1→6)-β-D-glucopyranoside (**6**).

Concinnoside B (compound **3**) was obtained as colorless

Table 2. ^{13}C-NMR Data (in Pyridine-d_5) for Compounds **2**—**10** (Sugar Moiety)

Carbon	2	3	4	12[a)]	5	6	7	8	9	10
	Glc	GluNAc	GluNAc	GluNAc	Glc	Glc	Glc	Glc	GluNAc	Glc
1′	105.1	104.9	104.8	104.7	104.9	107.0	105.0	105.1	104.8	105.0
2′	83.2	57.7	58.0	57.7	83.1	75.6	83.3	83.2	58.0	83.2
3′	78.0	75.6	75.7	75.5	77.81*	78.6	78.3	78.0*	75.9	77.2
4′	71.6*	72.3	73.0	72.8	71.7	71.9	71.6	71.5	72.6	71.5
5′	76.4	76.5	77.9	77.7	76.0	76.7	78.0*	76.5	77.0	77.6
6′	69.7	69.7	69.4	69.4	69.2	69.9	62.84#	70.0	69.9	69.4
COMe		170.1	170.1	170.5					170.1	
COMe		23.6	23.7	23.6					23.8	
	Glc	Ara	Ara	Ara	Ara	Ara	Glc	Fuc	Fuc	Fuc
1″	106.1	105.2	102.4	102.2	102.4	105.4	106.0	105.6	103.5	104.0
2″	77.1	72.1	80.5	80.4	80.6	72.3	77.0	72.1	82.4	82.5
3″	78.2	74.1	72.6	72.4	72.6	74.4	77.9	75.3	75.3	75.2
4″	71.7*	68.9	67.5	67.4	67.4	69.1	71.7	72.7	72.2	72.1
5″	78.3	66.3	64.3	64.2	64.4	66.4	78.1*	71.5	71.3	71.3
6″	62.7						62.77#	17.3	17.3	17.3
	Ara		Ara	Ara	Glc			Glc	Xyl	Glc
1‴	105.4		106.3	106.1	105.9			106.0	107.1	106.0
2‴	72.3		75.5	75.3	77.1			77.1	76.0	76.1
3‴	74.3		76.3	76.0	77.93*			78.2*	77.5	78.1
4‴	69.0		70.9	70.7	71.8			71.7	70.9	71.7
5‴	66.4		67.3	67.1	78.2			78.3	67.1	78.3
6‴					62.7			62.7		62.7
					Xyl					Xyl
1⁗					106.3					107.0
2⁗					75.4					76.7
3⁗					77.87*					77.9
4⁗					70.8					70.8
5⁗					67.2					67.2

*, #: These assignments are interchangeable in each column. *a*) In pyridine-d_5: $D_2O = 9:1$, see ref. 10.



12 **13a:** Δ^{22} **14a:** 22,23-dihydro

Chart 2. The Model Compound (**12**) and Phytosteryl Glucosides (**13a**, **14a**) in *A. concinna*

needles, mp 257—260 °C. It contained one nitrogen atom as evidenced by the elementary analysis. It has two sugars [anomeric protons: δ 4.33 (d, $J = 6.4$ Hz) and 4.44 (d, $J = 8.4$ Hz); anomeric carbons: δ 105.2 and 104.9], which showed a similar coupling pattern to that of concinnoside A (**6**). Detailed analysis of the ^{1}H–^{1}H COSY spectrum revealed that one is an α-arabinosyl group and the other is a β-hexosyl group with *gluco*-type substitution. The presence of an *N*-acetyl group [IR: 1639 and 1570 cm^{-1}, ^{1}H-NMR: 1.94 (3H, s, Ac) and δ 8.91 (1H, d, $J = 8.8$ Hz, NH in pyridine-d_5), ^{13}C-NMR δ: 23.6 and 170.1] suggested that this hexose is *N*-acetylglucosamine (GluNAc). A positive FAB-MS peak at *m/z* 828 $[M+Na]^+$, which is 41 mass units higher than the corresponding peak in concinnoside A (**6**), supported this conclusion. The structure of the sugar moiety was finally determined as Ara(1→6)-GluNAc by comparisons of the ^{13}C-NMR data with those of Me α-L-arabinopyranoside and julibroside A_3 (**9**)[7]: a glycosylation shift was observed at C-6′ of the *N*-acetylglucosamine moiety and the ^{13}C peaks of the arabinosyl moiety were in good agreement with those of Me α-L-arabinopyranoside. Thus, concinnoside B is acacic acid lactone-3-*O*-α-L-arabinopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranoside (**3**).

Concinnoside C (compound **7**) was obtained as colorless needles, mp 238—242 °C. The molecular formula $C_{42}H_{66}O_{14}$ was suggested from the positive FAB-MS peak at *m/z* 817 $[M+Na]^+$. The ^{1}H-NMR spectrum showed two anomeric signals at δ 4.88 (d, $J = 8.3$ Hz) and 5.35 (d, $J = 7.3$ Hz); anomeric carbons at δ 105.0 and 106.0, respectively. The negative FAB-MS peak at *m/z* 631 $[M-\text{hexosyl}]^-$ suggested that a hexose was present at

the terminal position of the sugar moiety. This hexose was proved to be glucose from the ^1H–^1H COSY spectrum and the identity of six ^{13}C peaks with those of Me β-D-glucopyranoside. The other sugar was also suggested to be glucose with a β-anomeric linkage from the ^1H–^1H COSY spectrum, which is substituted at C-2′, because its C-2′ signal (δ 83.3) is shifted down-field by 8.6 ppm compared to that of Me β-D-glucopyranoside. Thus, concinnoside C was determined to be acacic acid lactone-3-*O*-β-D-glucopyranosyl(1→2)-β-D-glucopyranoside (**7**).

Concinnoside D (compound **4**) was obtained as colorless needles, mp 214—218 °C. It contained an *N*-acetylglucosamine moiety as in **3**, as deduced from its spectral data. The positive FAB-MS ion peak at *m/z* 960 $[M+Na]^+$, which was 132 mass units higher than that of concinnoside B (**3**), and the negative FAB-MS peaks at *m/z* 936 $[M-H]^-$, 804 $[M-\text{pentosyl}]^-$, and 672 $[M-\text{pentosyl}-\text{pentosyl}]^-$ suggested the sequence of sugar moieties to be pentose–pentose–GluNAc. The ^1H-NMR spectrum showed three anomeric protons at δ 4.98, 5.05, 5.16, which corresponded to the ^{13}C signals at δ 106.3, 104.8, and 102.4. The ^{13}C-NMR data of the sugar moiety of concinnoside D were in good agreement with those of a known compound, echinocystic acid glycoside (**12**),[10] in which the sugar sequence is α-L-Ara(1→2)-α-L-Ara(1→6)-β-D-GluNAc. Thus, the structure of concinnoside D was concluded to be acacic acid lactone-3-*O*-α-L-arabinopyranosyl(1→2)-α-L-arabinopyranosyl(1→6)-2-acetamido-2-deoxy-β-D-glucopyranoside (**4**).

Concinnoside E (compound **8**) was a colorless crystalline powder, mp 256—261 °C. It contained three sugar moieties as evidenced from three anomeric proton signals at δ 5.34 (d, *J* = 7.8 Hz), 4.90 (d, *J* = 7.3 Hz), and 4.81 (d, *J* = 7.8 Hz), which corresponded to the ^{13}C signals at δ 106.0, 105.6, and 105.1 in the ^1H–^{13}C COSY spectrum. The negative FAB-MS peaks at *m/z* 939 $[M-H]^-$, 793 $[M-\text{deoxyhexosyl}]^-$ and 777 $[M-\text{hexosyl}]^-$ suggested that a deoxyhexose and a hexose are present at terminal positions of the sugar moiety. The former was proved to be a fucosyl group: the presence of a doublet *C*-Me signal at δ 1.53 (*J* = 6.4 Hz) was seen in the ^1H–^1H COSY spectrum and six ^{13}C peaks were identical with those of Me β-D-fucopyranoside.[9] The other terminus was a glucosyl moiety as evidenced from the identity of its ^{13}C signals with those of Me β-D-glucopyranoside. From the ^1H–^1H COSY spectrum the remaining sugar was suggested to be a glucose, which is substituted at C-2′ and C-6′, since these carbon signals are shifted down-field (δ 83.2 and 70.0, respectively) from the corresponding peaks in Me β-D-glucopyranoside. The linkage of the sugar moieties was determined by nuclear Overhauser enhancement spectroscopy (NOESY) and long-range ^{13}C–^1H COSY experiments. NOE correlation peaks were observed between H-3 of the aglycone moiety (δ 3.23) and the anomeric proton (H-1′) of the inner glucose (δ 4.81), and between the anomeric proton (H-1‴) of the outer glucose (δ 5.34) and H-2′ of the inner glucose (δ 4.17). A long-range C–H correlation peak was observed between C-2′ of the inner glucose (δ 83.2) and H-1‴ of the outer glucose (δ 5.34). These results established that the glucosyl and fucosyl moieties are attached to the C-2′ and C-6′ positions of the inner glucose, respectively. Thus, the structure of concinnoside E was determined to be acacic acid lactone-3-*O*-β-D-fucopyranosyl(1→6)-[β-D-glucopyranosyl(1→2)]-β-D-glucopyranoside (**8**).

Concinnoside F (compound **5**) was an amorphous powder. It contained four sugar moieties as evidenced from four anomeric proton signals at δ 5.35 (d, *J* = 7.3 Hz), 5.11 (d, *J* = 5.4 Hz), 4.94 (d, *J* = 7.3 Hz) and 4.85 (d, *J* = 6.4 Hz), which corresponded to anomeric carbons at δ 105.9, 102.4, 106.3 and 104.9 in the ^{13}C–^1H COSY spectrum. In the positive FAB-MS, it showed an ion peak $[M+Na]^+$ at *m/z* 1081. Parent and fragment ion peaks in the negative FAB-MS at *m/z* 1057 $[M-H]^-$, 925 $[M-\text{pentosyl}]^-$, 895 $[M-\text{hexosyl}]^-$, 793 $[M-\text{pentosyl}-\text{pentosyl}]^-$ indicated that a hexosyl and a pentosyl group must be at terminal positions, and the terminal pentose is attached to the other pentosyl moiety. The terminal hexosyl and pentosyl moieties were identified as β-glucopyranoside and β-xylopyranoside, because their ^{13}C-NMR peaks were in good agreement with those of Me β-D-glucopyranoside and Me β-D-xylopyranoside, respectively. One of the two inner sugars was identified as α-arabinopyranoside with substitution at C-2″, because this carbon signal (δ 80.6) was shifted down-field by 8.4 ppm and the C-3″ signal (δ 72.6), up-field by 1.6 ppm, when compared to those of Me α-L-arabinopyranoside. Similarly, the other inner sugar was suggested to be β-glucopyranoside with substitution at C-2′ and C-6′, because these carbon signals (δ 83.1 and 69.2) were almost identical with the corresponding carbon signals of julibroside A_1 (**10**). The linkages of the sugars were determined by means of a NOESY experiment: correlation peaks were observed between H-3 of the aglycone moiety (δ 3.44) and the anomeric proton (H-1′) of the inner glucose (δ 4.85), between the anomeric proton (H-1‴) of the outer glucose (δ 5.35) and H-2′ of the inner glucose (δ 4.22), and between the anomeric proton (H-1⁗) of the terminal xylose (δ 4.94) and H-2″ of the arabinose (δ 4.44) moieties, revealing that the outer glucosyl and xylosyl moieties were attached to C-2′ of the inner glucose and C-2″ of the arabinose, respectively. Therefore, the arabinose moiety substituted at C-2″ by a xylosyl moiety is attached to C-6′ of the inner glucose. Thus, the structure of concinnoside F is determined to be acacic acid lactone-3-*O*-β-D-xylopyranosyl(1→2)-α-L-arabinosyl(1→6)-[β-D-glucopyranosyl(1→2)]-β-D-glucopyranoside (**5**). The same structure was recently proposed for albiziasaponin C[8] isolated from *Albizia lebbeck*. The identity of these two compounds was confirmed by comparison of the ^{13}C-NMR data.

We consider that the γ-lactone moiety of the above prosapogenols may be produced during hydrolysis, and the corresponding hydroxy acids are connected to monoterpenoid moieties in the genuine saponins. Various combinations of so many prosapogenols (corresponding acids) and monoterpene-glycosides may afford a complex mixture of saponins.

Experimental

Unless otherwise noted, the following procedures were adopted. Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra were taken as KBr discs with

a Shimadzu IR-460 spectrometer and the data are given in cm^{-1}. NMR spectra were measured on a JEOL GSX-500 (500 MHz for ^1H, 125 MHz for ^{13}C) spectrometer in pyridine-d_5 solutions with tetramethylsilane as an internal standard and the chemical shifts are given in δ values. The FAB-MS were taken with a JEOL JMS-SX102 spectrometer and major peaks are indicated as m/z. Optical rotation was measured on a Horiba SEPA-300 polarimeter. Column chromatography was performed on LiChroprep RP-18 (ODS, 40—63 μm, Merck) for reversed phase and Micro Bead Silica Gel 4B (100—200 mesh, Fuji Silysia Chemical) for normal phase. Recycling HPLC was performed with a JAI LC-908 HPLC system (Japan Analytical Industry) on an Inertsil Prep-ODS column (20 × 250 mm, Gasukuro Kogyo) using 70% MeOH as a solvent. For thin-layer chromatography (TLC), Kieselgel 60 F_{254} and RP-18 $F_{254}S$ precoated plates (Merck) were used and the spots were developed by spraying 10% H_2SO_4 and heating the plates until coloration took place.

Extraction of Pods and Seeds of *Acacia concinna* Fruits of *A. concinna* were purchased from a Bangladeshi market. Pods and seeds were separated and pulverized separately. The pulverized pods (40 g) were defatted with hexane (60 ml × 2), then extracted with methanol–chloroform (2 : 1, 70 ml × 3). The extract (12.34 g) was treated with hot EtOAc to afford soluble (0.65 g) and insoluble (11.69 g) fractions.

Similar extraction of the seeds (40 g) gave the EtOAc-soluble (0.23 g) and insoluble (2.14 g) fractions.

Isolation of Prosapogenols From Pods: The EtOAc-insoluble fraction (10 g) from pods was hydrolyzed with 0.5 N NaOH (140 ml) and MeOH (20 ml) for 18 h at room temperature. The mixture was acidified with 10% HCl and extracted successively with EtOAc and BuOH. The EtOAc extract gave a mixture of monoterpene-glycosides (1.69 g). The BuOH extract (4.4 g) was subjected to ODS column chromatography to obtain the following 6 fractions: frs. A—D, 60% MeOH; fr. E, 70% MeOH; and fr. F, 100% MeOH eluates. These fractions were further separated by silica gel column chromatography using $CHCl_3$: MeOH : H_2O = 8 : 4 : 0.5 as an eluting solvent and monitoring with TLC.

Attempted separation of frs. A (130 mg) and E (340 mg) was unsuccessful. Fraction B (1.8 g) was a mixture of saccharides. Fraction F (400 mg) was purified by silica gel column chromatography ($CHCl_3$: MeOH = 30 : 1) and then preparative TLC to give compound **1** (acacic acid lactone, 36 mg).

Fraction C (530 mg) was concentrated, and when the residue was allowed to stand in a small amount of MeOH, a crystalline precipitate appeared (compound **2**, 187 mg) which was identical with acaciaside. The mother liquor (343 mg) was chromatographed over silica gel to afford 6 fractions. Fraction 2 (73 mg) afforded, on repeated silica gel chromatography, compound **2** (18 mg), compound **3** (concinnoside B, 7 mg), and compound **4** (concinnoside D, 16 mg). Fractions 3 (20 mg) and 4 (62 mg) similarly gave a further crop of **2** (48 mg). The mother liquors of **2** from fr. 4 and fr. 5 were combined (*ca.* 90 mg) and subjected to recycling HPLC to afford compound **5** (concinnoside F, 37 mg). Attempted purification of frs. 1 (77 mg) and 6 (52 mg) was fruitless.

Fraction D (758 mg) was chromatographed on silica gel to afford 10 fractions. Purification of fr. 1 (40 mg) with silica gel chromatography ($CHCl_3$: MeOH = 6 : 1) and recycling HPLC yielded compound **11** (13 mg). Fraction 3 (112 mg) gave, on repeated silica gel chromatography, compounds **3** (59 mg) and **6** (concinnoside A, 35 mg). Fraction 4 (65 mg), on repeated chromatography on silica gel and recycling HPLC, gave compounds **3** (24 mg), **6** (3 mg), **7** (concinnoside C, 10 mg), and **9** (julibroside A_3, 4 mg). Similarly, fr. 5 (75 mg) gave compounds **8** (concinnoside E, 4 mg), **3** (14 mg), **7** (7 mg), **4** (13 mg), and **9** (20 mg). Fraction 6 (122 mg) afforded compound **8** (60 mg) as crystals on standing in a small amount of MeOH. The mother liquor contained compounds **4** and **9** (from TLC). Fraction 7 (136 mg) was treated with MeOH to afford soluble and insoluble portions. The MeOH-soluble portion was crystallized from EtOAc–MeOH to give compound **10** (julibroside A_1, 100 mg). The MeOH-insoluble portion mainly consisted of compound **8** (from TLC).

Thus, the following eleven compounds were isolated in the approximate yields shown in parentheses: compounds **1** (0.10%), **2** (0.74%), **3** (0.30%), **4** (0.08%), **5** (0.11%), **6** (*ca.* 0.11%), **7** (0.05%), **8** (0.18%), **9** (0.07%), **10** (0.29%), and **11** (0.04%).

From Seeds: A portion of the EtOAc-insoluble fraction (1.4 g) from seeds was hydrolyzed and separated as described above to give compounds **2** (30 mg, 0.11%), **3** (*ca.* 11 mg, *ca.* 0.04%), **4** (63 mg, 0.24%), **5** (19 mg, 0.07%), and **10** (10 mg, 0.04%).

Compound 1 (Acacic Acid Lactone)[5a] Colorless needles from MeOH, mp 249—253 °C (lit. 255—256 °C,[5a] 250—252 °C[5b]). IR: 1751 (γ-lactone). Positive FAB-MS: 493 $[M+Na]^+$. Negative FAB-MS: 469 $[M-H]^-$. ^1H-NMR: 0.85, 0.90, 0.96, 1.01, 1.08, 1.24, 1.35 (each 3H, s, Me), 3.44 (1H, dd, J = 10.3, 5.9 Hz, H-3), 4.26 (1H, d, J = 5.4 Hz, H-21), 4.54 (1H, dd, J = 11.2, 5.1 Hz, H-16), 5.39 (1H, br s, H-12).

Compound 2 (Acaciaside)[5b] Colorless needles from MeOH–H_2O, mp 252—256 °C (lit.[5b] 245—248 °C). $[\alpha]_D$ −39.5° (c = 0.24, pyridine). Positive FAB-MS: 949 $[M+Na]^+$. Negative FAB-MS: 925 $[M-H]^-$, 793 $[M-pentosyl]^-$. ^1H-NMR: 0.77, 0.79, 0.94, 1.05, 1.09, 1.21, 1.30 (each 3H, s, Me), 3.19 (1H, dd, J = 11.7, 4.4 Hz, H-3), 4.81 (1H, d, J = 7.3 Hz, Glc H-1′), 4.91 (1H, d, J = 6.8 Hz, Ara H-1‴), 5.32 (1H, d, J = 7.3 Hz, Glc H-1″), 5.30 (1H, br s, H-12).

Compound 3 (Concinnoside B) Colorless needles from MeOH–H_2O, mp 257—260 °C. $[\alpha]_D$ −16.0° (c = 0.18, MeOH). IR: 1759 (γ-lactone), 1639, 1570 (CONH). Positive FAB-MS: 828 $[M+Na]^+$. Negative FAB-MS: 804 $[M-H]^-$. *Anal.* Calcd for $C_{43}H_{67}NO_{13}\cdot 5.5H_2O$: C, 60.69; H, 8.53; N, 1.65. Found: C, 60.96; H, 9.29; N, 1.67. ^1H-NMR (CD_3OD): 0.77, 0.92, 0.94, 0.97, 0.99, 1.00, 1.24 (each 3H, s, Me), 1.94 (3H, s, Ac), 3.11 (1H, dd, J = 12.0, 4.6 Hz, H-3), 3.32 (1H, t, J = 8.8 Hz, GluNAc H-4′), 3.42 (1H, m, GluNAc H-5′), 3.44 (1H, dd, J = 10.3, 8.8 Hz, GluNAc H-3′), 3.51 (1H, dd, J = 8.8, 3.4 Hz, Ara H-3″), 3.52 (1H, dd, J = 12.5, 1.4 Hz, Ara H-5″), 3.58 (1H, dd, J = 8.8, 6.4 Hz, Ara H-2″), 3.65 (1H, dd, J = 10.3, 8.3 Hz, GluNAc H-2′), 3.71 (1H, dd, J = 11.5, 5.7 Hz, GluNAc H-6′), 3.79 (1H, m, Ara H-4″), 3.85 (1H, dd, J = 12.5, 3.7 Hz, Ara H-5″), 3.90 (1H, dd, J = 12.2, 4.9 Hz, H-16), 4.06 (1H, dd, J = 11.5, 2.3 Hz, GluNAc H-6′), 4.25 (1H, d, J = 5.4 Hz, H-21), 4.33 (1H, d, J = 6.4 Hz, Ara H-1″), 4.44 (1H, d, J = 8.4 Hz, GluNAc H-1′), 5.41 (1H, br s, H-12). NHCO: 8.91 (1H, d, J = 8.8 Hz) in pyr-d_5.

Compound 4 (Concinnoside D) Colorless needles from MeOH–H_2O, mp 214—218 °C. $[\alpha]_D$ −12.2° (c = 0.3, MeOH). IR: 1761 (γ-lactone), 1656, 1558 (CONH). Positive FAB-MS: 960 $[M+Na]^+$. Negative FAB-MS: 936 $[M-H]^-$, 804 $[M-pentosyl]^-$, 672 $[M-pentosyl-pentosyl]^-$. *Anal.* Calcd for $C_{48}H_{75}NO_{17}\cdot 3H_2O$: C, 58.11; H, 8.23; N, 1.41. Found: C, 57.81; H, 8.28; N, 1.40. ^1H-NMR: 0.79, 0.80, 0.92, 1.00, 1.07, 1.21, 1.39 (each 3H, s, Me), 2.16 (3H, s, Ac), 3.42 (1H, dd, J = 11.7, 4.4 Hz, H-3), 3.59 (1H, t, J = 10.7 Hz, GluNAc H-4′), 3.75 (1H, dd, J = 11.2, 2.4 Hz, Ara H-5‴), 3.99-4.07 (3H, Ara H-2‴, 3‴, 5‴), 4.12 (2H, m, GluNAc H-5′, Ara H-4″), 4.23 (1H, d, J = 5.4 Hz, H-21), 4.19 (1H, dd, J = 11.2, 5.4 Hz, GluNAc H-6′), 4.29 (1H, dd, J = 11.7, 5.4 Hz, Ara H-5‴), 4.35—4.40 (4H, GluNAc H-3′, Ara H-3″, 5″, 4‴), 4.49—4.53 (3H, GluNAc H-2′, Ara H-2″, H-16), 4.61 (1H, d, J = 9.3 Hz, GluNAc H-6′), 4.98 (1H, d, J = 6.6 Hz, Ara H-1‴), 5.05 (1H, d, J = 8.3 Hz, GluNAc H-1′), 5.16 (1H, d, J = 4.9 Hz, Ara H-1″), 8.91 (1H, d, J = 8.8 Hz, NHCO).

Compound 5 (Concinnoside F = Albiziasaponin C)[8] Amorphous powder from MeOH–EtOAc. $[\alpha]_D$ −28.4° (c = 0.26, pyridine). IR: 1759 (γ-lactone). Positive FAB-MS: 1081 $[M+Na]^+$. Negative FAB-MS: 1057 $[M-H]^-$, 925 $[M-pentosyl]^-$, 895 $[M-hexosyl]^-$, 793 $[M-pentosyl-pentosyl]^-$. *Anal.* Calcd for $C_{52}H_{82}O_{22}\cdot 5.5H_2O$: C, 53.93; H, 8.0. Found: C, 53.87; H, 7.48. ^1H-NMR: 0.80, 0.84, 0.92, 1.06, 1.10, 1.28, 1.37 (each 3H, s, Me), 3.44 (1H, dd, J = 11.9, 4.6 Hz, H-3), 3.58 (1H, t, J = 10.8 Hz, Xyl H-5⁗), 3.74 (1H, dd, J = 11.2, 2.4 Hz, Ara H-5″), 3.91 (1H, m, Glc H-5‴), 3.96—4.01 (2H, Xyl H-2⁗, Glc H-5′), 4.01—4.05 (2H, Glc H-3′, Xyl H-3⁗), 4.08—4.12 (2H, Glc H-2‴, Xyl H-4⁗), 4.18 (1H, dd, J = 11.2, 5.6 Hz, Glc H-6′), 4.19—4.25 (4H, Ara H-5″, Glc H-2′, 3′, 3‴), 4.24 (1H, d, J = 5.6 Hz, H-21), 4.30 (1H, t, J = 9.0 Hz, Glc H-4‴), 4.32—4.38 (2H, Xyl H-5⁗, Ara H-4″), 4.38 (1H, dd, J = 10.7, 4.0 Hz, Ara H-3″), 4.42—4.51 (4H, H-16, Ara H-2″, Glc H-6‴ × 2), 4.60 (1H, d-like, J = 9.6 Hz, Glc H-6′), 4.85 (1H, d, J = 6.4 Hz, Glc H-1′), 4.94 (1H, d, J = 7.3 Hz, Xyl H-1⁗), 5.11 (1H, d, J = 5.4 Hz, Ara H-1″), 5.30 (1H, br s, H-12), 5.35 (1H, d, J = 7.3 Hz, Glc H-1‴).

Compound 6 (Concinnoside A) Colorless needles from MeOH–H_2O, mp 192—194 °C, $[\alpha]_D$ −1.2° (c = 0.23, MeOH). IR: 1761 (γ-lactone). Positive FAB-MS: 787 $[M+Na]^+$. Negative FAB-MS: 763 $[M-H]^-$. *Anal.* Calcd for $C_{41}H_{64}O_{13}\cdot 4H_2O$: C, 58.83; H, 8.67. Found: C, 58.51; H, 8.49. ^1H-NMR (CD_3OD): 0.87, 0.93, 0.96, 1.00, 1.01, 1.10, 1.24 (each 3H, s, Me), 3.16 (1H, dd, J = 11.2, 4.6 Hz, H-3), 3.19 (1H, t, J = 8.6 Hz, Glc H-2′), 3.29—3.31 (2H, Glc H-3′, 4′), 3.41 (1H, m, Glc H-5′), 3.51 (1H, dd, J = 12.7, 2.7 Hz, Ara H-5″), 3.53 (1H, dd, J = 8.3, 2.7 Hz, Ara H-3″), 3.58 (1H, dd, J = 8.8, 6.3 Hz, Ara H-2″), 3.71 (1H, dd, J = 11.3, 5.4 Hz, Glc H-6′), 3.80 (1H, m, Ara H-4″), 3.86 (1H, dd, J = 12.7, 3.9 Hz, Ara H-5″), 3.90 (1H, dd, J = 11.7, 4.6 Hz, H-16), 4.06 (1H, dd, J = 11.3, 2.2 Hz, Glc H-6′), 4.26 (1H, d, J = 5.4 Hz, H-21), 4.32 (1H, d, J = 7.8 Hz, Glc H-1′), 4.33 (1H, d, J = 6.3 Hz, Ara H-1″), 5.42 (1H, br s, H-12).

Compound 7 (Concinnoside C) Colorless needles from MeOH–H_2O,

mp 238—242 °C. $[\alpha]_D$ −11.8° (c=0.17, MeOH). IR: 1752 (γ-lactone). Positive FAB-MS: 817 $[M+Na]^+$. Negative FAB-MS: 793 $[M-H]^-$, 631 $[M-hexosyl]^-$. ^{1}H-NMR: 0.79, 0.80, 0.95, 1.07, 1.10, 1.28, 1.36 (each 3H, s, Me), 3.28 (1H, dd, J=11.7, 4.4 Hz, H-3), 3.91 (2H, m, Glc H-5′, 5″), 4.11 (1H, t, J= 8.3 Hz, Glc H-2″), 4.13 (1H, t, J=9.2 Hz, Glc H-4′), 4.23 (1H, t, J=9.2 Hz, Glc H-3″), 4.24 (1H, t, J=9.2 Hz, Glc H-2′), 4.25 (1H, d, J=5.4 Hz, H-21), 4.29 (1H, t, J=8.7 Hz, Glc H-3′), 4.30 (1H, t, J=9.6 Hz, Glc H-4″), 4.33 (1H, dd, J=11.9, 5.5 Hz, Glc H-6′ or 6″), 4.43 (1H, dd, J=11.0, 4.1 Hz, Glc H-6′ or 6″), 4.47 (1H, dd, J=11.0, 2.7 Hz, Glc H-6′ or 6″), 4.50—4.52 (1H, H-16), 4.54 (1H, dd, J=11.9, 1.8 Hz, Glc H-6′ or 6″), 4.88 (1H, d, J=8.3 Hz, Glc H-1′), 5.35 (1H, d, J=7.3 Hz, Glc H-1″), 5.36 (1H, br s, H-12).

Compound 8 (Concinnoside E) Colorless needles from MeOH, mp 256—261 °C. $[\alpha]_D$ −16.4° (c=0.32, MeOH). IR: 1759 (γ-lactone). Positive FAB-MS: 963 $[M+Na]^+$. Negative FAB-MS: 939 $[M-H]^-$, 793 $[M-deoxyhexosyl]^-$, 777 $[M-hexosyl]^-$. *Anal.* Calcd for $C_{48}H_{76}O_{18}\cdot 3H_2O$: C, 57.94; H, 7.93. Found: C, 57.73; H, 7.93. ^{1}H-NMR: 0.80, 0.83, 0.97, 1.09, 1.13, 1.24, 1.33 (each 3H, s, Me), 1.53 (3H, d, J=6.4 Hz, Fuc H-6″), 3.23 (1H, dd, J=11.2, 4.1 Hz, H-3), 3.81 (1H, q-like, J=6.4 Hz, Fuc H-5″), 3.93 (1H, m, Glc H-5‴), 4.01—4.10 (3H, Glc H-5′, Fuc H-3″, 4″), 4.10 (1H, t, J=9.5 Hz, Glc H-4′), 4.12 (1H, t, J=7.8 Hz, Glc H-2‴), 4.17 (1H, t, J=7.8 Hz, Glc H-2′), 4.27 (1H, d, J=4.9 Hz, H-21), 4.23—4.29 (4H, Glc H-3′, 6′, 3‴, 4‴), 4.40 (1H, t, J=8.5 Hz, Fuc H-2″), 4.48 (1H, dd-like, J=12.2, 2.2 Hz, Glc H-6‴), 4.52 (1H, dd-like, J=12.2, 4.9 Hz, Glc H-6‴), 4.54 (1H, dd, J=11.2, 4.9 Hz, H-16), 4.81 (1H, d, J=7.8 Hz, Glc H-1′), 4.81—4.83 (1H, Glc H-6′), 4.90 (1H, d, J=7.3 Hz, Fuc H-1″), 5.34 (1H, d, J=7.8 Hz, Glc H-1‴).

Compound 9 (Julibroside A_3)[7] Colorless prisms from MeOH–H_2O, mp 219—224 °C (lit.[7] amorphous powder). $[\alpha]_D$ −7.1° (c=0.17, MeOH). IR: 1773 (γ-lactone), 1655, 1572 (CONH). Positive FAB-MS: 974 $[M+Na]^+$. Negative FAB-MS: 950 $[M-H]^-$, 818 $[M-pentosyl]^-$. ^{1}H-NMR: 0.81, 0.83, 0.89, 1.03, 1.06, 1.24, 1.42 (each 3H, s, Me), 1.50 (3H, d, J=6.4 Hz, Fuc H-6″), 2.18 (3H, s, Ac), 3.58 (1H, dd, J=11.2, 4.3 Hz, H-3), 4.21 (1H, d, J=5.4 Hz, H-21), 5.03 (1H, d, J=7.8 Hz, GluNAc H-1′), 5.06 (1H, d, J=6.8 Hz, Fuc H-1″), 5.08 (1H, d, J=8.3 Hz, Xyl H-1‴), 5.28 (1H, br s, H-12), 8.92 (1H, d, J=8.8 Hz, NHCO).

Compound 10 (Julibroside A_1)[7] Amorphous powder, mp 204—208 °C (lit.[7] amorphous powder). IR: 1763 (γ-lactone). Positive FAB-MS: 1095 $[M+Na]^+$. ^{1}H-NMR: 0.81, 0.87, 0.89, 1.04, 1.14, 1.31, 1.40 (each 3H, s, Me), 1.50 (3H, d, J=6.4 Hz, Fuc H-6″), 3.59 (1H, dd, J=11.0, 3.7 Hz, H-3), 4.22 (1H, d, J=5.9 Hz, H-21), 4.54 (1H, m, H-16), 4.91 (1H, d, J=6.4 Hz, Glc H-1′), 5.00 (1H, d, J=7.3 Hz, Fuc H-1″), 5.01 (1H, d, J=6.3 Hz, Xyl H-1⁗), 5.30 (1H, br s, H-12), 5.40 (1H, d, J=7.3 Hz, Glc H-1‴).

Spinasteryl Glucoside (13a) and Stigmast-7-en-3-yl Glucoside (14a) The EtOAc-soluble fractions from pod and seed extracts were subjected to chromatography ($CHCl_3$–MeOH, 5:1) to yield glucoside-rich fractions (40 mg from pods, 20 mg from seeds), respectively. These fractions were treated with a small amount of MeOH to remove soluble materials, yielding mixtures of **13a** and **14a** as insoluble portions (7.5 mg from pods, 9 mg from seeds). The ratios of **13a** and **14a** (7.9:2.1 for the pod extract, 7.8:2.2 for the seed extract) were determined from the intensity ratios of the *C*10-Me peaks at δ 0.598 and 0.584 in the ^{1}H-NMR spectra.

Spinasteryl Glucoside (**13a**): Colorless fine needles after several crystallizations of the above mixture from $CHCl_3$–MeOH, mp 284—286 °C (lit. 279—283 °C,[11a] 292—294 °C[11b]). IR: 3515, 3435, 3425 (OH). Positive FAB-MS: 597 $[M+Na]^+$. *Anal.* Calcd for $C_{35}H_{58}O_6$: C, 73.13; H, 10.17. Found: C, 72.33; H, 10.00. ^{1}H-NMR: 0.598 (3H, s, H-18), 0.736 (3H, s, H-19), 0.873 (3H, d, J=6.8 Hz, H-27), 0.892 (3H, t, J=6.9 Hz, H-29), 0.919 (3H, d, J=6.8 Hz, H-26), 1.085 (3H, d, J=6.4 Hz, H-21), 3.96—4.05 (2H, m, H-3, 5′), 4.06 (1H, t, J=8.0 Hz, H-2′), 4.28 (1H, t, J=8.7 Hz, H-4′), 4.31 (1H, t, J=8.1 Hz, H-3′), 4.42 (1H, dd, J=11.7, 5.4 Hz, H-6′), 4.60 (1H, dd, J=11.7, 2.4 Hz, H-6′), 5.05 (1H, d, J=7.8 Hz, H-1′), 5.07, 5.21 (each 1H, dd, J=15.1, 9.0 Hz, H-22, 23), 5.19 (1H, br s, H-7).

The tetraacetate (**13b**) was obtained as colorless fine needles from MeOH, mp 169—172 °C (lit.[11a] 173—175 °C). ^{1}H-NMR ($CDCl_3$): 0.545 (3H, s, H-18), 0.777 (3H, s, H-19), 0.801 (3H, d, J=6.0 Hz, H-27), 0.806 (3H, t, J=7.3 Hz, H-29), 0.837 (3H, d, J=6.8 Hz, H-27), 1.025 (3H, d, J=6.8 Hz, H-21), 2.00, 2.02, 2.05, 2.08 (each 3H, s, Ac), 3.52—3.56 (1H, m, H-3), 3.69 (1H, ddd, J=9.8, 4.8, 2.4 Hz, H-5′), 4.12 (1H, dd, J=12.2, 2.5 Hz, H-6′), 4.25 (1H, dd, J=12.2, 4.9 Hz, H-6′), 4.61 (1H, d, J=8.0 Hz, H-1′), 4.95 (1H, dd, J=9.8, 8.0 Hz, H-2′), 5.03, 5.16 (each 1H, dd, J=16.1, 8.9 Hz, H-22, 23), 5.07 (1H, t, J=9.5 Hz, H-4′), 5.14 (1H, br s, H-7), 5.19 (1H, t, J=9.5 Hz, H-3′). The ^{13}C-NMR data for **13a** and **13b** were identical with those reported for spinasteryl glucoside and its tetraacetate,[12,13] respectively.

Stigmast-7-en-3β-yl Glucoside (Schottenyl Glucoside) (**14a**): This was obtained from the mother liquor of **13a** as a 1:2 mixture with **13a**, and gave the following spectral data. ^{1}H-NMR: *C*-Me 0.584 (s, H-18), 0.736 (s, H-19), 0.873 (d, J=6.8 Hz, H-27), 0.892 (t, J=6.9 Hz, H-29), 0.919 (d, J=6.8 Hz, H-26), 0.925 (d, J=6.4 Hz, H-21). The acetate (**14b**) gave the following data. ^{1}H-NMR ($CDCl_3$): *C*-Me 0.530 (s, H-18), 0.777 (H-19), 0.800 (d, J=6.0 Hz, H-27), 0.806 (t, J=7.3 Hz, H-29), 0.840 (d, J=6.8 Hz, H-26), 0.925 (d, J=6.4 Hz, H-21). The ^{13}C-NMR data were identical with those reported for stigmast-7-en-3β-yl glucoside and its tetraacetate.[12b]

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References and Notes

1) A part of this work was presented at the 94th Meeting of the Hokuriku Branch of the Pharmaceutical Society of Japan, Toyama, 1996, June.
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