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CARDIOACTIVE STEROID SAPONINS AND OTHER CONSTITUENTS FROM THE AERIAL PARTS OF *TRIBULUS CISTOIDES**

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Key Word Index— *Tribulus cistoides*; Zygophyllaceae; aerial parts; cistocardin; new cardioactive and other steroid saponins; neotigogenin; neogitogenin; neohecogenin; N-acyltyramines; 5′-(hydroxysulphonyloxy) jasmonic acid; D-(+)-pinitol; sucrose; partial synthesis of 5′-(hydroxysulphonyloxy) jasmonic acid.

Abstract—From the petrol extract of the aerial parts of *Tribulus cistoides* three steroid sapogenins and two N-acyltyramines were isolated, whereas the methanolic extract gave nine steroid saponins, among them the cardioactive cistocardin, saponin-3, saponin-4 and saponin-7. Furthermore, a furostanol diglycoside was isolated besides 5′-(hydroxysulphonyloxy) jasmonic acid, D-(+)-pinitol and sucrose. The structures were established by spectroscopic investigations of the isolated compounds and their hydrolysis products. 5′-(Hydroxysulphonyloxy) jasmonic acid has been prepared by partial synthesis.

INTRODUCTION

The genus *Tribulus* of the Zygophyllaceae comprises *ca* 20 species which grow as shrubs or herbs in subtropical areas around the world [2, 3]. Among the *Tribulus* species, only *T. terrestris* has been phytochemically investigated [4–7]. This plant is known in South Africa and the U.S.A. to be toxic for sheep and it causes major economic damage [3, 8]. On the other hand, *T. terrestris* is used in Ayurveda medicine against various diseases [9] and its extract constitutes the active component of a medicine traded in Bulgaria [10, 11].

Tribulus cistoides is a herb wide-spread in Middle America and the Southern U.S.A. Its local name in Mexico is 'Abrojo de tierra caliente' (thistle of the hot country) and aqueous extracts of the roots are applied against disorders of the kidney and bladder, but also against malaria [12, 13].

The starting point of our investigations was the observation that a methanolic extract of the leaves and stems of *T. cistoides* exhibits a significant positive inotropic effect in a biological test [M. Reiter, personal communication].

RESULTS AND DISCUSSION

The aerial parts of *T. cistoides* were extracted first with petrol and then with methanol. Chromatographic separation of these extracts yielded **1**–**17** and $Ca(NO_3)_2$ (Table 1). Repeated chromatography of the petrol extract on silica gel gave the sapogenins **1**–**3** and a mixture of **4** and **5**, whose separation was achieved by HPLC on silica gel RP-18.

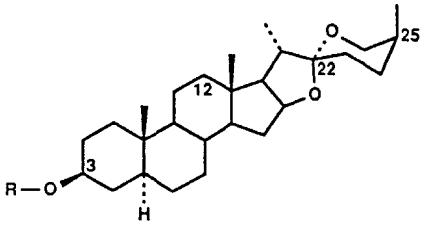
The structures of neotigogenin (**1**), neogitogenin (**2**) and neohecogenin (**3**), as well as the N-acyltyramines **4** and **5** were determined from their spectra and comparison with published data [4, 14–16, 18].

The methanolic extract was processed by dilution with water and partitioning first between chloroform and then *n*-butanol. MPLC of the $CHCl_3$ soluble part yielded 12 fractions (fractions 1–12) and fraction 3 gave by repeated CC on Sephadex® LH 20 **6**, while fractions 4–9 by HPLC on silica gel RP–18 yielded **7**–**13**. For **10**, we suppose the name cistocardin, since biological monitoring revealed this compound as the main cardiotonic active principle besides saponin-4 (**9**). Saponin-3 (**8**) also showed significant cardioactivity, whereas tribulosin (**7**) and saponin-7 (**12**) were only weakly active (Fig. 1, Table 4).

^1H and ^{13}C NMR studies established the structures of the aglycones in these compounds to be either **1**, **2** or **3** [15] with a sugar moiety linked at C-3 (Table 2). The size and basic information on the structure of the sugar moiety came from FAB mass spectroscopy. However, structure determination of the sugar parts was achieved by TLC-controlled partial hydrolysis in combination with ^1H NMR studies. In the presence of MeOH– 1 M H_2SO_4 at 80°, within 4–8 hr the genuine saponins **6**, **7** and **10**–**12** were hydrolysed to give the aglycone and a series of prosapogenins originating by successive loss of the sugar units. Chromatographic separation by CC or HPLC served to isolate the produced prosapogenins.

*Part 61 in the series 'Constituents of Tropical Medicinal Plants'. For Part 60 see ref. [1].

†Author to whom correspondence should be addressed.



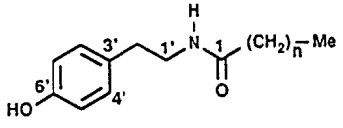
1 : R = H

6 : R = —β-Gal^{4}—β-Glc^{3}—β-Xyl
|^{2}
β-Xyl

7 : R = —β-D-Gal^{4}—β-D-Glc^{3}—β-D-Xyl
|^{2} |^{2}
α-L-Rha β-D-Xyl

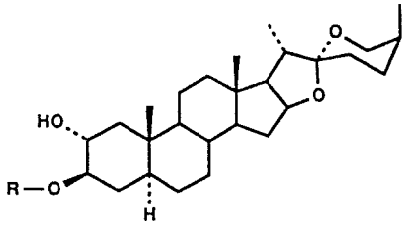
9 : R = —β-D-Gal^{4}—β-D-Glc^{3}—β-D-Glc
|^{2}
β-D-Glc

11 : R = —β-Gal^{4}—β-Glc^{3}—β-Glc^{4}—β-Xyl
|^{2}
β-Glc



4 : n = 20

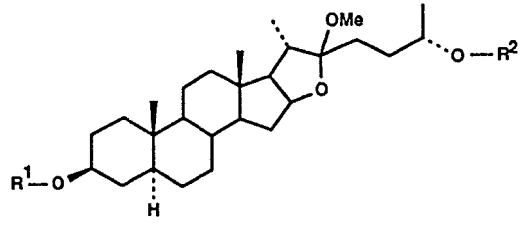
5 : n = 22



2 : R = H

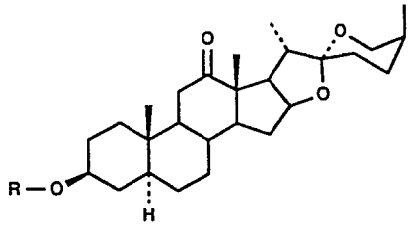
10 : R = —β-D-Gal^{4}—β-D-Glc^{3}—β-D-Glc
|^{2}
β-D-Glc

13 : R = —β-Gal^{4}—β-Glc^{3}—β-Glc^{4}—β-Xyl
|^{2}
β-Glc



14 : R^1 = —β-D-Gal^{4}—β-D-Glc^{3}—β-D-Xyl
|^{2} |^{2}
α-L-Rha β-D-Xyl

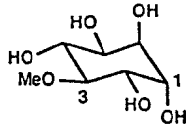
R^2 = —β-Glc



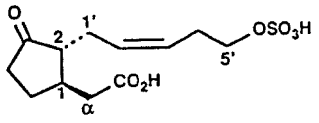
3 : R = H

8 : R = —β-D-Gal^{4}—β-D-Glc^{3}—β-D-Xyl
|^{2} |^{2}
α-L-Rha β-D-Xyl

12 : R = —β-Gal^{4}—β-Glc^{3}—β-Glc
|^{2} |^{2}
α-Rha β-Xyl



15



17

Table 1. Compounds isolated from extracts of the aerial parts of *T. cistoides*

Compound class	Compound	Fraction *	Content [%]†	Refs
Sapogenins	Neotigogenin (**1**)	PE	1.5	[4]
	Neogitogenin (**2**)	PE	1.5	[14, 15]
	Neohecogenin (**3**)	PE	0.5	[4, 15]
Acetogenins	N-Docosanoyltyramine (**4**)	PE	0.05	
	N-Tetracosanoyltyramine (**5**)	PE	0.1	[16]
Saponins				
(i) Spirostanol-type	Saponin-1 (**6**)	MeOH–$CHCl_3$	0.1	
	Tribulosin (**7**)	MeOH–$CHCl_3$	1.4	[4]
	Saponin-3 (**8**)	MeOH–$CHCl_3$	0.15	
	Saponin-4 (**9**)	MeOH–$CHCl_3$	0.05	
	Cistocardin (**10**)	MeOH–$CHCl_3$	0.2	
	Saponin-6 (**11**)	MeOH–$CHCl_3$	0.3	
	Saponin-7 (**12**)	MeOH–$CHCl_3$	0.07	
	Saponin-8 (**13**)	MeOH–$CHCl_3$	0.2	
(ii) Furostanol-type	Saponin-9 (**14**)	MeOH-BuOH	2	
Cyclitols	D-(+)-Pinitol (**15**)	MeOH–H_2O	10	[17]
Sugars	Sucrose (**16**)	MeOH–H_2O	15	
Inorganic	$Ca(NO_3)_2$	MeOH–H_2O	1	
Others	5′-(Hydroxysulphonyloxy)jasmonic acid (**17**)	MeOH–H_2O	0.005	

*PE: petrol extract; MeOH–$CHCl_3$: chloroform-soluble fraction of MeOH extract; MeOH–BuOH: *n*-butanol-soluble fraction of MeOH extract; MeOH–H_2O: residue after extraction with $CHCl_3$ and BuOH.

†Dry weight of extract = 100%.

^{1}H NMR studies of the acetylated prosapogenins and comparison of the spectra identified the individual sugar units [19] and revealed the positions of their linkage. As an example, the corresponding data are compiled for cistocardin (**10**) in Table 3.

Small coupling constants for H-1 to H-4 of the xylose moieties in the corresponding peracetylated compounds indicated that the conformation of the xylopyranosyl units had been changed by acetylation from $^4C_1$ to $^1C_4$ with all-axial acetoxy groups [20, 21]. This effect was observed particularly for saponin **12** and in the saponins **6–8**, but in the latter compounds it occurred only for the xylopyranosyl units linked to C-3 of the glucose as could be shown by $^3J^1H$–^{13}C experiments. To determine the absolute configurations of the sugar units, cistocardin (**10**) and tribulosin (**7**) were hydrolysed to give the aglycones and the mixture of the corresponding methyl glycosides, which was analysed by GC using a chiral column [22].

From the butanol-soluble fraction of the methanol extract were isolated **14**. NMR studies revealed the diglycosidic furostanol structure, which on treatment with β-glucosidase yielded tribulosin (**7**) and β-glucose.

Repeated chromatography of the methanol–water residue on Sephadex gels yielded D-(+)-pinitol (**15**) [17] and sucrose (**16**), besides a cardioactive fraction, which on HPLC gave calcium nitrate responsible for the cardioactivity (Fig. 1) in this fraction and 5′-(hydroxysulphonyloxy) jasmonic acid (**17**). Compounds **15** and **16** constitute the two major extractable components of the aerial parts of *T. cistoides*. Their structures derived from the spectral data for **15** [23], peracetyl-**15** and **16** [24], and from their optical properties [25, 26]. Structure **17** is the result of spectroscopic studies on the isolated compound and its methyl ester. The structure was corroborated by acidic hydrolysis, which yielded (−)-5′-hydroxyjasmonic acid methyl ester [27, 28], and by the synthesis of racemic **17** starting from (±)-jasmine ketolactone [29].

The cardioactive saponin-3 (**8**), saponin-4 (**9**) and cistocardin (**10**), and the steroid saponins **6** and **11–13** represent new natural products, as does the furostanol diglycoside **14**. However, it cannot be excluded that the methoxy group at C-22 in **14** may originate from the methanol used. N-Docosanoyltyramine (**4**) has also not been described previously and 5′-(hydroxysulphonyloxy)-jasmonic acid (**17**) constitutes a unique new natural product.

It may be pointed out that saponins deriving from neotigogenin or neohecogenin are rare natural products, and cistocardin (**10**) and **13** are the first saponins containing neogitogenin as the aglycone. Furthermore, except for the tetrasaccharide contained in **9** and **10**, and the pentasaccharide from **7** and **8**, the oligosaccharidic moieties from **6**, **11**, **12** and **13** have been described for the first time.

The biological test on inotropic cardioactivity uses the papillary muscle of guinea pigs [30]. The results show that cistocardin (**10**) and saponin-4 (**9**), and also saponin-3 (**8**) possess relatively strong activities at 10^{-6} to 10^{-5} M concentrations, whereas saponin-7 (**12**) and tribulosin (**7**) show considerably lower activities in concentrations of 10^{-5} to 10^{-4} M (Fig. 1 and Table 4). Half esters of sulphuric acid as in **17** represent a rare but characteristic structural group in constituents of higher plants, and are

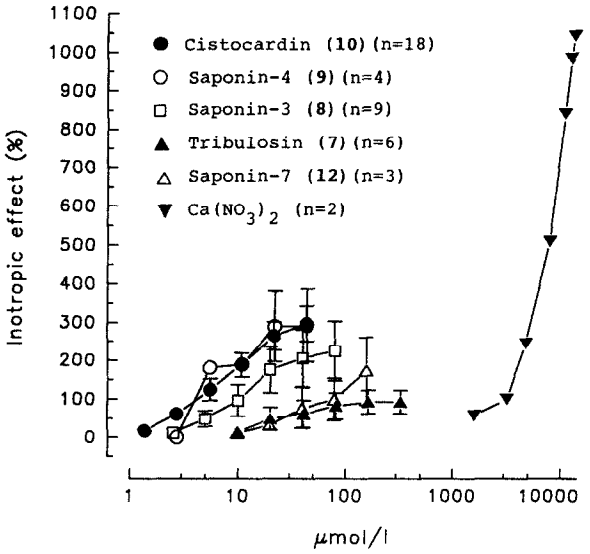


Fig. 1. Positive inotropic effects on isolated cardiac muscle of constituents from *Tribulus cistoides*. (Ordinate scale represents positive inotropic effect, expressed as per cent increase of force of contraction (ΔF_c) above control value. Symbols represent arithmetic means with s.e.)

typically present in plant hormones of the turgorin-type [31].

EXPERIMENTAL

Plant material. Plants were collected at the coast near Boca del Rio, Veracruz, Mexico, in August 1987. Identification was made at Herbario del Instituto Nacional de Investigaciones sobre Recursos Bioticos in Xalapa, Veracruz, Mexico; a voucher specimen is deposited in our institute in Erlangen under No. 88-01.

General. TLC was performed on ready-made plates (nano plates Sil-20 UV, Macherey-Nagel) using S−1 = $CHCl_3$; S−2 = $CHCl_3$–MeOH (9:1) S−3 = $CHCl_3$–MeOH–H_2O (7:4:1); S−4 = petrol–EtOH (7:3). Detection: anisaldehyde followed by heating [32] and Ehrlich reagent [33]. IR were run in KBr, if not otherwise stated. MS were recorded by EIMS (70 eV) using a direct inlet system, FABMS with glycerol as matrix (ionization gas: xenon, 8 kV). Unless otherwise stated, ^{1}H NMR were measured at 400 MHz and ^{13}C NMR at 100 MHz in pyridine-d_5 with TMS as int. standard. HPLC was done on Nucleosil® RP-18, Macherey-Nagel, if not stated otherwise.

Acetylation. The compound (1–20 mg) was dissolved in 0.5–2 ml pyridine–Ac_2O (1:1) and kept at room temp. for 15 hr. The solvents were removed by evapn and the product purified by either CC on silica gel using petrol–EtOH mixts or by HPLC using MeOH–H_2O mixts.

Total hydrolysis of glycosides. The glycoside (2 mg) was dissolved in 10 ml 2 M aq. CF_3CO_2H and refluxed for 2 hr. After evapn H_2O was added and the aglycones extracted with $CHCl_3$. The aq. phase was concd and subjected to HPLC for sugar analysis [34] {Nucleosil® 10 NH_2, Macherey-Nagel, using MeCN–H_2O (3:1)}.

Partial hydrolysis of glycosides. The glycoside (saponin) (50–150 mg) was dissolved in 50 ml 1 M H_2SO_4–MeOH (1:1) and kept at 70° for 4–8 hr under monitoring by TLC using S-3. Subsequent neutralization with 2 M NaOH and evapn of the MeOH precipitated the mixt. of prosapogenins together with the aglycone, which were filtered off and subjected to chromatographic sepn.

Extraction and chromatography. Aerial parts (1.4 kg) were extracted at room temp. successively with petrol yielding 9 g petrol extract (= PE extract) and then with MeOH. The MeOH extract (200 g) was redissolved in

Table 2. ^{13}C NMR data of the isolated saponins **6–14** (δ[ppm] in pyridine-d_5)

C	6	7	8	9	10	11	12	13	14
1	37.1	37.3	36.7	37.1	45.6	37.2	36.6	45.6	37.1
2	29.9	30.0	29.7	29.9	72.5	30.0	29.6	72.5	29.9
3	78.7	78.8	78.8	78.6	84.2	78.8	79.1	84.2	78.7
4	34.8	34.4	34.2	34.8	34.1	34.9	34.1	34.1	34.3[c]
5	44.6	44.7	44.4	44.6	44.6	44.7	44.3	44.6	44.6
6	28.9	29.0	28.6	28.9	28.1	29.0	28.6	28.1	28.9
7	32.1[b]	32.1[b]	31.4[b]	32.1[b]	32.1[b]	32.1[b]	31.4[b]	32.1[b]	32.1[b]
8	35.2	35.3	34.4	35.2	34.6	35.3	34.3	34.6	35.2
9	54.3	54.4	55.3	54.3	54.4	54.5	55.3	54.3	54.4
10	35.8	36.0	36.4	35.8	36.9	35.8	36.3	36.9	35.9
11	21.2	21.3	38.0	21.2	21.4	21.3	37.9	21.4	21.1
12	40.1	40.2	212.8	40.1	40.0	40.2	212.8	40.0	39.9
13	40.7	40.8	55.5	40.7	40.7	40.8	55.5	40.7	41.1
14	56.4	56.5	55.9	56.4	56.3	56.5	55.8	56.3	56.3
15	32.4[b]	32.5[b]	31.7[b]	32.4[b]	32.2[b]	32.4[b]	31.7[b]	32.2[b]	32.4[b]
16	81.2	81.2	79.8	81.2	81.2[h]	81.2	79.7	81.2[h]	81.3[i]
17	62.8	62.9	54.2	62.8	62.3[c]	62.5[c]	54.1	62.7[c]	64.3
18	16.6	16.6	16.0	16.6	16.6	16.6	16.0	16.6	16.3[a]
19	12.3	12.5	11.8	12.3	13.4	12.3	11.8	13.4	12.3

Table 2. *Continued*

C	6	7	8	9	10	11	12	13	14
20	42.4	42.5	43.1	42.4	42.5	42.5	43.1	42.5	40.4
21	14.9	14.9	13.8	14.8	14.8	14.9	13.7	14.9	16.4[a]
22	109.7	109.7	109.7	109.7	109.7	109.7	109.7	109.7	112.6
23	27.5	27.6	27.5	27.5	27.5	27.6	27.5	27.5	30.9
24	26.2[a]	26.2[a]	26.2[a]	26.2[a]	26.2[a]	26.2[a]	26.1[a]	26.2[a]	28.1
25	26.3[a]	26.4[a]	26.4[a]	26.3[a]	26.4[a]	26.4[a]	26.3[a]	26.4[a]	34.4[c]
26	65.0	65.1	65.2	65.0	65.1	65.1	65.1	65.1	74.9
27	16.3	16.3	16.3	16.3	16.3	16.3	16.2	16.3	17.5
MeO	—	—	—	—	—	—	—	—	47.3
1′	102.8	100.2	100.1	102.4	103.3	102.5	100.0	103.3	100.0
2′	73.2	81.4[e]	81.3[g]	73.2	71.3[e]	73.2	81.3[h]	70.4[d]	81.3[i]
3′	74.9	75.8	75.9	75.5[c]	75.3[f]	75.6[f]	75.8	74.8[e]	75.8
4′	80.3	79.1	79.4	80.2	79.7	80.1[i]	79.7	79.6	79.0
5′	76.1	77.8	77.8	76.1	76.0	76.2[g]	77.7	76.1[f]	77.7
6′	60.5	60.5	60.4	60.6	60.5	60.6	60.4	60.6	60.4
1″	106.3[f]	105.8[f]	105.9[h]	104.5[e]	104.6[i]	105.0[k]	105.9	104.1[i]	105.8
2″	82.1	81.5[e]	81.5[g]	81.5	81.3[h]	81.4	81.4[h]	81.3[h]	81.4[i]
3″	86.3	87.7	87.6	88.5	88.7	88.1	88.9	88.2	87.5
4″	70.5[c]	70.4[d]	70.4[d]	71.5	71.6[e]	70.8[d]	70.8[d]	70.7[d]	70.4[e]
5″	77.2	77.1	76.6[f]	77.9[d]	77.5	77.4[h]	76.5[g]	77.5	76.9
6″	63.1	62.9	62.9	63.0	62.6[c]	62.9[c]	62.3[c]	62.8[c]	62.8
1‴	105.6[f]	105.1[f]	105.1[h]	104.9[e]	104.7[i]	105.1[k]	104.6[i]	104.7[i]	105.0
2‴	75.3[d]	75.1	75.1	75.3[c]	75.5[f]	75.4[f]	75.0[f]	75.0[e]	75.0
3‴	77.8[e]	76.7	76.7[f]	78.6	78.2[g]	77.5[h]	76.6[g]	78.5[g]	76.5[g]
4‴	70.6[c]	70.7[d]	70.7[d]	70.8	70.4[d]	70.8[d]	70.9[d]	70.8[d]	70.7[e]
5‴	67.3	67.4[c]	67.4[c]	77.3[d]	78.6[g]	77.8[h]	67.6	78.3[g]	67.3[d]
6‴	—	—	—	62.3	62.8[c]	63.1[c]	—	63.0[c]	—
1⁗	105.2[f]	105.4[j]	105.4[h]	105.1[e]	104.9[i]	104.2	105.2[i]	104.9[i]	105.0
2⁗	75.5[d]	75.1	75.1	75.3[c]	75.7[f]	74.9[e]	75.3[f]	75.5[e]	75.0
3⁗	77.9[e]	76.7	76.7[f]	78.6	78.4[g]	76.4[g]	78.6	76.4[f]	76.6[g]
4⁗	70.7[c]	70.9[d]	70.9[d]	70.8	70.8[d]	80.4[i]	71.5	80.3	70.8[e]
5⁗	67.3	67.7[c]	67.7[c]	77.5[d]	78.6[g]	76.8[g]	78.6	76.7[f]	67.6[d]
6⁗	—	—	—	62.3	63.0[c]	61.3	63.0[c]	61.2	—
1⁗′		102.0	102.0			105.5[k]	102.0	105.5	101.9
2⁗′		72.5[g]	72.5[e]			75.0[e]	72.4[e]	75.7[e]	72.4[f]
3⁗′		72.7[g]	72.7[e]			78.3	72.7[e]	78.1	72.6[f]
4⁗′		74.0	74.0			71.0[d]	74.0	71.2[d]	73.9
5⁗′		69.4	69.4			67.4	69.3	67.4	69.3
6⁗′		18.5	18.5				18.4		18.4
1⁗″									105.3
2⁗″									75.2
3⁗″									78.5[h]
4⁗″									71.7
5⁗″									78.6[h]
6⁗″									62.8

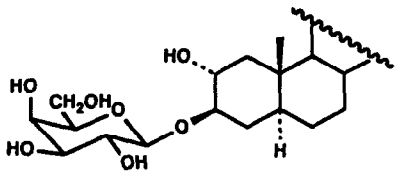
[a–k]Signals with the same letter may be interchangeable

350 ml MeOH, diluted with 700 ml H_2O and successively extracted with $CHCl_3$ (35 g residue = MeOH–$CHCl_3$ fr.) and then with *n*-BuOH (45 g residue = MeOH–BuOH fr.). The remaining aq. phase represents the MeOH–H_2O fr.

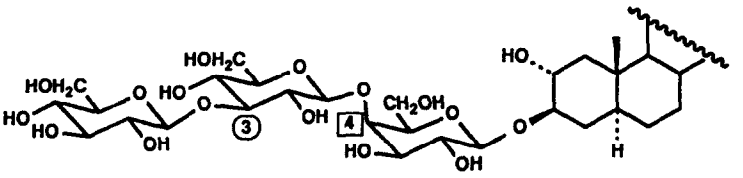
Repeated CC of the PE extract on silica gel (Macherey-Nagel) using cyclohexane–Me_2CO, $CHCl_3$–MeOH and $CHCl_3$–Me_2CO mixts yielded **1–3** besides a fr. whose sepn was achieved by HPLC using MeOH–H_2O (95:5) to yield **4** and **5**.

Repeated CC of the MeOH–$CHCl_3$ fr. on silica gel (MN 60, Macherey-Nagel) with $CHCl_3$–MeOH–H_2O mixts and subsequently HPLC on reversed phase silica gel (Nucleosil® RP-18, and LiChrosorb® RP-18, Merck, with MeOH–H_2O mixts) yielded **6–13**.

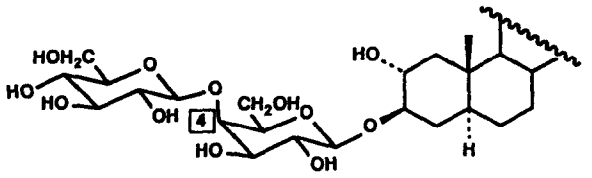
The MeOH–BuOH fr. was dissolved in 300 ml MeOH and added slowly to 3 l Me_2CO yielding a ppt. (*ca* 20 g), which was filtered off and redissolved in $CHCl_3$–MeOH–H_2O (65:45:10). CC of this soln on silica gel using $CHCl_3$–MeOH–H_2O (65:45:10) gave **14**.



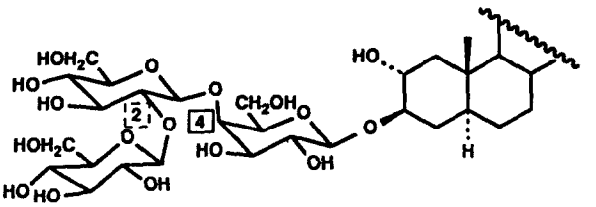
Prosapogenin **10.1**



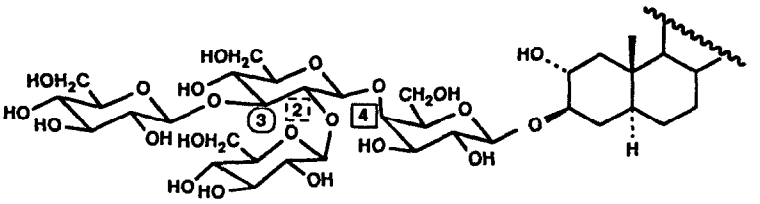
Prosapogenin **10.3**



Prosapogenin **10.2**



Prosapogenin **10.4**



Cistocardin (**10**)

Table 3. NMR shifts of the sugar protons in peracetylated cistocardin (**10**) and its prosapogenins **10.1**–**10.4** (δ[ppm] in C_6D_6)

H-Atoms	Peracetylated prosapogenins				Peracetyl-
	10.1	**10.2**	**10.3**	**10.4**	**10**
β-D-galactose					
1	4.42	4.46	4.44	4.33	4.36
2	5.64	5.40	5.38	5.69	5.70
3	5.23	5.02	5.06	4.98	5.06
4	5.52	3.89*	3.95*	3.74*	3.95*
5	3.46	3.42	3.45	3.41	3.48
$6_A/6_B$	4.15/4.23	4.40/4.48	4.43/4.47	4.43/4.45	~4.44/4.50
β-D-glucose					
1		4.58	4.59	4.24	4.43
2		5.15	~5.14	3.56†	3.97†
3		5.49	4.06‡	5.16	4.04‡
4		5.19	4.86	5.04	5.19
5		3.19	3.51	2.99	3.28
$6_A/6_B$		2 × 4.10	4.15/4.22	~4.10/4.13	2 × 4.20
β-D-glucose					
1			4.60		5.09
2			5.17		5.36
3			5.32		5.47
4			5.18		5.32
5			3.00		3.52
$6_A/6_B$			3.87/4.33		3.89/4.45
β-D-glucose					
1				4.56	5.24
2				~5.52	~5.70
3				~5.55	~5.70
4				5.86	5.87
5				3.85	4.13
$6_A/6_B$				4.67/4.76	4.71/4.78

*†‡Since not shifted by acetylation indicating the linkage.

Table 4. Positive inotropic activity* of the isolated saponins measured with the papillary muscle system [30]

Sugar moiety	Aglycone Neotigogenin (1)	Neogitogenin (2)	Neohecogenin (3)
β-D-Glc(1→3)[β-D-Glc(1→2)]β-D-Glc(1→4)β-D-Gal—	Saponin-4 (9)	Cistocardin (10)	
β-D-Glc	+++	+++	
β-Xyl(1→3)[β-Glc(1→2)]β-Gal—	Saponin-1 (6)		
β-Xyl	—		
β-Xyl(1→4)β-Glc(1→3)[β-Glc(1→2)]β-Gal—	Saponin-6 (11)	Saponin-8 (13)	
β-Glc	—	—	
β-D-Xyl(1→3)[β-D-Glc(1→2)β-D-Xyl]β-D-Gal(1→4)[α-L-Rha(1→2)]—	Tribulosin (7)		Saponin-3 (8)
	(+)		++
β-Glc(1→3)[β-Glc(1→2)β-Xyl]β-Gal(1→4)[α-Rha(1→2)]—			Saponin-7 (12)
			+

*Degree of activity: —, (+), +, ++, +++.

The MeOH–H_2O fr. was evapd and redissolved in MeOH–H_2O (1:2) and then subjected to CC on Sephadex® LH 20 with MeOH to give 2 frs. The faster fr. by CC on Sephadex® G 10 with MeOH yielded **15** and **16**. The slower fr. was sepd by MPLC on RP-18 (FC LiChroprep®, Merck with H_2O–MeOH (95:5) to give frs 1–4. Fr. 2 consisted of inorganic salts only as shown by its spectra. The result of an ion chromatographic analysis on Super Sep (Metrohm) was: Na^+ (11%), Ca^{2+} (15%), Cl^- (19%), NO_3^- (37%). HPLC of fr. 3 with H_2O–MeOH (95:5) yielded almost the same mixt of inorganic ions and **17**.

Neotigogenin (**1**). Crystals (40 mg). Mp 192–195° (lit. [4] mp 192–194°). TLC: R_f 0.26 (S-1); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −68° ($CHCl_3$; *c* 0.8) (lit. [4] $[\alpha]_D$ −65°). ^{1}H NMR: δ0.59 (1H, *ddd*, $J_1=12$, $J_2=10.5$, $J_3=4$ Hz), 0.80–2.20 (38H, *m*) within 0.82 and 0.85 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J=7$ Hz, Me-27), 1.16 (3H, *d*, $J=7$ Hz, Me-21), 3.37 (1H, *br d*, $J=11$ Hz, H-26_{ax}), 3.86 (1H, *m*, H-3), 4.07 (1H, *dd*, $J_1=11$, $J_2=3$ Hz, H-26_{eq}), 4.53 (1H, *ddd*, $J_1\sim J_2\sim 8$, $J_3=7$ Hz, H-16).

Neogitogenin (**2**). Crystals (21 mg). Mp 259–261° (lit. [14] mp 253–255°). TLC: R_f 0.26 (S-2); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −67° ($CHCl_3$; *c* 0.7) (lit. [14] $[\alpha]_D^{19}$ −66°). IR ν_{max} cm^{-1}: 3400, 2950, 990, 925, 895, 855. ^{1}H NMR: δ0.65–1.95 (34H, *m*) within 0.83 and 0.86 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J=7$ Hz, Me-27), 1.15 (3H, *d*, $J=7$ Hz, Me-21), 2.03 (1H, *ddd*, $J_1=12$, $J_2=7.5$, $J_3=5.5$ Hz), 2.14 (1H, *dddd*, $J_1\sim J_2\sim 13$, $J_3\sim J_4\sim 5$ Hz), 2.26 (1H, *dd*, $J_1=12$, $J_2=4.5$ Hz), 3.37 (1H, *br d*, $J=11$ Hz, H-26_{ax}), 3.86 (1H, *ddd*, $J_1=11$, $J_2=9$, $J_3=5$ Hz), [H-2 or H-3], 4.01–4.09 (2H, *m*) [H-3 or H-2 and H-26_{eq}], 4.53 (1H, *ddd*, $J_1\sim J_2\sim 8$, $J_3=7$ Hz, H-16). ^{13}C NMR (90 MHz): δ13.7 (C-19), 14.9 (C-21), 16.3 (C-27), 16.7 (C-18), 21.6 (C-11), 26.2 (C-24 or C-25), 26.4 (C-25 or C-24), 27.6 (C-23), 28.4 (C-6), 32.1 (C-7 or C-15), 32.4 (C-15 or C-7), 34.7 (C-8), 37.2 (C-4), 37.6 (C-10), 40.2 (C-12), 40.8 (C-13), 42.5 (C-20), 45.3 (C-1), 46.5 (C-5), 54.7 (C-9), 56.4 (C-14), 62.9 (C-17), 65.1 (C-26), 73.1 (C-2), 76.7 (C-3), 81.2 (C-16), 109.7 (C-22). EIMS *m/z* (rel. int.): 432 $[M]^+$ (5), 373 (2), 363 (5), 360 (10), 318 (19), 303 (15), 289 (38), 140 (12), 139 (100), 122 (9), 115 (26), 69 (18).

Neohecogenin (= *sisalagenin*) (**3**). Crystals (39 mg). Mp 240–243° (lit. [4] mp 245–246°). TLC: R_f 0.55 (S-2); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −3° ($CHCl_3$; *c* 1.1) (lit. [4] $[\alpha]_D$ −4.5°). ^{1}H NMR (360 MHz): δ0.70–2.19 (34H, *m*) within 0.83 (3H, *s*, Me-18), 1.08 (3H, *d*, $J=7$ Hz, Me-27), 1.11 (3H, *s*, Me-19), 1.38 (3H, *d*, $J=7$Hz, Me-21), 2.31 (1H, *dd*, $J_1=14$, $J_2=5$ Hz, H-11_{eq}), 2.45 (1H, *dd*, $J_1\sim J_2\sim 14$ Hz, H-11_{ax}), 2.76 (1H, *dd*, $J_1=9$, $J_2=7$ Hz, H-17), 3.37 (1H, *br d*, $J=11$ Hz, H-26_{ax}), 3.76–3.86 (1H, *m*, H-3), 4.05 (1H, *dd*, $J_1=11$, $J_2=3$ Hz, H-26_{eq}), 4.47 (1H, *ddd*, $J_1\sim J_2\sim 8$, $J_3=7$ Hz, H-16). ^{13}C NMR (90 MHz): δ12.0 (C-19), 13.6 (C-21), 16.1 (C-18 or C-27), 16.3 (C-27 or C-18), 26.3 (C-24 or C-25), 26.6 (C-25 or C-24), 27.6 (C-23), 28.8 (C-6), 31.5 (C-2), 31.9 (C-7 or C-15), 32.2 (C-15 or C-7), 34.7 (C-8), 36.5 (C-10), 37.1 (C-1), 38.1 (C-11), 39.1 (C-4), 43.3 (C-20), 45.2 (C-5), 54.4 (C-17), 55.5 (C-13), 56.0 (C-9 or C-14), 56.2 (C-14 or C-9), 65.3 (C-26), 70.4 (C-3), 79.9 (C-16), 109.8 (C-22), 212.4 (C-12).

N-Docosanoyltyramine (**4**). Crystals from $CHCl_3$ (3 mg). Mp 109–112°. TLC: R_f 0.53 (S-2); anisaldehyde: pink. IR ν_{max} cm^{-1}: 3400, 2920, 2850, 2465, 1625. UV λ_{max}^{EtOH} nm (log ε): 223 (4.02), 278 (3.32); +NaOH: 241 (4.26), 294 (3.71). ^{1}H NMR [$CDCl_3$–CD_3OD (1:1)]: δ0.89 (3H, *t*, $J=7$ Hz, Me-22), 1.26 (36H, *br s*, H-4 to H-21), 1.54–1.61 (2H, *m*, H-3), 2.14 (2H, *t*, $J=7.5$ Hz, H-2), 2.71 (2H, *t*, $J=7.5$ Hz, H-2′), 3.39 (2H, *t*, $J=7.5$ Hz, H-1′), 6.75 (2H, AA′BB′-system, H-5′ and H-7′), 7.04 (2H, AA′BB′-system, H-4′ and H-8′). ^{13}C NMR [$CDCl_3$–CD_3OD (1:1); 62.9 MHz]: δ14.0 (C-22), 22.9 (C-21), 26.2 (C-3), 29.6, 29.8, 29.9, 32.2 (C-20), 35.1 (C-2′),

36.9 (C-2), 41.3 (C-1'), 2 × 115.8 (C-4' and C-8'), 2 × 130.0 (C-5' and C-7'), 130.5 (C-3'), 155.9 (C-6'), 174.8 (C-1). DCIMS (isobutane) *m/z* (rel. int.): 460 $[M+H]^+$ (100); EIMS *m/z* (rel. int.) : 340 (13), 121 (10), 120 (100).

N-Tetracosanoyltyramine (**5**). Crystals from $CHCl_3$ (8 mg). Mp 111–114°. TLC: R_f 0.54 (S-2); anisaldehyde: pink. IR and UV identical with **4**. ^1H NMR [$CDCl_3$–CD_3OD (1:1)]: identical with **4** except for the assignments of the signals at δ0.89 (3H, *t*, *J* = 7 Hz, Me-24) and 1.26 (40H, *br s*, H-4 to H-23). ^{13}C NMR [$CDCl_3$–CD_3OD (1:1); 22.5 MHz] is identical with **4** except for the assignments of δ14.0 (C-24), 22.9 (C-23) and 32.2 (C-22), DCIMS (isobutane) *m/z* (rel. int.): 488 $[M+H]^+$ (100); EIMS *m/z* (rel. int.): 368.3900 (10) [calcd for $C_{24}H_{50}NO$: 368.3892], 120.0575 (100) [calcd for C_8H_8O: 120.0575].

Saponin-1 (= 3-O-[β-*xylopyranosyl*-(1→2)-[β-*xylopyranosyl*-(1→3)]-β-*glucopyranosyl*-(1→4)-β-*galactopyranosyl*]-*neotigogenin*) (**6**). Crystals from MeOH (45 mg). Mp 272–274°. TLC: R_f 0.51 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −47° (pyridine; *c* 1.0). (Found: C, 53.22; H, 8.42. Calcd for $C_{49}H_{80}O_{21} \cdot 5H_2O$: C, 53.74; H, 8.28%.) IR ν_{max} cm^{-1}: 3400, 2930, 990, 920, 895, 850. ^1H NMR: δ0.46–0.55 (1H, *m*), 0.63–2.19 (38H, various *m*) within 0.65 and 0.82 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, *J* = 7 Hz, Me-27), 1.16 (3H, *d*, *J* = 7 Hz, Me-21), 3.37 (1H, *br d*, *J* = 11 Hz), 3.67–4.26 (17H, *m*), 4.33–4.62 (6H, *m*), 4.76 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz), 4.89 (1H, *d*, *J* = 7.5 Hz), 5.17 (1H, *d*, *J* = 7.5 Hz) overlapped with 5.18 (1H, *d*, *J* = 7.5 Hz) and 5.28 (1H, *d*, *J* = 8 Hz) [4 anomeric protons]. Negative ions FABMS *m/z* (rel. int.): 1003 $[M-H]^-$ (14), 871 $[M-132-H]^-$ (7), 577 $[M-426-H]^-$ (13), 551 (27) and 459 (100) [both matrix peaks].

Peracetylsaponin-1(= *peracetyl*-**6**). Compound **6** (18 mg) was acetylated and purified by HPLC [MeOH–H_2O (9:1)] to yield 17 mg amorphous peracetyl-**6**. TLC: R_f 0.40 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −56° ($CHCl_3$; *c* 1.6). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750. ^1H NMR (C_6D_6): δ0.42–2.25 (72H, *m*) within 0.71 and 0.81 (3H each, *s*) [Me-18 and Me-19], 1.07 (3H, *d*, *J* = 7 Hz, Me-27), 1.21 (3H, *d*, *J* = 7 Hz, Me-21), 1.60, 1.65, 1.69, 1.76, 1.81, 1.82, 1.86, 1.96, 2.02, 2.06 and 2.18 (3H each, *s*, Ac), 3.03 (1H, *m*, H-5''), 3.34 (1H, *br d*, *J* = 11 Hz, H-26_{ax}), 3.48 (1H, *br dd*, $J_1 = 7$, $J_2 = 5$ Hz, H-5'), 3.53 (1H, *dd*, $J_1 = 12$, $J_2 = 4$ Hz, H-$5'''_A$), 3.58–3.70 (3H, *m*, H-3, H-2'' and H-$5'''_{ax}$), 3.96 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-3''), 4.01 (1H, *br d*, *J* = 3 Hz, H-4'), 4.06–4.14 (3H, *m*, H-$6''_A$, H-$5'''_B$ and H-26_{eq}) overlapped with 4.16 (1H, *dd*, $J_1 = 12.5$, $J_2 = 4$ Hz, H-$6''_B$), 4.34 (1H, *d*, *J* = 7.5 Hz, H-1''), 4.44–4.49 (2H, *m*, H-1' and H-$6'_A$) overlapped with 4.51 (1H, *dd*, $J_1 = 12$, $J_2 = 7$ Hz, H-$6'_B$), 4.60 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 6.5$ Hz, H-16), 4.71 (1H, *dd*, $J_1 = 11.5$, $J_2 = 5$ Hz, H-$5'''_{eq}$), 4.81 (1H, *ddd*, $J_1 \sim J_2 \sim 4$, $J_3 = 3$ Hz, H-4''''), 5.05–5.09 (2H, *m*, H-3' and H-1''') overlapped with 5.10 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4''), 5.17 (1H, *dd*, $J_1 = 4$, $J_2 = 2.5$ Hz, H-2''''), 5.29 (1H, *dd*, $J_1 \sim J_2 \sim 4$ Hz, H-3''''), 5.44 (1H, *d*, *J* = 2.5 Hz, H-1''''), 5.60 (1H, *dd*, $J_1 = 8.5$, $J_2 = 7$ Hz, H-2'''), 5.66 (1H, *dd*, $J_1 \sim J_2 \sim 8.5$ Hz, H-3'''), 5.77–5.86 (2H, *m*, H-4''' and H-2'). ^{13}C NMR (C_6D_6; 90 MHz): δ12.3 (C-19), 14.9 (C-21), 16.3 (C-27), 16.7 (C-18), 2 × 20.3, 4 × 20.4, 4 × 20.6 and 20.9 (all MeCO), 21.3 (C-11), 26.3 (C-24 or C-25), 26.5 (C-25 or C-24), 27.6 (C-23), 29.1 (C-6), 29.8 (C-2), 32.2 (C-7 or C-15), 32.5 (C-15 or C-7), 35.2 (C-4, C-8 or C-10), 35.3 (C-8, C-10 or C-4), 35.8 (C-10, C-4 or C-8), 37.3 (C-1), 40.3 (C-12), 40.8 (C-13), 42.6 (C-20), 45.0 (C-5), 54.6 (C-9), 56.6 (C-14), 58.6 (C-5''''), 62.0 (C-6''), 62.8 (C-17 or C-5'''), 63.1 (C-5''' or C-17), 64.3 (C-6'), 65.1 (C-26), 67.4 (C-4''''), 67.9 (C-3''''), 68.2 (C-2''''), 68.6 (C-4''), 69.3 (C-4'''), 70.8 (C-2'), 71.8 (C-5', C-5'' or C-3'''), 72.0 (C-5'', C-3''' or C-5'), 72.3 (C-3''', C-5' or C-5''), 72.9 (C-4' or C-2'''), 73.2 (C-2''' or C-4'), 74.1 (C-3'), 76.7 (C-3''), 79.0 (C-3), 79.9 (C-2''), 81.2 (C-16), 96.8 (C-1''''), 100.1 (C-1'''), 100.3 (C-1'), 101.4 (C-1''), 109.6 (C-22), 168.8, 3 × 169.1, 2 × 169.4, 2 × 169.8, 170.1, 170.4 and 170.5 (all MeCO).

Total hydrolysis of **6**. Total hydrolysis of **6** (1.7 mg) gave **1** as the aglycone (TLC). HPLC analysis of the aq. phase showed xylose, glucose and galactose in a 2:1:1 ratio.

Partial hydrolysis of **6**. Partial hydrolysis of **6** (16 mg) and subsequent CC on silica gel [$CHCl_3$–MeOH (9:1)] yielded prosapogenin-1.1 (1 mg).

Prosapogenin-1.1. Amorphous (1 mg). TLC: R_f 0.78 (S-3); anisaldehyde: yellow-green.

Peracetylprosapogenin-1.1. Acetylation of prosapogenin-1.1 (1 mg) yielded its peracetyl derivative [amorphous (1 mg)]. TLC: R_f 0.62 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −19° ($CHCl_3$; *c* 0.1). IR and ^1H NMR are identical with peracetylprotribulosin-1.

Tribulosin (= 3-O-[β-D-*xylopyranosyl*-(1→2)-[β-D-*xylopyranosyl*-(1→3)]-β-D-*glucopyranosyl*-(1→4)-[α-L-*rhamnopyranosyl*-(1→2)]-β-D-*galactopyranosyl*]-*neotigogenin*)(**7**) [4]. Crystals from MeOH (650 mg). Mp 273–276° (lit. [4] mp > 300°). TLC: R_f 0.37 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −66° (pyridine; *c* 1.2) [lit. [4] $[\alpha]_D$ −61° (pyridine)]. (Found: C, 52.26; H, 8.18. Calcd for $C_{55}H_{90}O_{25} \cdot 6H_2O$: C, 52.46; H, 8.16%.) ^1H NMR (360 MHz): δ0.46–0.55 (1H, *m*), 0.68–2.18 (41H, *m*) within 0.81 and 0.86 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, *J* = 7 Hz, Me-27), 1.15 (3H, *d*, *J* = 7 Hz, Me-21), 1.72 (3H, *d*, *J* = 6.5 Hz, Me-6''''), 3.37 (1H, *br d*, *J* = 11 Hz), 3.49 and 3.68 (1H each, *dd*, $J_1 \sim J_2 \sim 10$ Hz), 3.80–4.32 (17H, *m*), 4.46–5.02 (12H, *m*) within 4.86 and 5.00 (1H each, *d*, *J* = 8 Hz), 5.25 and 5.44 (1H each, *d*, *J* = 8 Hz), 6.20 (1H, *br s*) [5 anomeric protons]. Negative ions FABMS *m/z* (rel. int.): 1150 $[M]^-$ (10), 1149 $[M-H]^-$ (20), 1017 $[M-132-H]^-$ (10), 723 $[M-426-H]^-$ (5), 459 [glycerine–peak] (100).

Peracetyltribulosin (= *peracetyl*-**7**). Compound **7** (21 mg) was acetylated and purified by CC [petrol–EtOH (75:25)] to give 11 mg of peracetyltribulosin, amorphous. TLC: R_f 0.40 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −48° ($CHCl_3$; *c* 0.9). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1745. ^1H NMR (C_6D_6): δ from 0.46–0.55 (1H, *m*), 0.75–1.10 (9H, *m*) within 0.83 and 0.85 (3H each, *s*) [Me-18 and Me-19] and 1.08 (3H, *d*, *J* = 7 Hz, Me-27), 1.18–2.10 (67H, *m*) within 1.22 (3H, *d*, *J* = 7 Hz, Me-21), 1.47 (3H, *d*, *J* = 6 Hz, Me-6''''), 1.64, 1.65, 1.69, 1.71, 1.75, 1.78, 1.81, 1.84, 1.96, 1.97, 1.99 and 2.02 (3H each, *s*, Ac), 2.15–2.26 (1H, *m*), 2.49 (3H, *s*, Ac), 2.97 (1H, *ddd*, $J_1 = 9.5$, $J_2 = 4.5$, $J_3 = 3$ Hz, H-5''), 3.35 (1H, *br d*, *J* = 11 Hz, H-26_{ax}), 3.47–3.53 (2H, *m*, H-5' and H-$5'''_A$), 3.58 (1H, *dd*, $J_1 = 11.5$, $J_2 = 9$ Hz, H-$5'''_{ax}$)

overlapped with 3.62 (1H, *dd*, $J_1 = 9.5$, $J_2 = 8$ Hz, H-2''), 3.72–3.80 (1H, *m*, H-3), 3.93 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3''), 4.06 (1H, *dd*, $J_1 = 12$, $J_2 = 3$ Hz, H-$6''_A$), 4.09 (1H, *dd*, $J_1 = 13$, $J_2 = 3$ Hz, H-$5'''_B$), 4.12 (1H, *dd*, $J_1 = 11$, $J_2 = 3$ Hz, H-26_{eq}), 4.16 (1H, *dd*, $J_1 = 12$, $J_2 = 4.5$ Hz, H-$6''_B$), 4.21 (1H, *br d*, $J = 3$ Hz, H-4'), 4.25 (1H, *d*, $J = 8$ Hz, H-1''), 4.33 (1H, *d*, $J = 7$ Hz, H-1'), 4.40–4.47 (3H, *m*, H-2', H-$6'_A$ and -$5'''_{eq}$), 4.51 (1H, *dd*, $J_1 = 12$, $J_2 = 7$ Hz, H-$6'_B$), 4.62 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 6.5$ Hz, H-16), 4.81–4.88 (2H, *m*, H-4'''' and H-5''''), 4.99 (1H, *d*, $J = 7$ Hz, H-1''') overlapped with 5.01 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3'), 5.09 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-4''), 5.15 (1H, *dd*, $J_1 = 4$, $J_2 = 3$ Hz, H-2''''), 5.26 (1H, *dd*, $J_1 = 9$, $J_2 = 7$ Hz, H-2'''), 5.29 (1H, *dd*, $J_1 \sim J_2 \sim 4$ Hz, H-3''''), 5.34 (1H, *d*, $J = 3$ Hz, H-1''''), 5.39 (1H, *ddd*, $J_1 \sim J_2 \sim 9$, $J_3 = 5.5$ Hz, H-4''), 5.55–5.59 (3H, *m*, H-3''', H-1''''' and H-2'''''), 5.66 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4'''''), 5.87 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3'''''). ^{13}C NMR (C_6D_6; 90 MHz): δ12.3 (C-19), 14.9 (C-21), 16.3 (C-27), 16.7 (C-18), 17.6 (C-6''''''), 4 × 20.3, 2 × 20.4, 3 × 20.5, 3 × 20.6 and 21.0 (all MeCO), 21.4 (C-11), 26.3 (C-24 or C-25), 26.5 (C-25 or C-24), 27.6 (C-23), 29.1 (C-6), 29.9 (C-2), 32.2 (C-7 or C-15), 32.5 (C-15 or C-7), 34.6 (C-4), 35.4 (C-8 or C-10), 35.9 (C-10 or C-8), 37.3 (C-1), 40.3 (C-12), 40.8 (C-13), 42.6 (C-20), 44.8 (C-5), 54.5 (C-9), 56.6 (C-14), 59.0 (C-5''''''), 61.9 (C-6''), 63.0 (C-5''' or C-17), 63.1 (C-17 or C-5'''), 64.5 (C-6'), 65.1 (C-26), 67.0 (C-5''''''), 67.6 (C-3''''), 68.1 (C-4'', C-2'''' or C-4''''), 68.5 (C-2'''', C-4'''' or C-4''), 68.6 (C-4'''', C-4'' or C-2''''), 69.3 (C-4''' or C-3''''), 69.5 (C-3'''' or C-4'''), 71.2 (C-2''''''), 2 × 71.8 (C-5', C-5'', C-2''' or C-4''''''), 72.2 (C-2''', C-4'''', C-5' or C-5''), 72.3 (C-4'''', C-5', C-5'' or C-2'''), 73.1 (C-3'''), 73.7 (C-2' or C-4'), 74.0 (C-4' or C-2'), 76.7 (C-3'), 77.3 (C-3''), 77.7 (C-3), 80.1 (C-2''), 81.2 (C-16), 97.1 (C-1''''), 97.9 (C-1''''''), 99.4 (C-1'), 100.2 (C-1'''), 101.7 (C-1''), 109.6 (C-22), 168.9, 169.0, 169.1, 169.3, 169.4, 169.5, 169.6, 169.8, 2 × 169.9, 2 × 170.4 and 171.1 (all MeCO).

Total hydrolysis of **7**. Compound **7** (19 mg) was hydrolysed and the reaction mixt. worked-up as described. HPLC analysis [34] of the aq. phase afforded xylose, galactose, glucose and rhamnose in a 2:1:1:1 ratio; in the organic phase **1** was identified as the aglycone. Total hydrolysis with MeOH–2 M HCl (gas) yielded the methyl glycosides. The mixt. of methyl glycosides was derivatized and subjected to GC-analysis according to König *et al.* [22].

Partial hydrolysis of **7**. The reaction mixt. of 150 mg **7** was worked-up as described above. Repeated CC on Sephadex® LH 20 with MeOH and then on silica gel with $CHCl_3$–MeOH (9:1) yielded the aglycone **1** (9 mg) and the protribulosins-1 (5 mg) and -2 (22 mg), besides a further fr. of protribulosins. This mixt. was sepd by HPLC [RP-18; MeOH–H_2O (8:2)] into 3 crude protribulosins, which were finally purified after acetylation by CC [silica gel; petrol–EtOH (75:25)] to afford peracetylprotribulosin-3 (3 mg) and -4 (3.5 mg), and by HPLC [RP-18; MeOH–H_2O (9:1)] to afford in addition peracetylprotribulosin-5 (4 mg).

Protribulosin-1. Amorphous (5 mg). TLC: R_f 0.78 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −30° (MeOH; *c* 0.1). IR ν_{max} cm^{-1}: 3400, 2930, 990, 920, 895, 850. ^{1}H NMR: δ0.46–0.55 (1H, *m*), from 0.65–2.19 (38H, *m*) within 0.67 and 0.83 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.16 (3H, *d*, $J = 7$ Hz, Me-21), 3.37 (1H, *br d*, $J = 11$ Hz, H-26_{ax}), 3.96–4.05 (1H, *m*, H-3), 4.07 (1H, *dd*, $J_1 = 11$, $J_2 = 3$ Hz, H-26_{eq}), 4.18 (1H, *br dd*, $J_1 \sim J_2 \sim 6$ Hz, H-5'), 4.26 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3'), 4.47–4.57 (4H, *m*) [H-16, H-2', H-$6'_A$ and H-$6'_B$], 4.63 (1H, *br d*, $J = 3$ Hz, H-4'), 4.95–5.08 (*br s*, HOD-signal) overlapped with signal of the anomeric proton.

Peracetylprotribulosin-1. Acetylation of 3 mg protribulosin-1 gave peracetylprotribulosin-1 (amorphous, 3 mg). TLC: R_f 0.62 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −14° ($CHCl_3$; *c* 0.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750. ^{1}H NMR (C_6D_6; 360 MHz): δ0.40–2.25 (51H, *m*) within 0.62 and 0.81 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.22 (3H, *d*, $J = 7$ Hz, Me-21), 1.56, 1.64, 1.76 and 1.79 (3H each, *s*, Ac), 3.35 (1H, *br d*, J = 11 Hz, H-26_{ax}), 3.48 (1H, *ddd*, $J_1 \sim J_2 \sim 6.5$, $J_3 = 1$ Hz, H-5'), 3.56–3.65 (1H, *m*, H-3), 4.12 (1H, *dd*, $J_1 = 11$, $J_2 = 3$ Hz, H-26_{eq}), 4.18 (1H, *dd*, $J_1 = 11$, $J_2 = 6.5$ Hz, H-$6'_A$) overlapped with 4.21 (1H, *dd*, $J_1 = 11$, $J_2 = 6.5$ Hz, H-$6'_B$), 4.46 (1H, *d*, $J = 8$ Hz, H-1'), 4.61 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 6.5$ Hz, H-16), 5.24 (1H, *dd*, $J_1 = 10$, $J_2 = 3.5$ Hz, H-3'), 5.54 (1H, *dd*, $J_1 = 3.5$, $J_2 = 1$ Hz, H-4'), 5.69 (1H, *dd*, $J_1 = 10$, $J_2 = 8$ Hz, H-2').

Protribulosin-2. Amorphous (22 mg). TLC: R_f 0.65 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −36° (MeOH; *c* 1.1). IR ν_{max} cm^{-1}: 3400, 2930, 990, 920, 895, 850. ^{1}H NMR: δ0.46–0.55 (1H, *m*), 0.62–2.20 (38H, *m*) within 0.65 and 0.82 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.16 (3H, *d*, $J = 7$ Hz, Me-21), 3.37 (1H, *br d*, $J = 11$ Hz), 3.90–4.36 (10H, *m*), 4.43 (1H, *dd*, $J_1 \sim J_2 \sim 9$ Hz), 4.53 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 7$ Hz), 4.61–4.77 (3H, *m*), 4.91 and 5.33 (1H each, *d*, $J = 8$ Hz) [2 anomeric protons]. ^{13}C NMR: δ12.3 (C-19), 14.9 (C-21), 16.3 (C-27), 16.6 (C-18), 21.3 (C-11), 26.2 (C-24 or C-25), 26.4 (C-25 or C-24), 27.5 (C-23), 28.9 (C-6), 30.0 (C-2), 32.1 (C-7 or C-15), 32.4 (C-15 or C-7), 34.8 (C-4), 35.2 (C-8), 35.8 (C-10), 37.2 (C-1), 40.1 (C-12), 40.7 (C-13), 42.4 (C-20), 44.6 (C-5), 54.4 (C-9), 56.4 (C-14), 61.0 (C-6'), 62.8 (C-17), 63.1 (C-6''), 65.1 (C-26), 72.3 (C-4''), 73.5 (C-2'), 75.2 (C-2'' or C-3'), 75.5 (C-3' or C-2''), 76.0 (C-5'), 77.1 (C-3), 78.5 (C-3'' or C-5''), 78.7 (C-5'' or C-3''), 80.1 (C-4'), 81.2 (C-16), 102.5 (C-1'), 107.2 (C-1''), 109.7 (C-22).

Acetylation of protribulosin-2. Acetylation of protribulosin-2 (4 mg) gave 5 mg of peracetylprotribulosin-2, amorphous. TLC: R_f 0.50 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −28° ($CHCl_3$; *c* 0.5). IR and ^{1}H NMR identical with peracetylprosapogenin-6.1.

Peracetylprotribulosin-3. Amorphous (3 mg). TLC: R_f 0.44 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −22° ($CHCl_3$; *c* 0.2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750. ^{1}H NMR (C_6D_6): δ0.40–2.25 (69H, *m*) within 0.81 and 0.85 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.22 (3H, *d*, $J = 7$ Hz, Me-21), 1.40 (3H, *d*, $J = 6$ Hz, Me-6''''''), 1.60, 1.64, 1.66, 1.69, 1.73, 1.79, 1.85, 2.06 and 2.23 (3H each, *s*, Ac), 3.07 (1H, *ddd*, $J_1 = 10$, $J_2 = 4$, $J_3 = 3$ Hz, H-5''), 3.35 (1H, *br d*, $J = 11$ Hz, H-26_{ax}), 3.51 (1H, *br dd*, $J_1 = 7$, $J_2 = 4.5$ Hz, H-5'), 3.70–3.79 (1H, *m*, H-3), 4.05 (1H, *dd*, $J_1 = 13$, $J_2 = 3$ Hz, H-$6''_A$), 4.09–4.15 (3H, *m*, H-26_{eq}, H-4' and H-$6''_B$), 4.19 (1H, *dd*, $J_1 = 10$, $J_2 = 7.5$ Hz, H-2'), 4.34 (1H, *d*, $J = 7.5$ Hz, H-1'), 4.41 (1H,

dd, $J_1 = 11.5$, $J_2 = 7$ Hz, H-6′$_A$), 4.48 (1H, *d*, $J = 8$ Hz, H-1″) overlapped with 4.50 (1H, *dd*, $J_1 = 11.5$, $J_2 = 4.5$ Hz, H-6′$_B$), 4.61 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 6.5$ Hz, H-16), 4.79 (1H, *dq*, $J_1 = 10$, $J_2 = 6$ Hz, H-5‴″), 5.03 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3′), 5.10 (1H, *dd*, $J_1 = 10$, $J_2 = 8$ Hz, H-2″), 5.16 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4″), 5.43 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-3″) overlapped with 5.44 (1H, *dd*, $J_1 = 3$, $J_2 = 2$ Hz, H-2‴″) and 5.46 (1H, *d*, $J = 2$ Hz, H-1‴″), 5.63 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4‴″), 5.81 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3‴″).

Peracetylprotribulosin-4. Amorphous (3.5 mg). TLC: R_f 0.52 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −21° ($CHCl_3$; *c* 0.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750. ^1H NMR (C_6D_6): δ0.40–2.26 (66H, *m*) within 0.66 and 0.81 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.21 (3H, *d*, $J = 7$ Hz, Me-21), 1.63, 1.70, 1.72, 1.74, 1.76, 1.82, 1.92, 1.95 and 2.24 (3H each, *s*, Ac), 2.95 (1H, *ddd*, $J_1 = 9.5$, $J_2 = 4$, $J_3 = 2.5$ Hz, H-5″), 3.27 (1H, *dd*, $J_1 = 11.5$, $J_2 = 9.5$ Hz, H-5‴$_{ax}$), 3.34 (1H, *br d*, $J = 11$ Hz, H-26$_{ax}$), 3.46 (1H, *br dd*, $J_1 \sim J_2 \sim 6$ Hz, H-5′), 3.54 (1H, *dd*, $J_1 = 9.5$, $J_2 = 8$ Hz, H-2″), 3.56–3.65 (1H, *m*, H-3), 3.90 (1H, *br d*, $J = 3$ Hz, H-4′), 4.09 (1H, *dd*, $J_1 = 12.5$, $J_2 = 2.5$ Hz, H-6″$_A$) overlapped with 4.12 (1H, *dd*, $J_1 = 11$, $J_2 = 3$ Hz, H-26$_{eq}$) overlapped with 4.16 (1H, *dd*, $J_1 = 12.5$, $J_2 = 4$ Hz, H-6″$_B$), 4.22 (1H, *d*, $J = 8$ Hz, H-1‴), 4.42 (1H, *d*, $J = 8$ Hz, H-1′), 4.44–4.53 (3H, *m*, H-1‴, H-6′$_A$ and H-6′$_B$), 4.56–4.63 (2H, *m*, H-16 and H-5‴$_{eq}$), 5.01 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3′), 5.14 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-4″), 5.21 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3″), 5.42 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3‴), 5.48 (1H, *dd*, $J_1 = 9.5$, $J_2 = 7.5$ Hz, H-2‴), 5.80 (1H, *ddd*, $J_1 \sim J_2 \sim 9.5$, $J_3 = 5.5$ Hz, H-4‴), 5.87 (1H, *dd*, $J_1 = 10$, $J_2 = 8$ Hz, H-2′).

Peracetylprotribulosin-5. Amorphous (4 mg). TLC: R_f 0.46 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −19° ($CHCl_3$; *c* 0.4). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2945, 1750. ^1H NMR (C_6D_6): δ0.44–2.27 (75H, *m*) within 0.81 and 0.85 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.22 (3H, *d*, $J = 7$ Hz, Me-21), 1.48 (3H, *d*, $J = 6$ Hz, Me-6‴″), 1.65, 1.66, 1.70, 1.72, 1.73, 1.76, 1.81, 1.91, 1.93, 2.16 and 2.57 (3H each, *s*, Ac), 2.83 (1H, *ddd*, $J_1 = 10$, $J_2 = 3.5$, $J_3 = 2.5$ Hz, H-5″), 3.14 (1H, *dd*, $J_1 = 12$, $J_2 = 9.5$ Hz, H-5‴$_{ax}$), 3.35 (1H, *br d*, $J = 11$ Hz, H-26$_{ax}$), 3.43 (1H, *dd*, $J_1 = 9.5$, $J_2 = 8$ Hz, H-2″), 3.50 (1H, *br dd*, $J_1 = 7$, $J_2 = 5$ Hz, H-5′), 3.70–3.80 (1H, *m*, H-3), 4.02–4.07 (2H, *m*, H-6″$_A$ and H-4′), 4.10–4.15 (1H, *m*, H-26$_{eq}$) overlapped with 4.13 (1H, *d*, $J = 8$ Hz, H-1‴), 4.18 (1H, *dd*, $J_1 = 12.5$, $J_2 = 3.5$ Hz, H-6″$_B$), 4.34 (1H, *d*, $J = 8$ Hz, H-1′) overlapped with 4.34–4.39 (1H, *m*, H-5‴$_{eq}$) overlapped with 4.39 (1H, *d*, $J = 8$ Hz, H-1‴) overlapped with 4.42 (1H, *dd*, $J_1 = 11.5$, $J_2 = 5$ Hz, H-6′$_A$), 4.50 (1H, *dd*, $J_1 = 11.5$, $J_2 = 7$ Hz, H-6′$_B$) overlapped with 4.51 (1H, *dd*, $J_1 = 10$, $J_2 = 8$ Hz, H-2′), 4.62 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 6.5$ Hz, H-16), 4.86 (1H, *dq*, $J_1 = 10$, $J_2 = 6$ Hz, H-5‴″), 4.93 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3′), 5.07–5.15 (2H, *m*, H-3″ and H-4″) overlapped with 5.16 (1H, *dd*, $J_1 = 9.5$, $J_2 = 8$ Hz, H-2‴), 5.28 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3‴), 5.38 (1H, *ddd*, $J_1 \sim J_2 \sim 9.5$, $J_3 = 6$ Hz, H-4‴), 5.57–5.60 (2H, *m*, H-1‴″ and H-2‴″), 5.70 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4‴″), 5.89 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3‴″).

Saponin-3(= 3-O-[β-D-*xylopyranosyl*-(1→2)-[β-D-*xylopyranosyl*-(1→3)]-β-D-*glucopyranosyl*-(1→4)-[α-L-*rhamnopyranosyl*-(1→2)]-β-D-*galactopyranosyl*]-*neohecogenin*) (**8**). Crystals from MeOH (41 mg). Mp 272–278°. TLC: R_f 0.37 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −47° (pyridine; *c* 0.3). (Found: C, 51.63; H, 8.09. Calcd for $C_{55}H_{88}O_{26}\cdot 6H_2O$: C, 51.88; H, 7.91%.) IR ν_{max} cm^{-1}: 3435, 2930, 1708, 985, 920, 895, 850. ^1H NMR (360 MHz): δ0.70–2.18 (37H, *m*) within 0.87 (3H, *s*, Me-19), 1.06 (3H, *s*, Me-18) overlapped with 1.07 (3H, *d*, $J = 7$ Hz, Me-27), 1.37 (3H, *d*, $J = 7$ Hz, Me-21), 1.72 (3H, *d*, $J = 6.5$ Hz, Me-6‴″), 2.25 (1H, *dd*, $J_1 = 14$, $J_2 = 5$ Hz, H-11$_{eq}$), 2.40 (1H, *dd*, $J_1 \sim J_2 \sim 14$ Hz, H-11$_{ax}$), 2.74 (1H, *dd*, $J_1 = 9$, $J_2 = 7$ Hz, H-17), 3.37 (1H, *br d*, $J = 11$ Hz), 3.50 and 3.68 (1H each, *dd*, $J_1 \sim J_2 \sim 10$ Hz), 3.82–4.58 (23H, *m*), 4.65–5.05 (5H, *m*) within 4.85 (1H, *d*, $J = 8$ Hz) [anomeric proton], 4.96 (*br s*) [HOD-signal, overlapping with signal of one anomeric proton], 5.26 and 5.45 (1H each, *d*, $J = 8$ Hz) and 6.21 (1H, *br s*) [3 anomeric protons]. Negative ions FABMS *m/z* (rel. int.): 1165 (34), 1164 $[M]^-$ (31), 1163 $[M-H]^-$ (100), 1032 $[M-132]^-$ (30), 1031 $[M-132-H]^-$ (58), 1017 $[M-146-H]^-$ (12), 899 (11), 885 (12), 737 $[M-426-H]^-$ (26), 591 (16).

Peracetylsaponin-3(= *peracetyl*-**8**). Compound **8** (6 mg) was acetylated and purified by HPLC [MeOH–H_2O (8:2)] to obtain 3 mg of its peracetyl derivative (amorphous). TLC: R_f 0.37 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −26° ($CHCl_3$; *c* 0.2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1745, 1705. ^1H NMR (C_6D_6; 360 MHz): δ0.57–0.82 (7H, *m*) within 0.71 (3H, *s*) [Me-18 or Me-19], 0.93 (3H, *s*) [Me-19 or Me-18], 1.07 (3H, *d*, $J = 7$ Hz, Me-27), 1.15–2.24 (62H, *m*) within 1.49 (3H, *d*, $J = 6$ Hz, Me-6‴″), 1.52 (3H, *d*, $J = 7$ Hz, Me-21), 1.64, 1.65, 1.69, 1.71, 1.76, 1.78, 1.83, 1.84, 1.95, 1.98, 1.99, 2.01 (3H each, *s*, Ac), 2.47 (3H, *s*, Ac), 2.81 (1H, *dd*, $J_1 = 9$, $J_2 = 6.5$ Hz, H-17), 2.96–3.03 (1H, *m*, H-5″), 3.36 (1H, *br d*, $J = 11$ Hz, H-26$_{ax}$), 3.47–3.53 (2H, *m*, H-5′ and H-5‴$_A$), 3.58 (1H, *dd*, $J_1 = 11.5$, $J_2 = 9$ Hz, H-5‴$_{ax}$), 3.62–3.73 (2H, *m*, H-2″ and H-3), 3.94 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-3″), 4.05–4.12 (3H, *m*, H-5‴$_B$, H-26$_{eq}$ and H-6″$_A$), 4.16 (1H, *dd*, $J_1 = 12.5$, $J_2 = 4.5$ Hz, H-6″$_B$), 4.21 (1H, *br d*, $J = 3$ Hz, H-4′), 4.27 (1H, *d*, $J = 8$ Hz, H-1‴), 4.30 (1H, *d*, $J = 8$ Hz, H-1′), 4.40–4.54 (5H, *m*, H-2′, H-6′$_A$, H-6′$_B$, H-16 and H-5‴$_{eq}$), 4.74–4.85 (2H, *m*, H-4‴″ and H-5‴″), 5.01 (1H, *d*, $J = 7$ Hz, H-1‴″), overlapped with 5.01 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3′), 5.09 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4″), 5.16 (1H, *dd*, $J_1 = 4$, $J_2 = 3$ Hz, H-2‴″), 5.26 (1H, *dd*, $J_1 = 9$, $J_2 = 7$ Hz, H-2‴), 5.30 (1H, *dd*, $J_1 \sim J_2 \sim 4$ Hz, H-3‴″), 5.34 (1H, *d*, $J = 3$ Hz, H-1‴″), 5.39 (1H, *ddd*, $J_1 \sim J_2 \sim 9$, $J_3 = 5.5$ Hz, H-4‴), 5.54–5.60 (3H, *m*, H-3‴, H-1‴″ and H-2‴″), 5.65 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4‴″), 5.86 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3‴″).

Total hydrolysis of **8**. Compound **8** (1.5 mg) was hydrolysed as described. HPLC analysis of the aq. phase gave xylose, galactose, glucose and rhamnose in a 2:1:1:1 ratio; and **3** was identified as the aglycone (TLC).

Saponin-4 (=3-O-[β-D-*glucopyranosyl*-(1→2)-[β-D-*glucopyranosyl*-(1→3)]-β-D-*glucopyranosyl*-(1→4)-β-D-*galactopyranosyl*]-*neotigogenin*) (**9**). Crystals from MeOH (62 mg). TLC: R_f 0.36 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −38°

(pyridine; *c* 0.2). (Found: C, 52.52; H, 8.12. Calcd for $C_{51}H_{84}O_{23}\cdot 5H_2O$: C, 53.02; H, 8.20%.) All spectral and chromatographic properties identical with prosapogenin-6.4 (see below). Acetylation of **9** (25 mg) yielded on HPLC [MeOH–H_2O (87:13)] peracetyl-**9** (16 mg), which was identical with peracetylprosapogenin-6.4 (see below).

Cistocardin (= 3-O-[β-D-*glucopyranosyl*-(1→2)-[β-D-*glucopyranosyl*-(1→3)]-β-D-*glucopyranosyl*-(1→4)-β-D-*galactopyranosyl*]-*neogitogenin*) (**10**). Crystals from MeOH (247 mg). Mp 254°. TLC: R_f 0.33 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −47° (pyridine; *c* 1.2). (Found: C, 47.48; H, 7.74. Calcd for $C_{51}H_{84}O_{24}\cdot 8H_2O$: C, 47.22; H, 8.39%.) IR ν_{max} cm^{-1}: 3400, 2930, 990, 925, 895, 850. ^1H NMR: δ0.54–0.62 (1H, *m*), 0.67–0.83 (7H, *m*) within 0.70 and 0.80 (3H each, *s*) [Me-18 and Me-19], 0.93–1.65 (22H, *m*) within 1.08 (3H, *d*, *J* = 7 Hz, Me-27), 1.14 (3H, *d*, *J* = 7 Hz, Me-21), 1.75–2.22 (7H, *m*), 3.37 (1H, *br d*, *J* = 11 Hz), 3.81–4.69 (28H, *m*), 4.94, 5.20, 5.32 and 5.61 (1H each, *d*, *J* = 8 Hz) [4 anomeric protons]. Positive ion FABMS *m/z* (rel. int.): 1082 (51), 1081 $[M+H]^+$(16), 1080 $[M]^+$(32), 919 $[M-162+H]^+$ (5), 595 $[M-486+H]^+$ (65), 433 $[M-648+H]^+$ (100), 415 (48).

Peracetylcistocardin (= *peracetyl*-**10**). Compound **10** (10 mg) on acetylation and purification by HPLC [MeOH–H_2O (9:1)] gave peracetylcistocardin (amorphous, 12 mg). TLC: R_f 0.27 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −29° ($CHCl_3$; *c* 1.0). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750. ^1H NMR (C_6D_6): δ0.44–0.51 (1H, *m*), 0.63–2.24 (78H, *m*) within 0.75 and 0.87 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, *J* = 7 Hz, Me-27), 1.20 (3H, *d*, *J* = 7 Hz, Me-21), 1.65, 1.67, 1.69, 1.72, 1.80, 1.81, 1.82, 1.85, 1.95, 2.03, 2.04, 2.06, 2.09 and 2.20 (3H each, *s*, Ac), 3.28 (1H, *ddd*, J_1 = 10, $J_2 \sim J_3 \sim$ 3 Hz, H-5″), 3.34 (1H, *br d*, *J* = 11 Hz, H-26_{ax}), 3.48 (1H, *br dd*, J_1 = 7, J_2 = 5 Hz, H-5′), 3.52 (1H, *ddd*, J_1 = 10, J_2 = 4, J_3 = 2 Hz, H-5‴), 3.59 (1H, *ddd*, J_1 = 11, J_2 = 10, J_3 = 6 Hz, H-3), 3.89 (1H, *dd*, J_1 = 12.5, J_2 = 2 Hz, H-$6'''_A$), 3.95 (1H, *br d*, *J* = 3 Hz, H-4′) overlapped with 3.97 (1H, *dd*, J_1 = 9, J_2 = 7 Hz, H-2″), 4.04 (1H, *dd*, J_1 = 9.5, J_2 = 9 Hz, H-3″), 4.09–4.15 (2H, *m*, H-26_{eq}, H-5‴), 4.20 (2H, *d*, *J* = 3 Hz, H-$6''_A$, H-$6''_B$), 4.36 (1H, *d*, *J* = 8 Hz, H-1′), 4.41–4.52 (4H, *m*, H-1″, H-$6'_A$, H-$6'_B$, H-$6'''_B$), 4.59 (1H, *ddd*, $J_1 \sim J_2 \sim$ 8, J_3 = 7 Hz, H-16), 4.71 (1H, *dd*, J_1 = 12.5, J_2 = 5.5 Hz, H-$6'''_A$), 4.78 (1H, *dd*, J_1 = 12.5, J_2 = 4 Hz, H-$6'''_B$), 5.06 (1H, *dd*, J_1 = 10, J_2 = 3 Hz, H-3′), 5.09 (1H, *d*, *J* = 7 Hz, H-1⁗), 5.19 (1H, *dd*, J_1 = 10, J_2 = 9.5 Hz, H-4″) overlapped with 5.20–5.27 (2H, *m*, H-2 and H-1‴), 5.32 (1H, *dd*, J_1 = 10, J_2 = 9.5 Hz, H-4⁗) overlapped with 5.36 (1H, *dd*, J_1 = 9.5, J_2 = 7 Hz, H-2⁗), 5.47 (1H, *dd*, $J_1 \sim J_2 \sim$ 9.5 Hz, H-3⁗), 5.67–5.74 (3H, *m*, H-2′, H-2‴ and H-3‴), 5.87 (1H, *dd*, $J_1 \sim J_2 \sim$ 9.5 Hz, H-4‴).

Total hydrolysis of **10**. Compound **10** (2 mg) was hydrolysed. HPLC of the aq. phase gave glucose and galactose in a 3:1 ratio; from the organic layer **2** was identified as the aglycone (TLC). Total hydrolysis with MeOH–2 M HCl (gas) yielded the methyl glycosides; the mixt. of the methyl glycosides was derivatized and subjected to GC-analysis according to König *et al.* [22].

Partial hydrolysis of **10**. Compound **10** (48 mg) on partial hydrolysis and CC on Sephadex® LH 20 (MeOH) gave **2** (2 mg) and a mixt. of procistocardins, which was sepd by HPLC [MeOH–H_2O (82:18)] to yield prosapogenin **10.1** (= procistocardin-1, 1.5 mg), prosapogenin **10.2** (= procistocardin-2, 3 mg), prosapogenin **10.3** (= procistocardin-3, 3 mg) and prosapogenin **10.4** (= procistocardin-4, 2 mg).

Procistocardin-1 (**10.1**). Amorphous (1.5 mg). TLC: R_f 0.75 (S-3); anisaldehyde: yellow-green. ^1H NMR (CD_3OD): δ0.70–2.25 (37H, *m*) within 0.79 and 0.88 (3H each, *s*) [Me-18 and Me-19], 0.98 and 1.08 (3H each, *d*, *J* = 7 Hz) [Me-21 and Me-27], 3.44–3.54 (4H, *m*), 3.60–3.70 (3H, *m*), 3.76 (1H, *dd*, J_1 = 12, J_2 = 4 Hz), 3.80 (1H, *dd*, J_1 = 3, J_2 = 1 Hz), 3.92 (1H, *dd*, J_1 = 11, J_2 = 3 Hz), 4.31 (1H, *d*, *J* = 8 Hz) [anomeric proton], 4.39 (1H, *ddd*, $J_1 \sim J_2 \sim$ 8, J_3 = 7 Hz).

Peracetyl-**10.1**. Acetylation of **10.1** (1.4 mg) gave 2 mg of its peracetyl product (amorphous). TLC: R_f 0.54 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −22° ($CHCl_3$; *c* 0.1). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750. ^1H NMR (C_6D_6): δ0.59–2.25 (52H, *m*) within 0.63 and 0.77 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, *J* = 7 Hz, Me-27), 1.21 (3H, *d*, *J* = 7 Hz, Me-21), 1.54, 1.66, 1.75, 1.83 and 1.89 (3H each, *s*, Ac), 3.35 (1H, *br d*, *J* = 11 Hz, H-26_{ax}), 3.46 (1H, *ddd*, $J_1 \sim J_2 \sim$ 7, J_3 = 1 Hz, H-5′), 3.75 (1H, *ddd*, J_1 = 12, J_2 = 10, J_3 = 5.5 Hz, H-3), 4.12 (1H, *dd*, J_1 = 11, J_2 = 3.5 Hz, H-26_{eq}) overlapped with 4.15 (1H, *dd*, J_1 = 11, J_2 = 7 Hz, H-$6'_A$), 4.23 (1H, *dd*, J_1 = 11, J_2 = 7 Hz, H-$6'_B$), 4.42 (1H, *d*, *J* = 8 Hz, H-1′), 4.59–4.64 (1H, *m*, H-16), 5.23 (1H, *dd*, J_1 = 10, J_2 = 3 Hz, H-3′), 5.25–5.32 (1H, *m*, H-2), 5.52 (1H, *dd*, J_1 = 3, J_2 = 1 Hz, H-4′), 5.64 (1H, *dd*, J_1 = 10, J_2 = 8 Hz, H-2′).

Procistocardin-2 (**10.2**). Amorphous (3 mg). TLC: R_f 0.63 (S-3); anisaldehyde: yellow-green. ^1H NMR (CD_3OD): δ0.71–2.02 (37H, *m*) within 0.79 and 0.88 (3H each, *s*) [Me-18 and Me-19], 0.98 and 1.08 (3H each, *d*, *J* = 7 Hz) [Me-21 and Me-27], 3.18–3.68 (12H, *m*), 3.82–3.94 (3H, *m*), 4.04 (1H, *br d*, *J* = 3 Hz), 4.34 (1H, *d*, *J* = 7.5 Hz) [anomeric proton], 4.35–4.42 (1H, *m*), 4.51 (1H, *d*, *J* = 8 Hz) [anomeric proton].

Peracetyl-**10.2.** Compound **10.2** (3 mg) was acetylated as described yielding 2.5 mg of peracetyl-**10.2** (amorphous). TLC: R_f 0.40 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −24° ($CHCl_3$; *c* 0.2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750. ^1H NMR (C_6D_6): δ0.60–2.25 (61H, *m*) within 0.61 and 0.76 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, *J* = 7 Hz, Me-27), 1.21 (3H, *d*, *J* = 7 Hz, Me-21), 1.66, 1.68, 1.77, 1.81, 1.83, 1.86, 2.07 and 2.22 (3H each, *s*, Ac), 3.19 (1H, *ddd*, J_1 = 10, $J_2 \sim J_3 \sim$ 3 Hz, H-5″), 3.35 (1H, *br d*, *J* = 11 Hz, H-26_{ax}), 3.42 (1H, *br dd*, J_1 = 7, J_2 = 5 Hz, H-5′), 3.80 (1H, *ddd*, J_1 = 12, J_2 = 10, J_3 = 5 Hz, H-3), 3.89 (1H, *br d*, *J* = 3 Hz, H-4′), 4.10–4.14 (3H, *m*, H-$6''_A$, H-$6''_B$ and H-26_{eq}), 4.40 (1H, *dd*, J_1 = 11.5, J_2 = 7 Hz, H-$6'_A$), 4.46 (1H, *d*, *J* = 7.5 Hz, H-1′) overlapped with 4.48 (1H, *dd*, J_1 = 11.5, J_2 = 5 Hz, H-$6'_B$), 4.58 (1H, *d*, *J* = 8 Hz, H-1″) overlapped with 4.57–4.62 (1H, *m*, H-16), 5.02 (1H, *dd*, J_1 = 10, J_2 = 3 Hz, H-3′), 5.15 (1H, *dd*, J_1 = 10, J_2 = 8 Hz, H-2″), 5.19 (1H, *dd*, $J_1 \sim J_2 \sim$ 10 Hz, H-4″), 5.27 (1H, *ddd* J_1 = 12, J_2 = 10, J_3 = 5 Hz, H-2), 5.40 (1H, *dd*, J_1 = 10, J_2 = 7.5 Hz, H-2′), 5.49 (1H, *dd*, $J_1 \sim J_2 \sim$ 10 Hz, H-3″).

Procistocardin-3 (**10.3**). Amorphous (3 mg). TLC: R_f 0.49 (S-3); anisaldehyde: yellow-green. ^{1}H NMR (CD_3OD): δ0.71–1.46 (27H, *m*) within 0.79 and 0.88 (3H each, *s*) [Me-18 and Me-19], 0.98 and 1.08 (3H each, *d*, $J=7$ Hz) [Me-21 and Me-27], 1.52–2.03 (10H, *m*), 3.24–3.69 (17H, *m*), 3.81–3.94 (4H, *m*), 4.05 (1H, *br d*, $J=3$ Hz), 4.34 (1H, *d*, $J=8$ Hz) [anomeric proton], 4.39 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3=7$ Hz), 4.54 and 4.57 (1H each, *d*, $J=8$ Hz) [2 anomeric protons].

Peracetyl-**10.3.** Compound **10.3** (3 mg) was acetylated to obtain 3 mg of its peracetyl derivative (amorphous). TLC: R_f 0.35 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ $-39°$ ($CHCl_3$; *c* 0.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750. ^{1}H NMR (C_6D_6): δ0.40–2.25 (67H, *m*) within 0.61 and 0.76 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J=7$ Hz, Me-27), 1.21 (3H, *d*, $J=7$ Hz, Me-21), 1.65, 1.66, 1.69, 1.79, 1.81, 1.84, 1.85, 1.87, 1.97 and 2.14 (3H each, *s*, Ac), 2.42 (3H, *s*, Ac), 3.00 (1H, *ddd*, $J_1=10$, $J_2=4$, $J_3=2$ Hz, H-5''''), 3.35 (1H, *br d*, $J=11$ Hz, H-26$_{ax}$), 3.45 (1H, *br dd*, $J_1 \sim J_2 \sim 6$ Hz, H-5'), 3.48–3.54 (1H, *m*, H-5''), 3.76 (1H, *ddd*, $J_1=11.5$, $J_2=10$, $J_3=5$ Hz, H-3), 3.87 (1H, *dd*, $J_1=12.5$ Hz, $J_2=2$ Hz, H-6$'''_A$), 3.95 (1H, *br d*, $J=3$ Hz, H-4'), 4.06 (1H, *br dd*, $J_1 \sim J_2 \sim 10$ Hz, H-3''), 4.12 (1H, *dd*, $J_1=11$, $J_2=3$ Hz, H-26$_{eq}$) overlapped with 4.15 (1H, *dd*, $J_1=12.5$, $J_2=5$ Hz, H-6$''_A$), 4.22 (1H, *dd*, $J_1=12.5$, $J_2=3$ Hz, H-6$''_B$), 4.33 (1H, *dd*, $J_1=12.5$, $J_2=4$ Hz, H-6$'''_B$), 4.40–4.50 (3H, *m*, H-6$'_A$, H-6$'_B$ and H-1'), 4.57–4.63 (3H, *m*, H-1'', H-1'''', H-16), 4.86 (1H, *br dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4''), 5.06 (1H, *dd*, $J_1=10$, $J_2=3$ Hz, H-3'), 5.12–5.22 (3H, *m*, H-2'', H-2'''' and H-4''''), 5.26–5.33 (1H, *m*, H-2) overlapped with 5.32 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3''''), 5.38 (1H, *dd*, $J_1=10$, $J_2=8$ Hz, H-2').

Procistocardin-4 (**10.4**). Amorphous (2 mg). TLC: R_f 0.49 (S-3); anisaldehyde: yellow-green. ^{1}H NMR (CD_3OD): δ0.71–1.76 (33H, *m*) within 0.78 and 0.88 (3H each, *s*) [Me-18 and Me-19], 0.98 and 1.08 (3H each, *d*, $J=7$ Hz) [Me-21 and Me-27], 1.81–2.07 (4H, *m*), 3.16–4.04 (22H, *m*), 4.33–4.42 (2H, *m*) within 4.36 (1H, *d*, $J=8$ Hz), 4.56 and 4.66 (1H each, *d*, $J=8$ Hz) [3 anomeric protons.

Peracetyl-**10.4**. Compound **10.4** (2 mg) was acetylated to give peracetyl-**10.4** (amorphous, 2 mg). TLC: R_f 0.30 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ $-4°$ ($CHCl_3$; *c* 0.2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1755. ^{1}H NMR (C_6D_6): δ0.40–2.25 (70H, *m*) within 0.65 and 0.74 (3H each, *s*) [Me-18 and Me-19], 1.07 (3H, *d*, $J=7$ Hz, Me-27), 1.20 (3H, *d*, $J=7$ Hz, Me-21), 1.66, 1.67, 1.70, 1.76, 1.77, 1.81, 1.93, 1.96, 2.04, 2.09 and 2.24 (3H each, *s*, Ac), 2.99 (1H, *ddd*, $J_1=10$, $J_2 \sim J_3 \sim 3.5$ Hz, H-5''), 3.34 (1H, *br d*, $J=11$ Hz, H-26$_{ax}$), 3.41 (1H, *br dd*, $J_1=7$, $J_2=5.5$ Hz, H-5'), 3.53–3.61 (1H, *m*, H-3) overlapped with 3.56 (1H, *dd*, $J_1=10$, $J_2=8$ Hz, H-2''), 3.74 (1H, *br d*, $J=3$ Hz, H-4'), 3.85 (1H, *ddd*, $J_1=10$, $J_2=6$, $J_3=4.5$ Hz, H-5'''), 4.07–4.16 (3H, *m*, H-26$_{eq}$, H-6$''_A$ and H-6$''_B$), 4.24 (1H, *d*, $J=8$ Hz, H-1''), 4.33 (1H, *d*, $J=8$ Hz, H-1'), 4.43 (1H, *dd*, $J_1=11.5$, $J_2=5.5$ Hz, H-6$'_A$) overlapped with 4.45 (1H, *dd*, $J_1=11.5$, $J_2=7$ Hz, H-6$'_B$), 4.56 (1H, *d*, $J=8$ Hz, H-1''') overlapped with 4.59 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3=6.5$ Hz, H-16), 4.67 (1H, *dd*, $J_1=12$, $J_2=6$ Hz, H-6$'''_A$), 4.76 (1H, *dd*, $J_1=12$, $J_2=4.5$ Hz, H-6$'''_B$), 4.98 (1H, *dd*, $J_1=10$, $J_2=3$ Hz, H-3'), 5.04 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4''), 5.16 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-3''), 5.26 (1H, *ddd*, $J_1=11.5$, $J_2=9.5$, $J_3=5$ Hz, H-2), 5.48–5.57 (2H, *m*, H-2''' and H-3'''), 5.69 (1H, *dd*, $J_1=10$, $J_2=8$ Hz, H-2'), 5.86 (1H, *dd*, $J_1=10$, $J_2=9$ Hz, H-4''').

Saponin-6 (=3-O-[β-*xylopyranosyl*-(1→4)-β-*glucopyranosyl*-(1→3)-[β-*glucopyranosyl*-(1→2)]-β-*glucopyranosyl*-(1→4)-β-*galactopyranosyl*]-*neotigogenin*) (**11**). Crystals from MeOH (283 mg). Mp 286–290°. TLC: R_f 0.32 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ $-49°$ (pyridine; *c* 1.3). (Found: C, 52.17; H, 8.34. Calcd for $C_{56}H_{92}O_{27}\cdot 5H_2O$: C, 52.25; H, 7.99%.) IR ν_{max} cm^{-1}: 3400, 2930, 990, 920, 895, 850. ^{1}H NMR: δ0.45–0.54 (1H, *m*), 0.63 (3H, *s*) [Me-18 or Me-19], 0.74–2.20 (35H, *m*) within 0.81 (3H, *s*) [Me-19 or Me-18], 1.08 (3H, *d*, $J=7$ Hz, Me-27), 1.15 (3H, *d*, $J=7$ Hz, Me-21), 3.37 (1H, *br d*, $J=11$ Hz, H-26$_{ax}$), 3.67 (1H, *br dd*, $J_1 \sim J_2 \sim 10$ Hz), 3.77–4.30 (21H, *m*), 4.37–4.74 (10H, *m*), 4.89, 5.07, 5.15 and 5.27 (1H each, *d*, $J=8$ Hz), 5.57 (1H, *d*, $J=7.5$ Hz) [5 anomeric protons]. Positive ion FABMS *m/z* (rel. int.): 1197 $[M+H]^+$ (32), 613 (15), 579 $[M-618+H]^+$ (31), 418 (11), 417 $[M-780+H]^+$ (40).

Peracetyl-**11**. On acetylation **11** (16 mg) gave peracetyl-**11** (amorphous, 18 mg). TLC: R_f 0.28 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ $-23°$ ($CHCl_3$; *c* 0.7). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750. ^{1}H NMR (C_6D_6): from δ0.44–2.22 various *m*, within 0.79 and 0.81 (3H each, *s*) [Me-18 and Me-19], 1.07 (3H, *d*, $J=7$ Hz, Me-27), 1.21 (3H, *d*, $J=7$ Hz, Me-21), 1.60, 1.65, 1.69, 1.70, 1.76, 1.77, 1.82, 1.83, 1.85, 1.90, 1.92, 1.95, 2 × 2.09 and 2.18 (3H each *s*, Ac), 3.09 (1H, *dd*, $J_1=12$, $J_2=8$ Hz, H-5$''''_{ax}$), 3.27 (1H, *ddd*, $J_1=9.5$, $J_2=4.5$, $J_3=3.5$ Hz, H-5''), 3.34 (1H, *br d*, $J=11$ Hz, H-26$_{ax}$), 3.44–3.51 (2H, *m*, H-5' and H-5''''), 3.58–3.66 (1H, *m*, H-3) overlapped with 3.65 (1H, *dd*, $J_1=10$, $J_2=9$ Hz, H-4''''), 3.82 (1H, *dd*, $J_1=12$, $J_2=5$ Hz, H-5$''''_{eq}$), 4.00 (1H, *br d*, $J=3$ Hz, H-4'), 4.01–4.06 (2H, *m*, H-1'' and H-3''), 4.08–4.17 (3H, *m*, H-5''', H-26$_{eq}$ and H-6$'''_A$), 4.17 (1H, *dd*, $J_1=12$, $J_2=4.5$ Hz, H-6$''_A$), 4.21 (1H, *dd*, $J_1=12$, $J_2=3.5$ Hz, H-6$''_B$), 4.29 (1H, *dd*, $J_1=12.5$, $J_2=2$ Hz, H-6$'''_B$), 4.35 (1H , *d*, $J=7$ Hz, H-1''''), 4.41 (1H, *d*, $J=8$ Hz, H-1') overlapped with 4.38–4.51 (3H, *m*, H-6$'_{A/B}$ and H-2''), 4.60 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3=6.5$ Hz, H-16), 4.75 (1H, *dd*, $J_1=12$, $J_2=3.5$ Hz, H-6$''_A$), 4.84 (1H, *dd*, $J_1=12$, $J_2=6$ Hz, H-6$'''_B$), 4.92 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3=5$ Hz, H-4''''), 5.06–5.11 (3H, *m*, H-1'''', H-2'''' and H-3'), 5.20 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-4''), 5.25 (1H, *d*, $J=8$ Hz, H-1''') overlapped with 5.27 (1H, *dd*, $J_1=9$, $J_2=7.5$ Hz, H-2''''), 5.33 (1H, *dd*, $J_1 \sim J_2 \sim 8$ Hz, H-3''''), 5.47 (1H, *dd*, $J_1 \sim J_2 \sim 9$ Hz, H-3''''), 5.68–5.71 (2H, *m*, H-2''' and H-3'''), 5.76 (1H, *dd*, $J_1=10$, $J_2=8$ Hz, H-2'), 5.87 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4''').

Total hydrolysis of **11**. Compound **11** (2 mg) was hydrolysed and the aglycone from the organic layer was shown to be identical with **1** (TLC). Analysis of the aq. phase identified glucose, galactose and xylose as the sugars in a 3:1:1 ratio.

Partial hydrolysis of **11**. Partial hydrolysis of **11** (120 mg) afforded a mixt. of prosapogenins, which was

sepd by CC (Sephadex® LH 20; MeOH) into 2 frs. Subsequent HPLC of fr. 1 [MeOH–H_2O (83:17)] yielded the prosapogenins-6.1 (4 mg), -6.2 (8 mg), -6.3 (2 mg) and -6.4 (23 mg). CC of fr. 2 on silica gel [$CHCl_3$–MeOH (9:1)] gave the aglycone **1** (12 mg).

Prosapogenin-6.1. Amorphous (4 mg). TLC: R_f 0.65 (S-3); anisaldehyde: yellow-green. ^{1}H NMR [$CDCl_3$–CD_3OD (1:1)]: δ0.63–2.06 (39H, *m*) within 0.77 and 0.83 (3H each, *s*) [Me-18 and Me-19], 1.00 and 1.09 (3H each, *d*, J=7 Hz) [Me-21 and Me-27], 3.21–3.69 (11H, *m*), 3.89–3.96 (3H, *m*), 4.07 (1H, *br d*, J=3 Hz), 4.35 (1H, *d*, J=8 Hz) [anomeric proton], 4.42 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, J_3=6.5 Hz), 4.51 (1H) [anomeric proton] (overlapped with HOD-signal).

Peracetylprosapogenin-6.1. Prosapogenin-6.1 (4 mg) on acetylation gave its peracetyl derivative (amorphous, 5 mg). TLC: R_f 0.50 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −26° ($CHCl_3$; *c* 0.5). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750. ^{1}H NMR (C_6D_6): δ0.42–2.26 (60H, m) within 0.61 and 0.80 (3H each, *s*) [Me-18 and Me-19], 1.07 (3H, *d*, J=7 Hz, Me-27), 1.21 (3H, *d*, J=7 Hz, Me-21), 1.65, 1.67, 1.75, 1.78, 2×1.86, 2.19 (3H each, *s*, Ac), 3.15 (1H, *ddd*, J_1=10, $J_2 \sim J_3 \sim$3.5 Hz, H-5″), 3.34 (1H, *br d*, J=11 Hz, H-26$_{ax}$), 3.45 (1H, *br dd*, J_1=7, J_2=5 Hz, H-5′), 3.63–3.71 (1H, *m*, H-3), 3.86 (1H, *br d*, J=3 Hz, H-4′), 4.09–4.15 (3H, *m*, H-6″$_{A/B}$ and H-26$_{eq}$), 4.41 (1H, *dd*, J_1=12, J_2=7 Hz, H-6′$_A$), 4.48 (1H, *d*, J=8 Hz, H-1′), 4.52 (1H, *dd*, J_1=12, J_2=5 Hz, H-6′$_B$) overlapped with 4.52 (1H, *d*, J=8 Hz, H-1″), 4.60 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, J_3=6.5 Hz, H-16), 5.01 (1H, *dd*, J_1=10, J_2=3 Hz, H-3′), 5.13 (1H, *dd*, J_1=10, J_2=8 Hz, H-2″) overlapped with 5.16 (1H, *dd*, J_1=10, J_2=9.5 Hz, H-4″), 5.46–5.51 (2H, *m*, H-2′ and H-3″).

Prosapogenin-6.2. Amorphous (8 mg). TLC: R_f 0.50 (S-3); anisaldehyde: yellow-green. ^{1}H NMR [$CDCl_3$–CD_3OD (1:1)]: δ0.62–2.07 (39H, *m*) within 0.78 and 0.84 (3H each, *s*) [Me-18 and Me-19], 1.00 and 1.09 (3H each, *d*, J=7 Hz) [Me-21 and Me-27], 3.29–3.69 (16H, *m*), 3.88–3.96 (4H, *m*), 4.08 (1H, *br d*, J=3 Hz), 4.34 (1H, *d*, J=8 Hz) [anomeric proton], 4.42 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, J_3=7 Hz), 4.49 (1H, *d*, J=8 Hz) [anomeric proton], 4.55 (1H) [anomeric proton] (overlapped with HOD-signal).

Peracetylprosapogenin-6.2. Prosapogenin-6.2 (8 mg) on acetylation and purification by HPLC [MeOH–H_2O (9:1)] gave its peracetyl derivative (amorphous, 5 mg). TLC: R_f 0.38 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −18° ($CHCl_3$; *c* 0.5). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750. ^{1}H NMR (C_6D_6, 360 MHz): δ0.42–2.06 (65H, m) within 0.62 and 0.81 (3H each, *s*) [Me-18 and Me-19], 1.07 (3H, *d*, J=7 Hz, Me-27), 1.20 (3H, *d*, J=7 Hz, Me-21), 1.65, 1.66, 1.68, 1.76, 1.80, 1.85, 2×1.87, 1.97 (3H each, *s*, Ac), 2.15–2.25 (1H, *m*), 2.36 (3H, *s*, Ac), 3.04 (1H, *ddd*, J_1=10, J_2=4, J_3=2 Hz, H-5‴″), 3.33 (1H, *br d*, J=11 Hz, H-26$_{ax}$), 3.42–3.48 (2H, *m*, H-5′ and H-5″), 3.64–3.74 (1H, *m*, H-3), 3.85 (1H, *br d*, J=3 Hz, H-4′) overlapped with 3.86 (1H, *dd*, J_1=12, J_2=2 Hz, H-6‴′$_A$), 4.07 (1H, *br dd*, $J_1 \sim J_2 \sim$10 Hz, H-3″) overlapped with 4.11 (1H, *dd*, J_1=11, J_2=2.5 Hz, H-26$_{eq}$) overlapped with 4.14 (1H, *dd*, J_1=13, J_2=5 Hz, H-6″$_A$), 4.20 (1H, *dd*, J_1=13, J_2=2.5 Hz, H-6″$_B$), 4.31 (1H, *dd*, J_1=12, J_2=4 Hz, H-6‴″$_B$), 4.42 (1H, *dd*, J_1=12, J_2=7 Hz, H-6′$_A$) overlapped with 4.45 (1H, *br d*, J=8 Hz, H-1″), 4.48 (1H, *d*, J=8 Hz, H-1′), 4.52 (1H, *dd*, J_1=12, J_2=4 Hz, H-6′$_B$), 4.58 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, J_3=6 Hz, H-16), 4.62 (1H, *d*, J=8 Hz, H-1‴″), 4.85 (1H, *br dd*, $J_1 \sim J_2 \sim$10 Hz, H-4″), 5.04 (1H, *dd*, J_1=10, J_2=3 Hz, H-3′), 5.09–5.20 (3H, *m*, H-2″, H-2‴″ and H-4‴″), 5.33 (1H, *dd*, $J_1 \sim J_2 \sim$10 Hz, H-3‴″), 5.44 (1H, *dd*, J_1=10, J_2=8 Hz, H-2′).

Prosapogenin-6.3. Amorphous (2 mg). TLC: R_f 0.50 (S-3); anisaldehyde: yellow-green. ^{1}H NMR [$CDCl_3$–CD_3OD (1:1)]: δ0.64–2.20 (39H, *m*) within 0.78 and 0.85 (3H each, *s*) [Me-18 and Me-19], 0.99 and 1.09 (3H each, *d*, J=7 Hz) [Me-21 and Me-27], 3.21–3.70 (16H, *m*), 3.81 (1H, *dd*, J_1=12.5, J_2=4 Hz), 3.88–4.03 (4H, *m*), 4.37 (1H, *d*, J=8 Hz) [anomeric proton], 4.41 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, J_3=7 Hz), 4.52 and 4.63 (1H each, *d*, J=8 Hz) [2 anomeric protons].

Peracetylprosapogenin-6.3. Prosapogenin-6.3 was acetylated as described to give its amorphous peracetyl derivative (2 mg). TLC: R_f 0.45 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −15° ($CHCl_3$; *c* 0.2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750. ^{1}H NMR (C_6D_6): δ0.42–2.25 (69H, *m*) within 0.80 and 0.81 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, J=7 Hz, Me-27), 1.21 (3H, *d*, J=7 Hz, Me-21), 2×1.66, 1.69, 1.72, 1.76, 1.79, 1.88, 1.97, 1.98, 2.24 (3H each, *s*, Ac), 3.00 (1H, *ddd*, J_1=10, $J_2 \sim J_3 \sim$3 Hz, H-5″), 3.34 (1H, *br d*, J=11 Hz, H-26$_{ax}$), 3.41 (1H, *br dd*, $J_1 \sim J_2 \sim$6 Hz, H-5′), 3.54–3.63 (1H, *m*, H-3), 3.67 (1H, *dd*, J_1=10, J_2=8 Hz, H-2″), 3.74–3.80 (1H, *m*, H-5‴″) overlapped with 3.78 (1H, *br d*, J=3 Hz, H-4′), 4.06–4.14 (3H, *m*, H-26$_{eq}$, H-6″$_{A/B}$), 4.27 (1H, *d*, J=8 Hz, H-1″), 4.36 (1H, *d*, J=8 Hz, H-1′), 4.44 (2H, *d*, J=6 Hz, H-6′$_{A/B}$), 4.58–4.64 (1H, *m*, H-16) overlapped with 4.61 (1H, *d*, J=8 Hz, H-1‴″), 4.75 (1H, *dd*, J_1=12, J_2=4 Hz, H-6‴″$_A$), 4.80 (1H, *dd*, J_1=12, J_2=7 Hz, H-6‴″$_B$), 5.00 (1H, *dd*, J_1=10, J_2=3 Hz, H-3′), 5.03 (1H, *dd*, $J_1 \sim J_2 \sim$10 Hz, H-4″), 5.20 (1H, *dd*, $J_1 \sim J_2 \sim$10 Hz, H-3″), 5.49–5.59 (2H, *m*, H-2‴″ and H-3‴″), 5.76 (1H, *dd*, J_1=10, J_2=8 Hz, H-2′), 5.87 (1H, *dd*, J_1=10, J_2=9 Hz, H-4‴″).

Prosapogenin-6.4 (=*saponin*-4) (**9**). Crystals from MeOH (23 mg). Mp. 280–282°. TLC: R_f 0.36 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −41° (pyridine; *c* 1.4). IR ν_{max} cm^{-1}: 3400, 2930, 990, 920, 895, 850. ^{1}H NMR: δ0.45–0.54 (1H, *m*) 0.61–2.19 (38H, *m*) within 0.64 and 0.82 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, J=7 Hz, Me-27), 1.15 (3H, *d*, J=7 Hz, Me-21), 3.37 (1H, *br d*, J=11 Hz, H-26$_{ax}$), 3.83–4.75 (27H, *m*), 4.90, 5.17, 5.32 and 5.60 (1H each, *d*, J=8 Hz) [4 anomeric protons].

Peracetyl-**9** (=*peracetylprosapogenin*-6.4). Compound **9** (5 mg) on acetylation and purification by HPLC [MeOH–H_2O (9:1)] gave amorphous peracetyl-**9** (2 mg). TLC: R_f 0.33 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −15° ($CHCl_3$; *c* 0.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2945, 1750. ^{1}H NMR (C_6D_6): δ0.70–2.25 (78H, *m*) within 0.80 and 0.81 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, J=7 Hz, Me-27), 1.21 (3H, *d*, J=7 Hz, Me-21), 2×1.64, 1.69, 1.73, 1.76, 1.77, 1.81, 1.85, 1.91, 1.93, 2.04, 2.09, 2.18 (3H each, *s*, Ac), 3.29 (1H, *ddd*, J_1=9.5, J_2=4, J_3=3 Hz, H-5″), 3.34 (1H, *br d*, J=11 Hz, H-26$_{ax}$), 3.46 (1H, *br dd*,

$J_1=7$, $J_2=6$ Hz, H-5'), 3.54 (1H, *ddd*, $J_1=10$, $J_2=4$, $J_3=2$ Hz, H-5''''), 3.58–3.67 (1H, *m*, H-3), 3.89 (1H, *dd*, $J_1=12.5$, $J_2=2$ Hz, H-$6'''_A$), 3.98 (1H, *br d*, $J=3$ Hz, H-4'), 4.02–4.14 (4H, *m*, H-2'', H-3'', H-5''' and H-26_{eq}), 4.17 (1H, *dd*, $J_1=12.5$, $J_2=3$ Hz, H-$6''_A$), 4.21 (1H, *dd*, $J_1=12.5$, $J_2=4$ Hz, H-$6''_B$), 4.36–4.52 (5H, *m*, H-1', H-$6'''_B$, H-$6'_A$, H-$6'_B$, H-1''), 4.60 (1H, *ddd*, $J_1\sim J_2\sim 8$, $J_3=7$ Hz, H-16), 4.75 (1H, *dd*, $J_1=12$, $J_2=3$ Hz, H-$6'''_A$), 4.85 (1H, *dd*, $J_1=12$, $J_2=6.5$ Hz, H-$6'''_B$), 5.08 (1H, *dd*, $J_1=10$, $J_2=3$ Hz, H-3'), 5.13 (1H, *d*, $J=7$ Hz, H-1''''), 5.19 (1H, *dd*, $J_1\sim J_2\sim 9.5$ Hz, H-4''), 5.27 (1H, *d*, $J=8$ Hz, H-1'''), 5.33 (1H, *dd*, $J_1=10$, $J_2=9$ Hz, H-4''''), 5.36 (1H, *dd*, $J_1=9$, $J_2=7$ Hz, H-2''''), 5.48 (1H, *dd*, $J_1\sim J_2\sim 9$ Hz, H-3''''), 5.67–5.76 (2H, *m*, H-2''' and H-3'''), 5.79 (1H, *dd*, $J_1=10$, $J_2=8$ Hz, H-2'), 5.88 (1H, *dd*, $J_1\sim J_2\sim 9.5$ Hz, H-4''').

Saponin-7(=3-O-[β-*xylopyranosyl*-(1→2)-[β-*glucopyranosyl*-(1→3)]-β-*glucopyranosyl*-(1→4)-[α-*rhamnopyranosyl*-(1→2)]-β-*galactopyranosyl*]-*neohecogenin*) (**12**). Crystals from MeOH (53 mg). Mp 281–283°. TLC: R_f 0.28 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −37° (pyridine; *c* 0.3). (Found: C, 50.36; H, 9.24. Calcd for $C_{56}H_{90}O_{27}\cdot 7H_2O$: C, 50.90; H, 7.93%.) IR ν_{max} cm^{-1}: 3400, 2930, 1705, 985, 920, 895, 850. ^1H NMR: δ0.64–2.18 (37H, *m*) within 0.87 (3H, *s*, Me-19), 1.06 (3H, *s*, Me-18) overlapped with 1.07 (3H, *d*, $J=7$ Hz, Me-27), 1.37 (3H, *d*, $J=7$ Hz, Me-21), 1.72 (3H, *d*, $J=6.5$ Hz, Me-6''''), 2.25 (1H, *dd*, $J_1=14$, $J_2=5$ Hz, H-11_{eq}), 2.40 (1H, *dd*, $J_1\sim J_2\sim 14$ Hz, H-11_{ax}), 2.74 (1H, *dd*, $J_1=9$, $J_2=7$ Hz, H-17), 3.37 (1H, *br d*, $J=11$ Hz), 3.49 (1H, *dd*, $J_1\sim J_2\sim 11$ Hz), 3.80–4.31 (18H, *m*), 4.38–5.00 (13H, *m*) within 4.84 and 4.98 (1H each, *d*, $J=8$ Hz), 5.30 and 5.44 (1H each, *d*, $J=8$ Hz) and 6.23 (1H, *br s*) [5 anomeric protons]. Negative ion FABMS *m/z* (rel. int.): 1196 (30), 1194 $[M]^-$ (51), 1193 $[M-H]^-$ (100), 1062 $[M-132]^-$ (23), 1061 $[M-132-H]^-$ (60), 1047 $[M-146-H]^-$ (10), 1032 $[M-162]^-$ (11), 1031 $[M-162-H]^-$ (18), 899 (20), 738 $[M-456]^-$ (14), 737 $[M-456-H]^-$ (32), 590 (29).

Total hydrolysis of **12**. Hydrolysis of **12** (2 mg) gave in the aq. phase glucose, galactose, rhamnose and xylose in a 2:1:1:1 ratio, whereas from the organic layer **3** was isolated (identification by TLC).

Partial hydrolysis of **12**. Partial hydrolysis of **12** (38 mg) followed by CC on Sephadex® LH 20 (MeOH) gave 2 frs, which were acetylated. The acetylated fr. 1 on HPLC [MeOH–H_2O (85:15)] gave peracetyl-**12** (1.5 mg), peracetylprosapogenin-7.2 (4 mg) and peracetylprosapogenin-7.3 (0.5 mg). HPLC [MeOH–H_2O (85:15)] of the acetylated fr. 2 yielded peracetylprosapogenin-7.1 (3.5 mg).

Peracetylsaponin-7 (=*peracetyl*-**12**). Amorphous (1.5 mg). TLC: R_f 0.28 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −14° ($CHCl_3$; *c* 0.1). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750, 1705. ^1H NMR (C_6D_6): δ0.60–0.81 (6H, *m*) within 0.71 (3H, *s*) [Me-18 or Me-19], 0.94 (3H, *s*) [Me-19 or Me-18], 1.07 (3H, *d*, $J=7$ Hz, Me-27), 1.15–2.25 (66H, *m*) within 1.47 (3H, *d*, $J=6$ Hz, Me-6''''), 1.53 (3H, *d*, $J=7$ Hz, Me-21), 1.64, 2×1.69, 1.70, 1.76, 2×1.79, 2×1.80, 1.84, 1.88, 1.93, and 2.08 (3H each, *s*, Ac), 2.32 (3H, *s*, Ac), 2.81 (1H, *dd*, $J_1=8$, $J_2=6.5$ Hz, H-17), 3.37 (1H, *br d*, $J=11$ Hz, H-26_{ax}), 3.40–3.45 (1H, *m*, H-5''), 3.48 (1H, *br dd*, $J_1=7$, $J_2=5$ Hz, H-5'), 3.56 (1H, *ddd*, $J_1=10$, $J_2=4$, $J_3=2$ Hz, H-5''''), 3.59–3.66 (1H, *m*, H-3), 3.69 (1H, *dd*, $J_1=13$, $J_2=2$ Hz, H-$6'''_A$), 3.80 (1H, *dd*, $J_1=13$, $J_2=5$ Hz, H-$5'''_A$), 3.98 (1H, *dd*, $J_1=9$, $J_2=8$ Hz, H-2''), 4.11 (1H, *dd*, $J_1=11$, $J_2=3$ Hz, H-26_{eq}), 4.14–4.24 (3H, *m*, H-3'', H-$6''_A$ and H-$6''_B$), 4.27 (1H, *d*, $J=8$ Hz, H-1'), 4.32–4.38 (2H, *m*, H-$6'_A$ and H-2'), 4.41 (1H, *dd*, $J_1=13$, $J_2=4$ Hz, H-$6'''_B$), 4.45–4.53 (3H, *m*, H-16, H-4', H-$6'_B$), 4.65 (1H, *d*, $J=8$ Hz, H-1''), 4.73 (1H, *dq*, $J_1=10$, $J_2=6$ Hz, H-5''''), 4.81 (1H, *dd*, $J_1=13$, $J_2=3.5$ Hz, H-$5'''_B$), 5.07–5.13 (3H, *m*, H-3', H-4'', H-1''''), 5.28 (1H, *dd*, $J_1=9.5$, $J_2=7.5$ Hz, H-2'''') overlapped with 5.30 (1H, *dd*, $J_1=10$, $J_2=9.5$ Hz, H-4'''') overlapped with 5.31–5.36 (2H, *m*, H-1''' and H-4'''), 5.39 (1H, *dd*, $J_1\sim J_2\sim 5.5$ Hz, H-2'''), 5.43–5.47 (2H, *m*, H-3''' and H-2''''), 5.50 (1H, *d*, $J=1.5$ Hz, H-1''''), 5.63 (1H, *dd*, $J_1\sim J_2\sim 10$ Hz, H-4'''') overlapped with 5.64 (1H, *dd*, $J_1\sim J_2\sim 9.5$ Hz, H-3''''), 5.81 (1H, *dd*, $J_1=10$, $J_2=3$ Hz, H-3'''').

Peracetylprosapogenin-7.1. Amorphous (3.5 mg). TLC: R_f 0.53 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −3° ($CHCl_3$; *c* 0.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750, 1705. ^1H NMR (C_6D_6): δ0.40–2.20 (57H, *m*) within 0.47 and 0.88 (3H each, *s*) [Me-18 and Me-19], 1.06 (3H, *d*, $J=7$ Hz, Me-27), 1.51 (3H, *d*, $J=7$ Hz, Me-21), 1.65, 1.66, 1.76, 1.78, 2×1.85, and 2.19 (3H each, *s*, Ac), 2.77 (1H, *dd*, $J_1=9$, $J_2=7$ Hz, H-17), 3.15 (1H, *ddd*, $J_1=10$, $J_2\sim J_3\sim 3.5$ Hz, H-5''), 3.36 (1H, *br d*, $J=11$ Hz, H-26_{ax}), 3.44 (1H, *br dd*, $J_1=7$, $J_2=4.5$ Hz, H-5'), 3.56–3.65 (1H, *m*, H-3), 3.83 (1H, *br d*, $J=3$ Hz, H-4'), 4.07–4.11 (1H, *m*, H-26_{eq}) overlapped with 4.10 (2H, *d*, $J=3.5$ Hz, H-$6''_A$ and H-$6''_B$), 4.41 (1H, *dd*, $J_1=12$, $J_2=7$ Hz, H-$6'_A$), 4.44–4.49 (1H, *m*, H-16) overlapped with 4.45 (1H, *d*, $J=8$ Hz, H-1') and 4.49 (1H, *d*, $J=8$ Hz, H-1'') overlapped with 4.51 (1H, *dd*, $J_1=12$, $J_2=4.5$ Hz, H-$6'_B$), 4.99 (1H, *dd*, $J_1=10$, $J_2=3$ Hz, H-3'), 5.12–5.18 (2H, *m*, H-2'' and H-4''), 5.45–5.51 (2H, *m*, H-2' and H-3'').

Peracetylprosapogenin-7.2. Amorphous (4 mg). TLC: R_f 0.35 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −9° ($CHCl_3$; *c* 0.3). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750, 1705. ^1H NMR (C_6D_6): δ0.42–2.22 (63H, *m*) within 0.49 and 0.88 (3H each, *s*) [Me-18 and Me-19], 1.07 (3H, *d*, $J=7$ Hz, Me-27), 1.50 (3H, *d*, $J=7$ Hz, Me-21), 1.63, 1.67, 1.69, 1.78, 1.81, 1.85, 2×1.87, and 1.99 (3H each, *s*, Ac), 2.37 (3H, *s*, Ac), 2.78 (1H, *dd*, $J_1=9$, $J_2=6.5$ Hz, H-17), 3.04 (1H, *ddd*, $J_1=10$, $J_2=4$, $J_3=2$ Hz, H-5''''), 3.35 (1H, *br d*, $J=11$ Hz, H-26_{ax}), 3.42–3.48 (2H, *m*, H-5' and H-5''), 3.60–3.68 (1H, *m*, H-3), 3.80 (1H, *br d*, $J=3$ Hz, H-4'), 3.86 (1H, *dd*, $J_1=12.5$, $J_2=2$ Hz, H-$6'''_A$), 4.02–4.08 (1H, *m*, H-3'') overlapped with 4.08 (1H, *dd*, $J_1=11$, $J_2=3$ Hz, H-26_{eq}), 4.13 (1H, *dd*, $J_1=12.5$, $J_2=5$ Hz, H-$6'_A$), 4.20 (1H, *dd*, $J_1=12.5$, $J_2=2.5$ Hz, H-$6''_B$), 4.30 (1H, *dd*, $J_1=12.5$, $J_2=4$ Hz, H-$6'''_B$), 4.41 (1H, *br d*, $J=8$ Hz, H-1'') overlapped with 4.44 (1H, *dd*, $J_1=12$, $J_2=7$ Hz, H-$6'_A$), 4.40–4.50 (1H, overlapped *m*, H-16), 4.49 (1H, *d*, $J=8$ Hz, H-1') overlapped with 4.52 (1H, *dd*, $J_1=12$, $J_2=4$ Hz, H-$6'_B$), 4.62 (1H, *d*, $J=8$ Hz, H-1''''), 4.81 (1H, *br dd*, $J_1\sim J_2\sim 9.5$ Hz, H-4''), 5.02 (1H, *dd*, $J_1=10$, $J_2=3$ Hz, H-3'), 5.10–5.20 (3H, *m*, H-2'', H-2'''' and H-

4''''), 5.33 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3''''), 5.44 (1H, *dd*, $J_1 = 10$, $J_2 = 8$ Hz, H-2').

Peracetylprosapogenin-7.3. Oil (0.5 mg). TLC: R_f 0.41 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −32° ($CHCl_3$; *c* 0.05). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 1750, 1705. ^1H NMR (C_6D_6): δ0.42–2.23 (72H, *m*) within 0.59 and 0.89 (3H each, *s*) [Me-18 and Me-19], 1.07 (3H, *d*, $J = 7$ Hz, Me-27), 1.51 (3H, *d*, $J = 7$ Hz, Me-21), 1.64, 1.68, 1.70, 1.74, 1.75, 1.78, 1.83, 1.87, 1.89, 1.90, 1.96 and 2.10 (3H each, *s*, Ac), 2.80 (1H, *dd*, $J_1 = 8.5$, $J_2 = 6.5$ Hz, H-17), 3.36 (1H, *br d*, $J = 11$ Hz, H-26_{ax}), 3.44–3.54 (3H, *m*, H-3, H-5' and H-5''), 3.63 (1H, *ddd*, $J_1 = 10$, $J_2 = 4$, $J_3 = 2$ Hz, H-5''''), 3.73 (1H, *dd*, $J_1 = 12.5$, $J_2 = 2$ Hz, H-$6''''_A$), 3.91 (1H, *dd*, $J_1 = 13$, $J_2 = 4.5$ Hz, H-$5''_A$), 3.99 (1H, *dd*, $J_1 = 9$, $J_2 = 8$ Hz, H-2''), 4.10 (1H, *dd*, $J_1 = 11$, $J_2 = 3$ Hz, H-26_{eq}), 4.16–4.25 (3H, *m*, H-3'', H-$6''_A$ and H-$6''_B$), 4.33 (1H, *dd*, $J_1 = 12$, $J_2 = 5$ Hz, H-$6'_A$), 4.38 (1H, *br d*, $J = 3$ Hz, H-4'), 4.45 (1H, *dd*, $J_1 = 12.5$, $J_2 = 4$ Hz, H-$6''''_B$) overlapped with 4.47 (1H, *d*, $J = 7.5$ Hz, H-1'), 4.45–4.51 (1H, overlapped *m*, H-16), 4.53 (1H, *dd*, $J_1 = 12$, $J_2 = 7$ Hz, H-$6'_B$), 4.80 (1H, *d*, $J = 8$ Hz, H-1''), 4.98 (1H, *dd*, $J_1 = 13$, $J_2 = 3$ Hz, H-$5''''_B$), 5.06 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4''), 5.15 (1H, *d*, $J = 8$ Hz, H-1''''), 5.19 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3'), 5.30 (1H, *dd*, $J_1 = 9.5$, $J_2 = 8$ Hz, H-2'''') overlapped with 5.33 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-4''''), 5.40–5.44 (2H, *m*, H-1''' and H-2''' or H-3'''), 5.48–5.53 (1H, *m*, H-4''''), 5.56–5.61 (2H, *m*, H-2' and H-3''' or H-2'''), 5.68 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3'''').

Saponin-8 (=3-O-[β-*xylopyranosyl*-(1→4)-β-*glucopyranosyl*-(1→3)-[β-*glucopyranosyl*-(1→2)]-β-*glucopyranosyl*-(1→4)-β-*galactopyranosyl*]-*neogitogenin*) (**13**). Crystals from MeOH (89 mg). Mp 261–264°. TLC: R_f 0.29 (S-3); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −45° (pyridine; *c* 1.2). (Found: C, 50.12; H, 7.81. Calcd for $C_{56}H_{92}O_{28} \cdot 6H_2O$: C, 50.90; H, 7.93%.) IR ν_{max} cm^{-1}: 3400, 2930, 990, 920, 895, 850. ^1H NMR: δ0.54–0.62 (1H, *m*), 0.67–0.82 (7H, *m*) within 0.70 and 0.80 (3H each, *s*) [Me-18 and Me-19], 0.95–1.64 (22H, *m*) within 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.14 (3H, *d*, $J = 7$ Hz, Me-21), 1.74–2.22 (7H, *m*), 3.37 (1H, *br d*, $J = 11$ Hz), 3.62–4.65 (33H, *m*), 4.93 (1H, *d*, $J = 8$ Hz), 5.06 (1H) [overlapped with HOD-signal], 5.18 (1H, *d*, $J = 8$ Hz), 5.29 (1H, *d*, $J = 8$ Hz) and 5.58 (1H, *d*, $J = 8$ Hz) [5 anomeric protons]. Positive ions FABMS *m/z* (rel. int.): 1213 $[M+H]^+$ (25), 1081 $[M-132+H]^+$ (6), 1051 $[M-162+H]^+$ (6), 596 (27), 595 $[M-618+H]^+$ (100), 433 $[M-780+H]^+$ (65), 415 (30).

Peracetylsaponin-8 (=*peracetyl*-**13**). Compound **13** (18 mg) on acetylation and HPLC [MeOH–H_2O (9:1)] yielded peracetyl-**13** (amorphous, 17 mg). TLC: R_f 0.25 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −36° ($CHCl_3$; *c* 1.5). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2940, 1750. ^1H NMR (C_6D_6): δ0.42–0.50 (1H, *m*), 0.65–2.24 (84H, *m*) within 0.75 and 0.85 (3H each, *s*) [Me-18 and Me-19], 1.08 (3H, *d*, $J = 7$ Hz, Me-27), 1.20 (3H, *d*, $J = 7$ Hz, Me-21), 1.61, 1.68, 1.69, 1.72, 1.81, 2 × 1.82, 1.85, 1.86, 1.92, 1.95, 2.04, 2.07, 2.09, 2.11 and 2.20 (3H each, *s*, Ac), 3.10 (1H, *dd*, $J_1 = 12$, $J_2 = 8$ Hz, H-$5''''_{ax}$), 3.27 (1H, *ddd*, $J_1 = 10$, $J_2 \sim J_3 \sim 3$ Hz, H-5''), 3.34 (1H, *br d*, $J = 11$ Hz, H-26_{ax}), 3.46–3.52 (2H, *m*, H-5', H-5''''), 3.56–3.63 (1H, *m*, H-3), 3.66 (1H, *dd*, $J_1 = 9$, $J_2 = 8$ Hz, H-4''''), 3.83 (1H, *dd*, $J_1 = 12$, $J_2 = 5$ Hz, H-$5''''_{eq}$), 3.95–4.02 (3H, *m*, H-4', H-2'', H-3''), 4.09–4.23 (5H, *m*, H-26_{eq}, H-5''', H-$6''_A$, H-$6''_B$, H-$6''''_A$), 4.29 (1H, *dd*, $J_1 = 12$, $J_2 = 2$ Hz, H-$6''''_B$), 4.34 (1H, *d*, $J = 7$ Hz, H-1''''), 4.39 (1H, *d*, $J = 8$ Hz, H-1'), 4.41–4.46 (2H, *m*, H-1'', H-$6'_A$), 4.50 (1H, *dd*, $J_1 = 12$, $J_2 = 5$ Hz, H-$6'_B$), 4.59 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 6.5$ Hz, H-16), 4.70 (1H, *dd*, $J_1 = 12$, $J_2 = 5.5$ Hz, H-$6''_A$), 4.79 (1H, *dd*, $J_1 = 12$, $J_2 = 4$ Hz, H-$6''''_B$), 4.93 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, $J_3 = 5$ Hz, H-4''''), 5.04 (1H, *d*, $J = 7$ Hz, H-1''''), 5.07 (1H, *dd*, $J_1 = 10$, $J_2 = 3$ Hz, H-3') overlapped with 5.08 (1H, *dd*, $J_1 = 9$, $J_2 = 7$ Hz, H-2''''), 5.18–5.29 (4H, *m*, H-2, H-4'', H-1''', H-2''''), 5.34 (1H, *dd*, $J_1 = 9$, $J_2 = 8$ Hz, H-3''''), 5.47 (1H, *dd*, $J_1 \sim J_2 \sim 9$ Hz, H-3''''), 5.66 (1H, *dd*, $J_1 = 10$, $J_2 = 8$ Hz, H-2') overlapped with 5.67 (1H, *dd*, $J_1 = 9.5$, $J_2 = 7.5$ Hz, H-2'''), 5.73 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3'''), 5.86 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-4''').

Total hydrolysis of **13**. Compound **13** (2 mg) was hydrolysed. The aq. phase when subjected to HPLC gave glucose, galactose and xylose in a 3:1:1 ratio, whereas from the organic layer **2** was isolated and identified by TLC.

Saponin-9 (=3-[β-D-*xylopyranosyl*-(1→2)-[β-D-*xylopyranosyl*-(1→3)]-β-D-*glucopyranosyl*-(1→4)-[α-L-*rhamnopyranosyl*-(1→2)]-β-D-*galactopyranosyl*]-26-(β-*glucopyranosyl*)-22-*methoxy*-(3β,5α,25S)-*furostan*-3,26-*diol*) (**14**). Crystals from MeOH (125 mg). Mp 208–211°. TLC: R_f 0.23 (S-3); anisaldehyde: yellow-green; Ehrlich reagent [33]: red. $[\alpha]_D^{20}$ −58° (pyridine; *c* 0.8). (Found: C, 50.43; H, 8.02. Calcd for $C_{62}H_{104}O_{31} \cdot 7H_2O$: C, 50.60; H, 8.08%.) IR ν_{max} cm^{-1}: 3400, 2930. ^1H NMR: δ0.46–0.54 (1H, *m*), 0.74–2.07 (40H, *m*) within 0.79 and 0.86 (3H each, *s*) (Me-18 and Me-19), 1.06 and 1.18 (3H each, *d*, $J = 7$ Hz) [Me-21 and Me-27], 1.73 (3H, *d*, $J = 6$ Hz, Me-6''''), 2.18–2.26 (1H, *m*), 3.26 (3H, *s*, MeO), 3.47–3.56 (2H, *m*), 3.69 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz), 3.82–4.33 (20H, *m*), 4.39–4.62 (8H, *m*), 4.66–4.98 (7H, *m*) within 4.87 and 4.88 (1H each, *d*, $J = 8$ Hz), 5.00–5.04 (*m*) overlapped with HOD-peak at δ5.01, 5.26 and 5.45 (1H each, *d*, $J = 8$ Hz) and 6.21 (1H, *br s*) [6 anomeric protons]. Negative ion FABMS *m/z* (rel. int.): 1344 $[M]^-$ (54), 1343 $[M-H]^-$ (100), 1212 $[M-132]^-$ (37), 1211 $[M-132-H]^-$ (69), 1197 $[M-146-H]^-$ (13), 1181 $[M-162-H]^-$ (11), 1079 (16), 917 $[M-426-H]^-$ (32), 609 $[M-734-H]^-$ (21).

Peracetylsaponin-9 (=*peracetyl*-**14**). Compound **14** (15 mg) was acetylated and purified by HPLC [MeOH–H_2O (85:15)] to afford 15 mg of its peracetyl derivative (amorphous). TLC: R_f 0.25 (S-4); anisaldehyde: yellow-green. $[\alpha]_D^{20}$ −29° ($CHCl_3$; *c* 1.4). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1750. ^1H NMR (C_6D_6): δ0.40–0.58 (1H, *m*) overlapped with HOD-peak, 0.76–1.09 (14H, *m*) within 0.85 and 0.88 (3H each, *s*) [Me-18 and Me-19], 0.93 (3H, *d*, $J = 7$ Hz, Me-27), 1.22–2.10 (74H, *m*) within 1.29 (3H, *d*, $J = 7$ Hz, Me-21), 1.48 (3H, *d*, $J = 6$ Hz, Me-6''''), 1.64, 1.65, 2 × 1.68, 1.69, 1.70, 1.71, 1.75, 1.78, 2 × 1.83, 1.84, 1.95, 1.98, 2.00 and 2.03 (3H each, *s*, Ac), 2.20–2.28 (1H, *m*), 2.49 (3H, *s*, Ac), 2.94–2.99 (1H, *m*, H-5''), 3.14 (1H, *dd*, $J_1 = 10$, $J_2 = 6$ Hz, H-26_A), 3.25 (3H, *s*, MeO) overlapped with 3.27 (1H, *ddd*, $J_1 = 10$, $J_2 = 4$,

J_3 = 2.5 Hz, H-5''''''), 3.47–3.53 (2H, *m*, H-5$''''_A$ and H-5'), 3.59 (1H, *dd*, J_1 = 12, J_2 = 8 Hz, H-5$'''_{ax}$) overlapped with 3.63 (1H, *dd*, J_1 = 9, J_2 = 8 Hz, H-2''), 3.72–3.81 (1H, *m*, H-3) overlapped with 3.76 (1H, *dd*, J_1 = 10, J_2 = 5.5 Hz, H-26$_B$), 3.93 (1H, *dd*, $J_1 \sim J_2 \sim 9$ Hz, H-3''), 4.04–4.11 (3H, *m*, H-6$''_A$, H-5$''''_B$ and H-6$''''_A$''''''), 4.16 (1H, *dd*, J_1 = 12.5, J_2 = 5 Hz, H-6$''_B$), 4.21 (1H, *br d*, J = 3 Hz, H-4'), 4.25 and 4.26 (1H each, *d*, J = 8 Hz) [H-1'' and H-1''''''] overlapped with 4.28 (1H, *dd*, J_1 = 12.5, J_2 = 4 Hz, H-6$''''_B$''''''), 4.34 (1H, *d*, J = 8 Hz, H-1'), 4.40–4.55 (5H, *m*, H-2', H-6'$_A$, H-6'$_B$, H-16 and H-5$'''_{eq}$), 4.80–4.88 (2H, *m*, H-4'''' and H-5''''''), 5.00 (1H, *d*, J = 7 Hz, H-1''') overlapped with 5.01 (1H, *dd*, J_1 = 10, J_2 = 3 Hz, H-3'), 5.09 (1H, *dd*, $J_1 \sim J_2 \sim 9$ Hz, H-4''), 5.16 (1H, *dd*, J_1 = 4, J_2 = 3 Hz, H-2''''), 5.24–5.31 (3H, *m*, H-2''', H-3'''' and H-4''''''), 5.34 (1H, *d*, J = 3 Hz, H-1'''') overlapped with 5.35 (1H, *dd*, J_1 = 9.5, J_2 = 8 Hz, H-2''''''') overlapped with 5.39 (1H, *ddd*, $J_1 \sim J_2 \sim 8$, J_3 = 5.5 Hz, H-4''') overlapped with 5.44 (1H, *dd*, $J_1 \sim J_2 \sim 9.5$ Hz, H-3''''''), 5.54–5.60 (3H, *m*, H-3''', H-1'''' and H-2''''''), 5.66 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4''''''), 5.87 (1H, *dd*, J_1 = 10, J_2 = 3 Hz, H-3''''').

Total hydrolysis of **14**. Compound **14** (3 mg) was hydrolysed with CF_3CO_2H. HPLC analysis of the aq. phase gave glucose, xylose, galactose and rhamnose in a 2:2:1:1 ratio; from the organic layer **1** was isolated and identified by TLC.

Enzymatic hydrolysis of **14**. Compound **14** (11 mg) was suspended in 13 ml H_2O and 20 mg β-glucosidase (6 U mg^{-1}, Fluka) was added. After stirring for 18 hr at 37–39° the mixt. was extracted with EtOAc. The solvent was evapd and the residue purified by HPLC [MeOH–H_2O (78:22)] to yield 3 mg of the prosapogenin -14.1 (amorphous), which was found to be identical with tribulosin (7).

D-(+)-*Pinitol* (**15**). Crystals from MeOH (210 mg). Mp 179° (lit. [17] mp 185–186°). TLC: R_f 0.18 (S-3); anisaldehyde: light blue. $[\alpha]_D^{20}$ +60° (H_2O; *c* 6.5). {lit. [25] $[\alpha]_D^{20}$ +64.6° (H_2O; *c* 1.0)}. IR ν_{max} cm^{-1}: 3400, 2935. ^{1}H and ^{13}C NMR in agreement with published data [23].

Pentaacetylpinitol. Compound **15** (4 mg) was acetylated to yield 5 mg of pentaacetylpinitol (oil). TLC: R_f 0.54 (S-4); anisaldehyde: light blue. $[\alpha]_D^{20}$ −5° ($CHCl_3$; *c* 0.4). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755. ^{1}H NMR ($CDCl_3$): δ1.99, 2.05, 2.10, 2.16 and 2.17 (3H each, *s*, Ac), 3.63 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-3), 5.20 (1H, *dd*, J_1 = 10, J_2 = 3 Hz, H-2) overlapped with 5.22 (1H, *dd*, J_1 = 10, J_2 = 3 Hz, H-5), 5.31–5.36 (2H, *m*, H-1 and H-6) overlapped with 5.38 (1H, *dd*, $J_1 \sim J_2 \sim 10$ Hz, H-4).

Sucrose (**16**). Crystals from MeOH (100 mg). Mp 172°. TLC: R_f 0.15 (S-3); anisaldehyde: brown-blue. $[\alpha]_D^{20}$ +65° (H_2O; *c* 9.9) {lit. [26] $[\alpha]_D^{22}$ +66.5° (H_2O)}. Substance identical with an authentic sample.

5'-(*Hydroxysulphonyloxy*) *jasmonic acid* (= 1R, 2R (2'Z)-3-*oxo*-2-(5-*hydroxysulphonyloxy*-2-*pentenyl*) *cyclopentane acetic acid* (**17**). Amorphous (5 mg). TLC: R_f 0.17 (S-3); anisaldehyde: red-brown. $[\alpha]_D^{20}$ −24° (MeOH; *c* 0.2). IR ν_{max} cm^{-1}: 3430, 2985, 1735. CD λ_{max}^{MeOH} nm ($\Delta\varepsilon$: 295 (−0.92). ^{1}H NMR (CD_3OD): δ1.46–1.58 (1H, *m*, H-5$_A$), 1.93–1.99 (1H, *m*, H-2), 2.03–2.41 (7H, *m*), 2.46 (2H, *dt*, J_1 = 5.5, J_2 = 7 Hz, H-4'), 2.54 (1H, *dd*, J_1 = 14, J_2 = 5 Hz, H−α_A), 3.98 (2H, *t*, J = 7 Hz, H-5'), 5.34–5.54 (2H, *m*, H-2' and H-3'). ^{13}C NMR (CD_3OD): δ26.4 (C-1'), 28.3 (C-5), 28.6 (C-4'), 38.8 (C-4), 40.0 (C-1), 43.5 (C-α), 55.1 (C-2), 68.5 (C-5'), 127.9 (C-3'), 129.8 (C-2'), 182.0 ($\underline{C}O_2H$), 222.6 (C-3). Negative ions FABMS *m/z* (rel. int.): 344 $[M+K-H]^-$ (93), 343 $[M+K-2H]^-$ (100), 327 $[M+Na-2H]^-$ (42), 306 $[M]^-$ (47), 305 $[M-H]^-$ (53), 283 (57).

Methylation of **17**. Compound **17** (2.5 mg) was dissolved in 1 ml MeOH and CH_2N_2 in Et_2O was added until the soln showed a yellow colour. After 12 hr the solvent was evapd to yield 3 mg **17** monomethyl ester (amorphous). TLC: R_f 0.62 (S-3); anisaldehyde: red-brown. $[\alpha]_D^{20}$ −22° (MeOH; *c* 0.1). CD λ_{max}^{MeOH} nm ($\Delta\varepsilon$): 297 (−0.51). ^{1}H NMR (CD_3OD): δ1.53 (1H, *dddd*, J_1 = 12, J_2 = 11, J_3 = 10, J_4 = 9 Hz, H-5$_A$), 2.00 (1H, *ddt*, J_1 = 11, J_2 = 1.5, J_3 = 6 Hz, H-2), 2.10 (1H, *ddd*, J_1 = 19, J_2 = 11, J_3 = 9 Hz, H-4$_A$), 2.15–2.24 (1H, *m*, H-5$_B$), 2.27–2.38 (2H, *m*, H-1 and H-4$_B$) overlapped by 2.38 (2H, *dd*, J_1 = 6, J_2 = 5.5 Hz, H-1') and 2.39 (1H, *dd*, J_1 = 14, J_2 = 9 Hz, H-α_B), 2.45 (2H, *dt*, $J_1 \sim J_2 \sim 7$ Hz, H-4'), 2.73 (1H, *dd*, J_1 = 14, J_2 = 4 Hz, H-α_A), 3.71 (3H, *s*, CO_2Me), 3.98 (2H, *t*, J = 7 Hz, H-5'), 5.40–5.55 (2H, *m*, H-2' and H-3'). ^{13}C NMR (CD_3OD): δ26.4 (C-1'), 28.1 (C-5), 28.7 (C-4'), 38.6 (C-4), 39.2 (C-1), 39.5 (C-α), 52.1 (CO_2Me), 55.0 (C-2), 68.4 (C-5'), 128.3 (C-3'), 129.6 (C-2'), 174.5 (CO_2Me) and 220.3 (C-3). Negative ion FABMS *m/z* (rel. int.): 321 (52), 320 $[M]^-$ (34), 319 $[M-H]^-$ (100).

Hydrolysis of **17** *monomethyl ester*. Compound **17** monomethyl ester (1.2 mg) was dissolved in 1 ml MeOH–2 M HCl (1:1) and refluxed for 10 hr at 80°. After evapn of the MeOH the aq. phase was extracted with $CHCl_3$ (5 ml). Work-up of the organic layer yielded 5'-hydroxyjasmonic acid methyl ester [27] (0.8 mg, amorphous). TLC: R_f 0.80 (S-3); anisaldehyde: red-brown. $[\alpha]_D^{20}$ *ca* −35° (MeOH; *c* 0.08). ^{1}H NMR (CD_3OD): δ1.47–1.63 (1H, *m*, H-5$_A$), 1.98 (1H, *ddt*, J_1 = 11, J_2 = 1.5, J_3 = 9 Hz, H-2), 2.04–2.15 (1H, *m*, H-4$_A$), 2.15–2.24 (1H, *m*, H-5$_B$), 2.26–2.41 (7H, *m*), 2.72 (1H, *dd*, J_1 = 15, J_2 = 4 Hz, H-α_A), 3.55 (2H, *t*, J = 7 Hz, H-5'), 3.68 (3H, *s*, $CO_2\underline{Me}$), 5.40–5.51 (2H, *m*, H-2' and H-3'). EIMS *m/z* (rel. int.): 240 $[M]^+$(2), 222 $[M-18]^+$ (2), 210 (27), 156 (65), 83 (100). In the aq. phase sulphate was detected besides chloride by ion chromatography (Super Sep Anionensäule, Metrohm).

Compound (±)-**17** *by partial synthesis*. Aq. KOH (0.5 M, 2 ml) was slowly added to a soln of 20 mg (±)-jasmine ketolactone in 4 ml MeOH and stirred for 3 hr at room temp. The reaction mixt. was neutralized, the solvent evapd and the residue subjected to CC on silica gel [$CHCl_3$–MeOH (95:5)] to yield (±)-5'-hydroxyjasmonic acid methyl ester (18 mg).

Chlorosulphuric acid (550 mg) was added dropwise to a soln of (±)-5'-hydroxyjasmonic acid methyl ester (15 mg) in 10 ml $CHCl_3$ at 0° under stirring. After stirring for 4 hr the mixt. was adjusted to pH 6 with 2 M NaOH, the solvent evapd and the residue subjected to CC on silica gel [$CHCl_3$–MeOH–H_2O (75:25:2)] to yield (±)-**17** monomethyl ester (16 mg).

(±)-**17** monomethyl ester (15 mg) was stirred in 12 ml 0.1 M aq. KOH for 5 hr at room temp. After adjusting to pH 6 with 2 M H_2SO_4 the solvent was evapd and the residue subjected to MPLC (LiChroprep® RP-18, Merck) using H_2O–MeOH (85:15), which gave (±)-**17** (11 mg). Except for the optical properties ($[\alpha]_D$, CD), all physical and spectral data of synthetic (±)-**17** were found in agreement with those of (−)-**17** isolated from the plant material.

Pharmacological methods. Guinea pigs of either sex weighing 250–350 g were killed by cervical dislocation. Right ventricular papillary muscles (diameter, 0.5–0.8 mm) were rapidly excised from the isolated heart and mounted in a 2-chambered organ bath [30] with a vol. of 17 ml. The bath soln was constantly gassed and kept in circulation by 95% O_2–5% CO_2; temp. 35°, pH 7.5. The composition of the bath soln was (mM): NaCl 115, KCl 4.7, $MgSO_4$ 1.2, $CaCl_2$ 3.2, $NaHCO_3$ 25, KH_2PO_4 1.2, and glucose 10.

The muscles were stimulated at their base through 2 punctate platinum electrodes with square wave pulses of 1 msec and an intensity slightly above threshold. Force of contraction was recorded isometrically by means of an inductive force transducer (Q-11, 10p, Hottinger Baldwin Messtechnik, Darmstadt, F.R.G.) connected to an oscilloscope and a pen recorder. The resting force was kept constant at 4 mN throughout the experiment. An equilibration period of at least 1 hr at a stimulation frequency of 1 Hz preceded each experiment. Subsequently, the frequency of stimulation was lowered to 0.2 Hz, and the substance to be tested was added as soon as force of contraction had reached a steady state.

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