Four Acylated Triterpenoid Saponins from *Albizia procera*

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Received December 1, 1997

Four new oleanane-type triterpene glycosides, proceraosides A−D (**1**−**4**), were isolated from the seeds of *Albizia procera*. Their structures were established by extensive NMR experiments and chemical methods. Compounds **1**−**3** comprised acacic acid as the aglycon and a monoterpenic carboxylic acid linked to a monoterpene quinovoside as the acyl moiety at C-21. The common oligosaccharide moiety linked to C-28 in **1**−**3** was determined as α-L-arabinofuranosyl-(1→4)-[β-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester. These compounds differed in the C-3-linked sugar unit or in the configuration of C-6′ of the inner monoterpene moiety in the C-21-linked acyl unit. Compound **4** was established as the 16-deoxy analogue of **1**.

Albizia procera Benth. belonging to the Leguminosae and commonly known as "Safed Siris" in Hindi, is widely distributed in India. This species has been used for hedges, street trees, and as an animal feed.[1] Previous phytochemical studies on the saponins of this plant have been limited to the structure elucidation of the acid hydrolysates of the extract.[2] Therefore, we initiated a phytochemical investigation of the saponins of this species, in which complex mixtures of these compounds were purified using modern phytochemical techniques. We describe here the isolation of proceraosides A−D (**1**−**4**), whose structures were determined by various NMR techniques, including COSY, HMQC, HMBC, TOCSY, and ROESY experiments, as well as by chemical degradation.

Results and Discussion

Proceraoside A (**1**) was obtained as a white powder. The molecular formula was deduced as $C_{96}H_{154}O_{44}$ from a $[M + Na]^+$ peak observed at *m/z* 2034 in the FABMS and from its ^{13}C NMR data. The IR spectrum showed carbonyl group (1735 cm^{-1}) and α,β-unsaturated carbonyl group (1710 cm^{-1}) absorptions. The ^1H and ^{13}C NMR spectra obtained for **1** contained resonances that were characteristic of an oleanene-type triterpenoidal saponin. The NMR data of **1**−**3** were in good agreement with those of julibrosides I−III, which are represented by an acacic acid 3,21,28-*O*-trisdesmoside acylated with two monoterpenic acids, and were isolated from the stem bark of *Albizia julibrissin*.[3] The acid hydrolysis of **1** with 5% H_2SO_4 afforded an acacic acid lactone (**5**), which was identified by comparison with published data,[4] and L-arabinose, D-fucose, D-glucose, D-quinovose, L-rhamnose, and D-xylose, which were confirmed by specific rotation using chiral detection by HPLC analysis.[5] In the ^1H NMR spectrum of **1**, eight anomeric proton signals appeared at δ 6.26 [1H, br s, ara(*f*)], 6.07 (1H, d, *J* = 8.0 Hz, glc_2), 5.88 (1H, br s, rha), 5.33 (1H, d, *J* = 7.7 Hz, glc_3), 5.06 (1H, d, *J* = 6.9 Hz, xyl), 5.01 (1H, d, *J* = 7.1 Hz, fuc), 4.93 (1H, d, *J* = 7.7 Hz, glc_1), and 4.85 (1H, d, *J* = 7.7 Hz, qui), respectively. The corresponding eight anomeric carbons were observed at δ 111.1 [ara(*f*)], 95.6 (glc_2), 101.9 (rha), 105.7 (glc_3), 107.0 (xyl), 103.4 (fuc), 106.7 (glc_1), and 99.4 (qui) in the ^{13}C NMR spectrum. The chemical shift at δ 111.1 of the arabinose unit demonstrated that this sugar was in the α-furanose form.[6] The configuration of all of the other sugars in the pyranose form in **1** was fully defined from the chemical shift and the coupling constant of each of the remaining anomeric protons. Accordingly, three glucoses and a unit each of fucose, quinovose, and xylose were established as having the β configuration, with a rhamnose moiety having an α configuration. The ^{13}C NMR spectrum of **1** showed three carbonyl carbons at δ 167.9, 176.3, and 174.5 that could be assignable to C-28 of the aglycon. Upon alkaline hydrolysis of the crude saponin with 0.6 N NaOH in MeOH, three prosapogenins (**6**−**8**) and a mixture of monoterpene glycosides (**9a** and **9b**), and a monoterpenic acid (**10**) were obtained as major components (Chart 1).

Compounds **6**, **7**, and **10** were found to be identical with the known compounds, acacic acid lactone 3-*O*-β-D-xylopyranosyl-(1→2)-β-D-fucopyranosyl-(1→6)-β-D-glucopyranoside (julibroside A_2), [7] acacic acid lactone 3-*O*-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranoside [prosapogenin-3 (**6**)′][8] (albiziasaponin A),[9] and (6*S*),(2*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoic acid [(6*S*)-menthiafolic acid],[3] respectively, by comparison of their NMR and optical rotation data to literature values.

Prosapogenin **8** showed in the FABMS a $[M - H]^-$ peak at *m/z* 911, consistent with having a molecular formula of $C_{47}H_{76}O_{17}$. Acid hydrolysis of **8** afforded machaerinic acid lactone (**11**),[10] as the aglycon, and the sugar components, D-fucose, D-glucose, and D-xylose. The ^{13}C NMR signals of the aglycon in **8** exhibited a glycosylation shift of +8.0 ppm at the C-3 carbon in comparison with that of machaerinic acid, suggesting that **8** was a machaerinic acid 3-*O*-glycoside.[11] Meanwhile, the ^{13}C NMR sugar signals of **8** and **6** at the C-3

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S0163-3864(97)00538-7 CCC: $15.00
Published on Web 03/28/1998

Chart 1

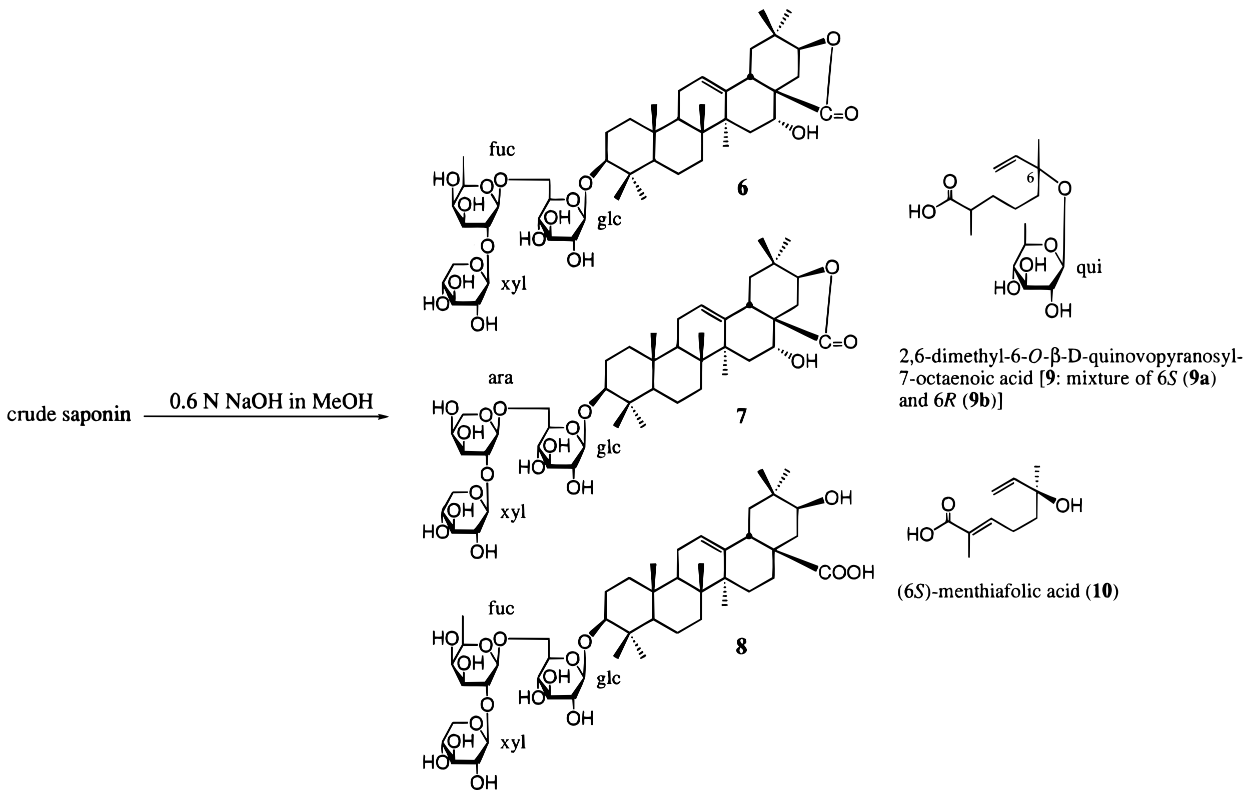


Table 1. ^{13}C NMR Data of the Aglycon Moieties of Compounds **1**−**4** and **6**−**8** in C_5D_5N

position	1	2	3	4	6	7	8
C-1	38.9	39.1	39.2	39.0	38.9	38.9	38.9
2	26.9	26.9	27.0	26.9	26.9	27.1	27.0
3	88.4	88.8	88.8	88.1	88.7	88.2	88.2
4	39.7	39.7	39.8	39.8	39.7	39.8	39.8
5	56.0	56.2	56.1	56.0	56.2	56.2	56.1
6	18.9	18.9	18.9	18.9	18.6	18.7	18.8
7	33.6	33.7	33.8	33.5	32.7	32.8	33.4
8	39.9	40.1	40.3	39.9	40.6	40.6	40.0
9	47.2	47.3	47.3	48.2	47.5	47.5	48.3
10	37.1	37.2	37.3	37.2	37.2	37.3	37.3
11	23.9	24.0	24.1	24.0	24.0	24.0	24.1
12	123.1	123.1	123.1	123.2	124.8	124.6	123.3
13	143.3	143.4	143.3	143.0	140.3	140.0	144.0
14	42.1	42.2	42.2	42.4	43.5	43.6	42.4
15	35.9	35.9	36.1	28.6	38.3	38.4	28.7
16	73.9	73.9	74.0	24.8	67.0	67.3	25.4
17	51.6	51.8	51.8	48.8	50.2	50.2	48.8
18	40.9	40.9	41.1	41.4	41.9	41.9	41.9
19	47.9	47.9	48.1	46.6	43.2	43.1	47.5
20	35.2	35.3	35.4	35.4	34.3	34.3	37.1
21	77.0	77.1	77.1	75.2	83.7	83.2	72.7
22	36.5	36.5	36.6	36.5	27.3	27.3	41.8
23	28.2	28.4	28.4	28.2	28.4	28.4	28.5
24	17.0	17.0	17.3	17.0	17.3	17.3	17.3
25	15.9	16.0	16.1	15.9	16.0	16.0	15.8
26	17.4	17.5	17.6	17.5	16.5	16.5	17.7
27	27.3	27.4	27.4	26.0	29.1	29.2	26.5
28	174.5	174.6	174.5	175.0	181.5	181.4	179.6
29	29.3	29.4	29.5	29.0	28.8	28.8	30.1
30	19.1	19.2	19.3	18.6	24.5	24.5	18.1

position in each pair were very similar in position and appearance (Table 2). Therefore, **8** was formulated as machaerinic acid 3-*O*-*β*-D-xylopyranosyl-(l→2)-*β*-D-fucopyranosyl-(1→6)-*β*-D-glucopyranoside.

Compound **9** gave a $[M - H]^-$ peak at m/z 331 in the FABMS, appropriate for a molecular formula of $C_{16}H_{28}O_7$. Hydrolysis of **9** with 5% H_2SO_4 allowed in the idetification of D-quinovose. On comparison of the ^{13}C NMR spectra of **9** and **10**, the signals of one double bond and a vinyl methyl group out of the 10 carbon signals of the monoterpenic acid observed in **10** were missing in **9**. In turn, one secondary methyl, a methylene, and a methine signal could be seen at δ 17.9, 35.2, and 40.1, respectively, in **9**, including a glycosylation shift of +7.3 ppm at the C-6 carbon (Table 3). Therefore, the structure of **9** was established as 2,6-dimethyl-6-*O*-*β*-D-quinovopyranosyl-7-octaenoic acid. However, in the ^{1}H NMR spectrum of **9**, pairs of resonances of equal intensity for H-7 (δ 6.23 and 6.33), H_2-8 (δ 5.22, 5.43 and 5.15, 5.28), H_3-9 (δ 1.56 and 1.43), and H-1 (δ 4.88 and 4.82) of quinovose were observed and were assigned to the (6*S*)- and (6*R*)-isomers of menthiafolic acid-6-*O*-*β*-D-quinovoside reported by Kiuchi et al.,[12] respectively. This finding suggested that **9** was a mixture of the (6*S*)-(**9a**) and (6*R*)-(**9b**) isomers in the ratio of 1:1.

The alkaline hydrolysis of **1** under the same conditions also afforded **6** and **10** as major products. The binding sites of the two ester linkages (δ 167.9 and 176.3) in **1** were revealed by two acylation shifts observed at δ 6.20 (1H, dt, J = 11.1, 5.6 Hz) and 5.36 (1H, t, J = 9.6 Hz). Using both ROESY and HMBC experiments, these signals were assigned to H-21 of the aglycon and H-4 of quinovose, respectively. Further, the HMBC spectrum exhibited significant correlations between H-21 of the aglycon and the carbonyl carbon (δ 176.3) of the inner monoterpene unit (MTA_1), and between H-1 (δ 4.85) of quinovose and C-6′ (δ 80.2) of the inner monoterpene unit (MTA_1), and between H-4 (δ 5.36, t, J = 9.6 Hz) of quinovose and the carbonyl carbon (δ 167.9) of the outer monoterpene unit (MTA_2) (Figure 1). The chemical shifts observed for H-7′ (δ 6.21), H_2-8′ (δ 5.27 and 5.43), and H_3-9′ (δ 1.54) of the

Table 2. ^{13}C NMR Data of Sugar Moieties of Compounds **1**−**4** and **6**−**8** in C_5D_5N

C-3	sugar	1	2	3	4	6	7	8	C-28	sugar	1	2	3	4
glc$_1$	1	106.7	106.9	106.9	106.6	106.8	106.9	106.8	glc$_2$	1	95.6	95.7	95.7	95.5
	2	75.8	75.7	75.7	75.8	75.9	75.7	75.9		2	76.8	76.8	76.7	76.8
	3	78.4	78.4	78.3	78.4	78.5	78.5	78.6		3	78.4	78.4	78.5	78.4
	4	71.8	72.3	72.4	71.9	71.8	72.2	71.8		4	71.2	71.3	71.4	71.3
	5	76.6	76.2	76.2	77.0	77.1	76.4	77.1		5	79.1	79.1	79.2	79.0
	6	70.1	69.7	69.7	70.0	70.1	69.6	70.1		6	62.0	62.2	62.2	62.1
ara	1	103.4	102.4	102.3	103.5	103.6	10.25	103.6	rha	1	101.9	102.0	102.0	101.8
or	2	82.2	80.5	80.5	82.4	82.4	80.7	82.4		2	70.6	70.7	70.7	71.0
fuc	3	75.3	72.6	72.7	75.2	75.3	72.8	75.3		3	81.9	82.1	82.1	81.9
	4	72.2	67.3	67.4	72.2	72.3	67.4	72.3		4	79.1	79.0	79.2	79.3
	5	71.4	64.6	64.4	71.4	71.5	64.5	71.4		5	69.2	69.2	69.3	69.0
	6	17.2			17.3	17.5		17.4	glc$_3$	6	18.9	19.0	19.1	18.9
xyl	1	107.0	106.3	106.2	107.1	107.1	106.4	107.0		1	105.7	105.8	105.7	105.7
	2	75.8	75.5	75.5	76.0	76.0	75.6	76.0		2	75.4	75.5	75.5	75.5
	3	77.5	78.1	78.0	77.6	77.6	77.9	77.6		3	78.0	78.0	78.2	78.2
	4	70.8	70.9	71.0	70.8	70.9	71.0	70.9		4	71.7	71.8	71.9	71.8
	5	67.2	67.5	67.4	67.3	67.0	67.7	67.3		5	78.4	78.4	78.5	78.4
										6	62.8	62.8	62.9	62.8
									ara(*f*)	1	111.1	111.1	111.1	111.0
										2	84.5	84.5	84.6	84.9
										3	78.2	78.4	78.5	78.4
										4	85.4	85.4	85.5	84.7
										5	62.5	62.6	62.6	62.5

Table 3. ^{13}C NMR Data of C-21 Portions of Compounds **1**−**4**, **9a**, **9b**, and **10** in C_5D_5N

position		1	2	3	4	9a(6*S*)		9b(6*R*)	10
MAT$_1$[a]	1′	176.3	176.5	176.3	176.3		179.3		
	2′	40.2	40.3	40.3	40.0		40.1		
	3′	34.7	34.8	34.9	34.6		35.2		
	4′	21.9	22.1	22.1	21.9		22.2		
	5′	42.1	42.2	40.6	42.2	40.8		40.1	
	6′	80.2	80.3	80.2	80.2		79.7		
	7′	144.3	144.4	144.4	144.4	144.2		144.8	
	8′	115.0	115.1	114.2	115.0	114.9		114.0	
	9′	23.2	23.4	24.2	23.4	24.0		24.5	
	10′	17.2	17.2	17.3	17.0		17.9		
qui	1	99.4	99.4	99.2	99.4	99.5		99.3	
	2	75.6	75.7	75.5	75.6	75.7		75.6	
	3	75.7	75.7	75.6	75.7		78.5		
	4	77.3	77.4	77.4	77.3		77.0		
	5	70.1	70.2	70.3	70.2		72.7		
	6	18.5	18.6	18.6	18.5		19.1		
MAT$_2$[b]	1″	167.9	167.9	167.8	167.9				170.7
	2″	127.9	128.0	127.9	127.9				129.3
	3″	143.6	143.8	143.6	143.6				142.5
	4″	24.1	24.2	24.2	24.1				24.3
	5″	41.5	41.6	41.7	41.5				41.9
	6″	72.1	72.3	72.2	72.2				72.4
	7″	146.6	146.6	146.6	146.6				146.8
	8″	111.7	111.9	111.7	111.8				111.8
	9″	28.6	28.6	28.7	28.6				28.7
	10″	12.6	12.7	12.8	12.7				13.0

[a] (6′*S* or (6*R*)-2′,6′-Dimethyl-7′-octenic acid. [b] (6*S*)-Methiafolic acid.

inner monoterpene unit (MTA_1) in **1** were very similar to those of the (6*S*)-isomer (**9a**). Therefore, a (6′*S*)-2′,6′-dimethyl-6′-*O*-(menthiafolyl-*β*-D-quinovopyranosyl)-7′-octenoyl residue was located at C-21 of the aglycon.

The FABMS of **1** showed a [M + Na − 602]$^+$ peak at *m*/*z* 1432, in which 602 mass units were accounted for by the C-28-linked sugar residues consisting of one arabinose, one rhamnose, and two glucose units. The carbon signals observed for the sugar moiety linked at C-28 of the ^{13}C NMR spectrum for **1** were superimposable on those of pithedulosides H−J,[12] indicating that **1** possesses the same sugar sequence in the oligosaccharide moiety at C-28 as those of pithedulosides H−J. Thus, the structure of the sugar moiety at C-28 of **1** was determined as α-L-arabinofuranosyl-(1→4)-[*β*-D-glucopyranosyl-(l→3)]-α-L-rhamnopyranosyl-(l→2)-*β*-D-glucopyranoside. Consequently, the whole structure of proceraoside A (**1**) was concluded to be 3-*O*-*β*-D-xylopyranosyl-(l→2)-*β*-D-fucopyranosyl-(l→6)-*β*-D-glucopyranosyl-21-*O*-{(6′*S*)−(2′,6′-dimethyl-6′-*O*-[4-*O*-(6*S*)-menthiafolyl-*β*-D-quinovopyranosyl]-7′-octenoyl} acacic acid 28-*O*-α-L-arabinofuranosyl-(1→4)-[*β*-D-glucopyranosyl-(l→3)]-α-L-rhamnopyranosyl-(l→2)-*β*-D-glucopyranosyl ester.

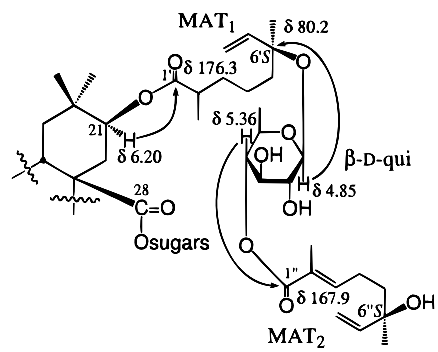
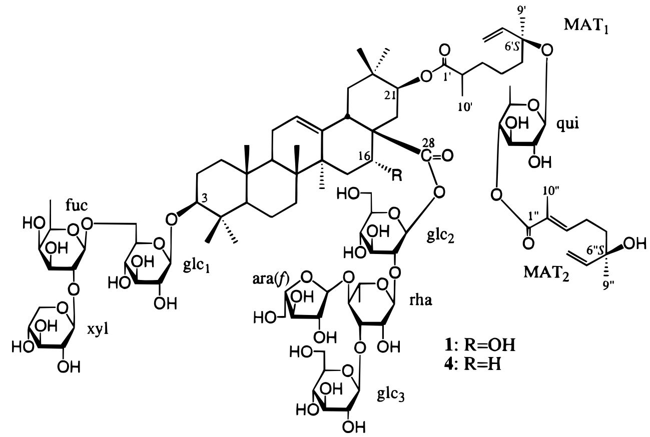


Figure 1. HMBC experiment of acyl moieties at C-21 of **1**.

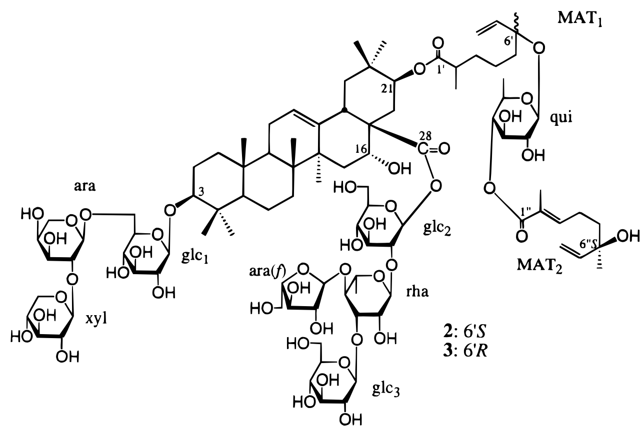
Proceraoside B (**2**) gave, in the FABMS, a [M + Na]$^+$ peak at *m*/*z* 2020 and a [M + Na − 602]$^+$ peak at *m*/*z* 1418, 14 mass units lower than those of **1**. Hydrolysis of **2** with 5% H_2SO_4 again gave acacic acid lactone (**5**), and the sugar units determined by chiral HPLC analysis were L-arabinose, D-glucose, D-quinovose, L-rhamnose, and D-xylose. Alkaline hydrolysis of **2** gave the prosapogenin **7** and the monoterpenic acid **10**. The hydrolysis results combined with the MS data suggested that proceraoside B (**2**) differed from proceraoside A (**1**) only by the replacement of fucose with arabinose in the C-3-linked sugar unit. Indeed, comparison of the ^{1}H and ^{13}C NMR spectra for **2** with those of **1** revealed that they had a common sugar substitution pattern at C-28, and the same acyl substitution pattern at C-21 (Tables 2 and 3). The configuration of C-6′ of the inner monoterpene unit (MTA_1) at C-21 for **2** was determined as *S* because the proton resonances of H-7′ (*δ* 6.21), H_2-8′ (*δ* 5.27 and 5.42), and H_3-9′ (*δ* 1.54) were identical to those of **1**. From an analysis of the data obtained, the structure of proceraoside B (**2**) was concluded to be 3-*O*-*β*-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(l→6)-*β*-D-glucopyranosyl-21-*O*-{(6′*S*)-2′,6′-dimethyl-6′-*O*-[4-*O*-(6*S*)-menthiafolyl-*β*-D-quinovopyranosyl]-7′-octenoyl}-acacic acid 28-*O*-α-L-arabinofuranosyl-(1→4)-[*β*-D-glucopyranosyl-(l→3)]-α-L-rhamnopyranosyl-(l→2)-*β*-D-glucopyranosyl ester.

Proceraoside C (**3**) gave a $[M + Na]^+$ peak at *m/z* 2020 in the FABMS, consistent with a molecular formula of $C_{95}H_{152}O_{44}$, identical with that of proceraoside B (**2**). Acid hydrolysis of **3** allowed the identification of the same sugar components as **2**, that is, L-arabinose, D-glucose, D-quinovose, L-rhamnose, and D-xylose, as determined by HPLC analysis. Alkaline hydrolysis of **3** led to prosapogenin **7** and the monoterpenic acid **10**, as found in **2**. The NMR data for the sugar parts of **3** and **2** indicated that they had identical saccharide chains at C-3 and C-28 but differed in their C-21 acyl units (Tables 1−3). On detailed ^{13}C NMR data comparison of the acyl moieties at C-21 for **3** and **2**, the resonances of C-5′, C-6′, C-8′, and C-9′ centering around C-6′ of the inner monoterpene unit (MTA_1) exhibited slight differences. This observation was further clarified from the ^{1}H NMR data. The corresponding proton resonances, H-7′ (*δ* 6.32), H_2-8′ (*δ* 5.22 and 5.32), and H_3-9′ (*δ* 1.46) revealed that the configuration of C-6′ of the inner monoterpene moiety (MTA_1) in **3** was *R*. Hence, the structure of **3** was concluded to be 3-*O*-*β*-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(l→6)-*β*-D-glucopyranosyl-21-*O*-{(6′*R*)-2′,6′-dimethyl-6′-*O*-[4-*O*-(6*S*)-menthiafolyl-*β*-D-quinovopyranosyl]-7′-octenoyl}-acacic acid 28-*O*-α-L-arabinofuranosyl-(1→4)-[*β*-D-glucopyranosyl-(l→3)]-α-L-rhamnopyranosyl-(l→2)-*β*-D-glucopyranosyl ester.

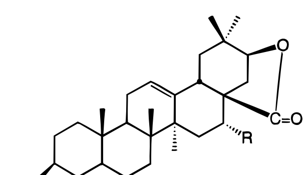
Proceraoside D (**4**) gave a $[M + Na]^+$ peak at *m/z* 2018, appropriate for a molecular formula of $C_{96}H_{154}O_{43}$ that differed from the molecular formula of proceraoside A (**1**) simply by the loss of one oxygen atom. Acid hydrolysis of **4** afforded machaerinic acid lactone (**11**)[10] as the aglycon, and the same sugar components shown in **1** were determined by chiral HPLC analysis (L-arabinose, D-glucose, D-quinovose, L-rhamnose, and D-xylose). However, alkaline hydrolysis of **4** gave the prosapogenin **8** and the monoterpenic acid **10**. The detailed NMR spectral comparison of **4** with that of **1** strongly suggested that proceraoside D (**4**) differed from proceraoside A (**1**) only in the absence of an α-hydroxyl group at C-16 (Tables 1−3). Accordingly, **4** contained the same sugar moieties at C-3 and C-28, and the same acyl moieties at C-21 as **1**. Thus, the structure of proceraoside D (**4**) was shown to be 3-*O*-*β*-D-xylopyranosyl-(l→2)-*β*-D-fucopyranosyl-(l→6)-*β*-D-glucopyranosyl-21-*O*-{(6′*S*)−(2′,6′-dimethyl-6′-*O*-[4-*O*-(6*S*)-menthiafolyl-*β*-D-quinovopyranosyl]-7′-octenoyl} machaerinic acid 28-*O*-α-L-arabinofuranosyl-(1→4)-[*β*-D-glucopyranosyl-(l→3)]-α-L-rhamnopyranosyl-(l→2)-*β*-D-glucopyranosyl ester.



1: R=OH
4: R=H



2: 6′*S*
3: 6′*R*



5 : R=OH
11: R=H

Experimental Section

General Experimental Procedures. Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were taken on a JASCO DIP-360 polarimeter. IR spectra were recorded on a JASCO FT/IR-5300, and NMR spectra were run on Varian UNITY 600 and/or a JEOL GSX-400 spectrometer in C_5D_5N solution, using TMS as internal standard. NMR experiments included ^{1}H−^{1}H COSY, HMQC, HMBC, TOCSY, and ROESY. Coupling constants (*J* values) are given in Hz. The FABMS (Xe gun, 10 kV, triethylene glycol as the matrix) was measured on a JEOL JMS−HX-100 mass spectrometer. HPLC separations were performed with a Hitachi HPLC system (L-6200 Pump, L-4000 UV).

Plant Material. The seeds of *A. procera* were collected from Lucknow, India, in August 1995. A voucher specimen is deposited in the Herbarium of the Upgraded Department of Pharmacology and Therapeutics, King George's Medical College, Lucknow, India.

Extraction and Isolation. The dried seeds (10.0 kg) of *A. procera* were pulverized and percolated with EtOH. The alcoholic extractive was partitioned in solvent, with hexane and Et_2O in turn. The EtOH-soluble extract, on removal of solvent, gave a golden white amorphous powder (crude saponins, 200 g). An aliquot (100 g) was passed through an Amberlite XAD-2 column, following elution with 80 and 100% MeOH. The 80% MeOH eluate (11.0 g) was subjected to HPLC on ODS with 36% CH_3CN in H_2O to give five fractions in decreasing polarity. Fraction 2 (2.57 g) was purified by HPLC on ODS with 37% CH_3CN in H_2O to furnish proceraosides B (**2**, 125 mg) and C (**3**, 30 mg). Fraction 4 (1.89 g) was subjected to HPLC on ODS with 36% CH_3CN in H_2O to yield proceraoside A (**1**, 150 mg). Fraction 5 (2.13 g) was subjected to HPLC on ODS with 38% CH_3CN in H_2O to yield proceraoside D (**4**, 135 mg).

Proceraoside A (1): colorless needles; mp 202−204 °C; $[\alpha]^{25}_D$ −23.0° (*c* 1.5, MeOH); FT-IR (dry film) ν_{max} 3400 (OH), 1740, 1710 (C=O) cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 0.97 (3H, s, H_3-25), 1.02 (3H, s, H_3-29), 1.04 (3H, s, H_3-30), 1.07 (3H, s, H_3-24), 1.18 (3H, s, H_3-26), 1.32 (3H, s, H_3-23), 1.35 (3H, d, J = 6.0 Hz, Me of qui), 1.49 (3H, d, J = 6.0 Hz, Me of fuc), 1.77 (3H, d, J = 5.8 Hz, Me of rha), 1.90 (3H, s, H_3-27), 3.44 (1H, dd, J = 13.4, 5.0 Hz, H-18), 3.62 (1H, dd, J = 11.5, 4.9 Hz, H-3), 5.22 (1H, m, H-16), 5.36 (1H, t, J = 9.6 Hz, H-4 of qui), 5.62 (1H, m, H-12), 6.20 (1H, dd, J = 11.1, 5.6 Hz, H-21), anomeric H 4.85 (1H, d, J = 7.7 Hz, qui), 4.93 (1H, d, J = 7.7 Hz, glc_1), 5.01 (1H, d, J = 7.1 Hz, fuc), 5.06 (1H, d, J = 6.9 Hz, xyl), 5.33 (1H, d, J = 7.7 Hz, glc_3), 5.88 (1H, br s, rha), 6.07 (1H, d, J = 8.0 Hz, glc_2), 6.26 [1H, br s, ara(*f*)], $MTA_1$1.06 (3H, d, J = 7.1 Hz, H_3-10), 1.54 (3H, s, H_3-9), 5.27 (1H, dd, J = 11.3, 1.1 Hz, H_2-8), 5.43 (1H, dd, J = 17.8, 1.1 Hz, H_2-8), 6.21 (1H, dd, J = 17.8, 11.3 Hz, H-7), MTA_2 1.45 (3H, s, H_3-9), 1.91 (3H, s, H_3-10), 5.17 (1H, dd, J = 10.7, 1.6 Hz, H_2-8), 5.56 (1H, dd, J = 17.3, 1.6 Hz, H_2-8), 6.10 (1H, dd, J = 17.3, 10.7 Hz, H-7), 7.13 (1H, t, J = 7.5 Hz, H-3); ^{13}C NMR data, see Tables 1−3; FABMS *m/z* $[M + Na]^+$ 2034, $[M + Na - 602]^+$ 1432.

Proceraoside B (2): colorless needles; mp 194−196 °C; $[\alpha]^{25}_D$ −20.4° (*c* 1.8, MeOH); FT-IR (dry film) ν_{max} 3400 (OH), 1740, 1710 (C=O) cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 0.96 (3H, s, H_3-25), 1.02 (3H, s, H_3-29), 1.05 (3H, s, H_3-30), 1.08 (3H, s, H_3-24), 1.17 (3H, s, H_3-26), 1.30 (3H, s, H_3-23), 1.35 (3H, d, J = 6.3 Hz, Me of qui), 1.78 (3H, d, J = 6.0 Hz, Me of rha), 1.88 (3H, s, H_3-27), 3.44 (1H, dd, J = 13.3, 4.0 Hz, H-18), 3.51 (1H, dd, J = 11.5, 4.9 Hz, H-3), 5.22 (1H, m, H-16), 5.36 (1H, t, J = 9.6 Hz, H-4 of qui), 5.64 (1H, m, H-12), 6.20 (1H, dd, J = 11.1, 5.6 Hz, H-21), anomeric H 4.85 (1H, d, J = 7.7 Hz, qui), 4.90 (1H, d, J = 8.0 Hz, glc_1), 5.00 (1H, d, J = 7.1 Hz, xyl), 5.17 (1H, d, J = 6.0 Hz, ara), 5.34 (1H, d, J = 7.7 Hz, glc_3), 5.89 (1H, br s, rha), 6.08 (1H, d, J = 8.0 Hz, glc_2), 6.26 [1H, d, J = 1.4 Hz, ara(*f*)], $MTA_1$1.06 (3H, d, J = 7.1 Hz, H_3-10), 1.54 (3H, s, H_3-9), 5.27 (1H, dd, J = 11.0, 1.4 Hz, H_2-8), 5.42 (1H, dd, J = 17.6, 1.4 Hz, H_2-8), 6.21 (1H, dd, J = 17.6, 11.0 Hz, H-7), MTA_2 1.45 (3H, s, H_3-9), 1.91 (3H, s, H_3-10), 5.17 (1H, dd, J = 10.7, 2.0 Hz, H_2-8), 5.56 (1H, dd, J = 17.3, 2.0 Hz, H_2-8), 6.12 (1H, dd, J = 17.3, 10.7 Hz, H-7), 7.13 (1H, dt, J = 7.4, 1.4 Hz, H-3); ^{13}C NMR data, see Tables 1−3; FABMS *m/z* $[M + Na]^+$ 2020, $[M + Na - 602]^+$ 1418.

Proceraoside C (3): colorless needles; mp 185−187 °C; $[\alpha]^{25}_D$ −26.6° (*c* 1.4, MeOH); FT-IR (dry film) ν_{max} 3410 (OH), 1740, 1700 (C=O) cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 0.96 (3H, s, H_3-25), 1.02 (3H, s, H_3-29), 1.05 (3H, s, H_3-30), 1.08 (3H, s, H_3-24), 1.17 (3H, s, H_3-26), 1.30 (3H, s, H_3-23), 1.35 (3H, d, J = 6.0 Hz, Me of qui), 1.78 (3H, d, J = 6.0 Hz, Me of rha), 1.88 (3H, s, H_3-27), 3.45 (1H, dd, J = 14.0, 4.5 Hz, H-18), 3.51 (1H, dd, J = 11.5, 4.9 Hz, H-3), 5.23 (1H, m, H-16), 5.37 (1H, t, J = 9.5 Hz, H-4 of qui), 5.64 (1H, m, H-12), 6.21 (1H, dd, J = 11.1, 5.6 Hz, H-21), anomeric H 4.80 (1H, d, J = 7.7 Hz, qui), 4.90 (1H, d, J = 7.7 Hz, glc_1), 5.00 (1H, d, J = 7.1 Hz, xyl), 5.16 (1H, d, J = 6.0 Hz, ara), 5.34 (1H, d, J = 8.0 Hz, glc_3), 5.89 (1H, br s, rha), 6.07 (1H, d, J = 8.0 Hz, glc_2), 6.27 [1H, d, J = 1.4 Hz, ara(*f*)], $MTA_1$1.09 (3H, d, J = 6.8 Hz, H_3-10), 1.46 (3H, s, H_3-9), 5.22 (1H, dd, J = 11.0, 1.1 Hz, H_2-8), 5.32 (1H, dd, J = 17.6, 1.1 Hz, H_2-8), 6.32 (1H, dd, J = 17.6, 11.0 Hz, H-7), MTA_2 1.45 (3H, s, H_3-9), 1.92 (3H, s, H_3-10), 5.17 (1H, dd, J = 10.7, 2.1 Hz, H_2-8), 5.56 (1H, dd, J = 17.3, 2.1 Hz, H_2-8), 6.12 (1H, dd, J = 17.3, 10.7 Hz, H-7), 7.14 (1H, dt, J = 7.4, 1.4 Hz, H-3); ^{13}C NMR data, see Tables 1−3; FABMS *m/z* $[M + Na]^+$ 2020, $[M + Na - 602]^+$ 1418.

Proceraoside D (4): colorless needles; mp 194−196 °C; $[\alpha]^{25}_D$ −12.9° (*c* 1.8, MeOH); FT-IR (dry film) ν_{max} 3410 (OH), 1740, 1710 (C=O) cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 0.95 (3H, s, H_3-29), 0.97 (6H, s, H_3-25 and H_3-30), 1.07 (3H, s, H_3-24), 1.17 (3H, s, H_3-26), 1.34 (3H, s, H_3-23), 1.35 (3H, d, J = 6.3 Hz, Me of qui), 1.39 (3H, s, H_3-27), 1.49 (3H, d, J = 6.3 Hz, Me of fuc), 1.80 (3H, d, J = 5.8 Hz, Me of rha), 3.20 (1H, dd, J = 13.4, 5.2 Hz, H-18), 3.67 (1H, dd, J = 11.5, 4.9 Hz, H-3), 5.13 (1H, dd, J = 11.1, 5.6 Hz, H-21), 5.36 (1H, t, J = 9.5 Hz, H-4 of qui), 5.47 (1H, m, H-12), anomeric H 4.86 (1H, d, J = 8.0 Hz, qui), 4.91 (1H, d, J = 7.7 Hz, glc_1), 5.03 (1H, d, J = 7.7 Hz, fuc), 5.06 (1H, d, J = 7.1 Hz, xyl), 5.34 (1H, d, J = 7.1 Hz, glc_3), 6.03 (1H, br s, rha), 6.09 (1H, d, J = 8.0 Hz, glc_2), 6.21 [1H, d, J = 1.6 Hz, ara(*f*)], $MTA_1$1.06 (3H, d, J = 6.9 Hz, H_3-10), 1.56 (3H, s, H_3-9), 5.31 (1H, dd, J = 11.0, 1.1 Hz, H_2-8), 5.45 (1H, dd, J = 17.8, 1.1 Hz, H_2-8), 6.24 (1H, dd, J = 17.8, 11.0 Hz, H-7), MTA_2 1.46 (3H, s, H_3-9), 1.91 (3H, s, H_3-10), 5.17 (1H, dd, J = 10.7, 1.9 Hz, H_2-8), 5.56 (1H, dd, J = 17.3, 1.9 Hz, H_2-8), 6.13 (1H, dd, J = 17.3, 10.7 Hz, H-7), 7.13 (1H, dt, J = 7.5, 1.4 Hz, H-3); ^{13}C NMR data, see Tables 1−3; FABMS *m/z* $[M + Na]^+$ 2018, $[M + Na - 602]^+$ 1416.

Acid Hydrolysis of Proceraoside A (1). A solution of **1** (30 mg) in 5% H_2SO_4−dioxane (1:1) was heated at 100 °C for 6 h. The reaction mixture was diluted with H_2O, and extracted with EtOAc. The EtOAc layer was subjected to Si gel column chromatography with CH_2Cl_2−MeOH (30:1) to give acacic acid lactone (**5**, 5 mg) of mp 255−257 °C; $[\alpha]^{25}_D$ +1.7° (*c* 0.5, $CHCl_3$), whose IR, ^1H NMR, ^{13}C NMR, and FABMS data were consisted with literature values.[13] The aqueous layer was neutralized with Amberlite IRA-35 and evaporated *in vacuo* to dryness. The identification and the D or L configuration of each sugar was determined by using RI detection (Waters 410) and chiral detection (Shodex OR-1) by HPLC (Shodex RSpak NH_2P-50 4D, CH_3CN−H_2O−H_3PO_4, 95:5:1, 1 mL/min, 47 °C) by comparison with an authentic sugar (10 mmol each of L-ara, D-fuc, D-glc, D-qui, L-rha, and D-xyl). The sugar portion gave the following peaks: L-(+)-rha 6.40 min; D-(+)-qui 6.70 min; D-(+)-fuc 8.10 min; D-(+)-xyl 9.10 min; L-(+)-ara 10.80 min and D-(+)-glc 20.70 min.

Alkaline Hydrolysis of Crude Saponin. A solution of crude saponin (2.0 g) in 0.6 N NaOH (80 mL) in MeOH (20 mL) was heated at 30 °C for 6 days. The reaction mixture was adjusted to pH 1.0 with 10% H_2SO_4, and extracted with *n*-BuOH. The *n*-BuOH layer was subjected to Si gel column chromatography, eluting with CH_2C1_2−MeOH−H_2O (25:2:0.1−25:8:0.1) to afford fractions 1 to 6. Fraction 3 (0.25 g) was purified by HPLC on ODS (18−15% CH_3CN) to afford a mixture of monoterpene quinovoside (**9**: mixture of **9a** and **9b**, 35 mg), and (6*S*)-menthiafolic acid (**10**, 60 mg). Fraction 5 (0.91 g) was purified by HPLC on ODS (29−28% CH_3-

CN) to give three prosapogenins, julibroside A_2 (**6**, 120 mg), albiziasaponin A (**7**, 160 mg), and **8** (400 mg).

Julibroside A_2 (6): colorless needles; mp 188−190 °C; $[\alpha]^{25}_D$ −17.3° (*c* 2.9, MeOH) exhibited comparable ^{1}H NMR, ^{13}C NMR, and FABMS data consistent with literature values.[7]

Albiziasaponin A (7): colorless needles; mp 195−197 °C; $[\alpha]^{25}_D$ −21.9° (*c* 1.6, MeOH) exhibited ^{1}H NMR, ^{13}C NMR, and FABMS data consistent with literature values.[8,9]

Compound 8: colorless needles; mp 186−188 °C; $[\alpha]^{25}_D$ +9.7° (*c* 2.6, MeOH); FT-IR (dry film) ν_{max} 3450 (OH), 1700 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, C_5D_5N) δ 0.86 (3H, s, H_3-25), 0.97 (3H, s, H_3-24), 1.01 (3H, s, H_3-26), 1.23 (3H, s, H_3-29), 1.25 (3H, s, H_3-30), 1.35 (3H, s, H_3-23), 1.37 (3H, s, H_3-27), 1.48(3H, d, J = 5.9 Hz, Me of fuc), 3.39 (1H, dd, J = 12.3, 4.5 Hz, H-18), 3.67 (1H, dd, J = 11.8, 4.4 Hz, H-3), 3.92 (1H, dd, J = 12.3, 6.5 Hz, H-21), 5.46 (1H, m, H-12), anomeric H 4.91 (1H, d, J = 7.4 Hz, glc), 5.00 (1H, d, J = 6.6 Hz, xyl), 5.01 (1H, d, J = 6.6 Hz, fuc); ^{13}C NMR data, see Tables 1 and 2; FABMS m/z [M − H]$^-$ 911, [M − H − xyl]$^-$ 779.

Compound 9: colorless oil; $[\alpha]^{25}_D$ −14.2° (*c* 3.6, MeOH); ^{1}H NMR (400 MHz, C_5D_5N) **9a** (6*S*) δ 1.31 (1H, d, J = 6.9 Hz, H_3-10), 1.56 (3H, s, H_3-9), 1.60 (1H, d, J = 5.9 Hz, Me of qui), 5.22 (1H, d, J = 10.7 Hz, H_2-8), 5.43 (1H, d, J = 17.7 Hz, H_2-8), 6.23 (1H, dd, J = 17.7, 10.7 Hz, H-7), 4.88 (1H, d, J = 7.8 Hz, H-1 of qui), **9b** (6*R*) δ 1.31 (1H, d, J = 6.9 Hz, H_3-10), 1.43 (3H, s, H_3-9), 1.60 (1H, d, J = 5.9 Hz, Me of qui), 5.15 (1H, d, J = 11.3 Hz, H_2-8), 5.28 (1H, d, J = 17.5 Hz, H_2-8), 6.33 (1H, dd, J = 17.5, 11.3 Hz, H-7), 4.82 (1H, d, J = 7.8 Hz, H-1 of qui); ^{13}C NMR data, see Table 3; FABMS m/z [M − H]$^-$ 331.

(6*S*)-Menthiafolic Acid (10): colorless oil; $[\alpha]^{25}_D$ +14.8° (*c* 0.3, MeOH); ^{1}H NMR (400 MHz, C_5D_5N) δ 1.46 (3H, s, H_3-9), 1.82 (2H, t, J = 7.8 Hz, H_2-5), 2.05 (3H, s, H_3-10), 2.50 (2H, q, J = 7.8, 7.3 Hz, H_2-4), 5.17 (1H, d, J = 10.8 Hz, H_2-8), 5.57 (1H, d, J = 17.8 Hz, H_2-8), 6.15 (1H, dd, J = 17.8, 10.8 Hz, H-7), 7.24 (1H, t, J = 7.3 Hz, H-3); ^{13}C NMR data, see Table 3; FABMS m/z [M − H]$^-$ 183.

Acid Hydrolysis of Monoterpene Quinovoside (9). Acid hydrolysis of **9** (4 mg) was carried out as described for **1** to afforded D-quinovose on HPLC analysis.

Acid Hydrolysis of Proceraosides B and C (2 and 3). Acid hydrolysis of **2** and **3** (each 5 mg) was carried out in the same manner as described for **1** to yield acacic acid lactone (**5**) on TLC: **5**, R_f 0.23 (CH_2Cl_2−MeOH, 25:1). The aqueous layer was analyzed in the same way as described for **1** to give L-ara, D-glc, D-qui, L-rha, and D-xyl.

Acid Hydrolysis of Proceraoside D (4). Acid hydrolysis of **4** (40 mg) was carried out in the same manner as described for **1** to yield machaerinic acid lactone (**11**, 15 mg) of mp 258−260 °C; $[\alpha]^{25}_D$ −15.0° (*c* 0.5, $CHCl_3$), whose IR, ^{1}H NMR, ^{13}C NMR, and FABMS data were consisted with literature values.[10] The aqueous layer afforded L-ara, D-fuc, D-glc, D-qui, L-rha, and D-xyl on HPLC analysis, as described for **1**.

Alkaline Hydrolysis of Proceraosides A−D (1−4). Compounds **1**−**4** (each 5 mg) was hydrolyzed in same way as described for the crude saponin fraction to yield a prosapogenin (**6**) and a monoterpene (**10**) from **1**, prosapogenin **7** and **10** from **2** and **3**, and prosapogenin **8** and **10** from **4**. TLC data: **6**, R_f 0.51; **7**, R_f 0.46; **8**, R_f 0.33 (CH_2Cl_2−MeOH−H_2O, 25:8:0.1); **10**, R_f 0.55 (CH_2Cl_2−MeOH−H_2O, 25:2:0.1).

Acknowledgment. We are grateful to Dr. T. Miyase, School of Pharmaceutical Sciences, University of Shizuoka, for mass spectral measurements.

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NP970538R