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SAPONINS FROM *ALBIZIA LEBBECK*

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Key Word Index—*Albizia lebbeck*; Leguminosae; Mimosaceae; oleanane glycoside; acacic acid lactone; albiziasaponin.

Abstract—Three main saponins named albiziasaponins A, B, and C were isolated from the barks of *Albizia lebbeck*. Their structures were established through spectral analyses as acacic acid lactone 3-*O*-*β*-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-*β*-D-glucopyranoside, 3-*O*-*β*-D-glucopyranosyl-(1 → 2)-*O*-[α-L-arabinopyranosyl-(1 → 6)]-*β*-D-glucopyranoside and 3-*O*-*β*-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-*O*-[*β*-D-glucopyranosyl-(1 → 2)]-*β*-D-glucopyranoside.

INTRODUCTION

Albizia lebbeck Benth is widely distributed in India and is also found in South Africa and Australia. It is a host of lac insect [1] and is reported [2] to have antiseptic, antidysentric and anti-tubercular activities. The saponins of seeds exhibit antiovulatory properties. The seeds were also studied because of their lipid composition and their use as food [3]. The saponin constituents of this genus so far described are echinocystic acid glycosides [4, 5]. We now report the isolation and structure elucidation of three main saponins (**1**–**3**) from the barks of the title plant.

RESULTS AND DISCUSSION

The dried barks of *A. lebbeck* were extracted successively with petrol and methanol. The methanol extract was partitioned between H_2O and EtOAc, and the water layer was then extracted with *n*-BuOH to afford a saponin fraction. Repeated separation of the saponin fraction by chromatography over ordinary phase silica gel and reversed-phase silica gel furnished three novel saponins, named albiziasaponins A (**1**), B (**2**) and C (**3**). Analysis by ^1H–^1H COSY, ^1H–^{13}C COSY, HMBC, TOCSY and ROESY led to determination of the complete structures of **1**–**3**, inclusive of the sequence of the sugar moieties and the position of attachment of the sugar chains to the aglycone.

Albiziasaponin A (**1**), $[\alpha]_D$ − 22.0°, was obtained as needles and deduced to have the molecular formula $C_{46}H_{72}O_{17}$ from the observation of quasi-molecular ion at *m/z* 895 $[M - H]^-$ in the negative FAB-mass spectrum and carbon counts in the ^{13}C NMR spectrum. The IR absorption band at 1760 cm^{-1} and the peak at δ181.3 in the ^{13}C NMR spectrum showed the presence of a *γ*-lactone ring. The acid hydrolysis of **1** afforded L-arabinose, D-glucose and D-xylose in a ratio of 1:1:1 confirmed by specific rotation using chiral detection in HPLC. The ^1H and ^{13}C NMR spectra of **1** indicated the presence of one α-arabinopyranosyl unit [H-1: δ5.18 (*d*, *J* = 5.1 Hz), C-1: δ102.4], one *β*-glucopyranosyl unit [H-1: δ4.91 (*d*, *J* = 7.8 Hz), C-1: δ106.8] and one *β*-xylopyranosyl unit [H-1: δ5.00 (*d*, *J* = 6.8 Hz), C-1: δ106.4]. The molecular formula $C_{46}H_{72}O_{17}$ implied 11 degrees of unsaturation. Six can be assigned to one carbonyl group (δ181.3), one lactone ring, one olefinic bond (δ140.1 and 124.6), and three hemiacetal linkages of the sugar parts. The remaining five are due to the pentacyclic triterpene ring system indicated by the positive Salkowsky reaction. ^1H–^1H COSY, ^1H–^{13}C COSY, and HMBC, experiments enabled us to construct the aglycone skeleton. The ^1H–^1H connectivity from the COSY spectrum of **1** suggested the isolated spin systems (H-1–3, H-5–7, H-9–12, H-15–16, H-18–19, H-21–22).

The gross structure of the aglycone of **1** was determined by analysis of NMR data including ^1H–^1H COSY, ^1H–^{13}C COSY, HMBC, and ROESY experiments (Table 1), and by referring to the NMR data of acacic acid lactone [6–8] and echinocystic acid 3-*O*-glycosides [4, 5]. The cross-peaks from the proton signal (δ4.52) of C-16 (δ66.8) to the carbon signal at δ50.0 (C-17) and 181.3 (C-28) located a hydroxy group at C-16, and the cross-peak from the proton signal (δ4.23) of C-21 (δ83.5) to the carbonyl signal at δ181.3 (C-28) indicated that a 28, 21*β* olide is over the E-ring, which was consistent with the observed band (1760 cm^{-1}) in the IR spectrum. The NOEs between H-16 (δ4.52) and H-26 (δ0.78), and H-16 and H*β*-15 (δ2.30) indicated an α-configuration of the C-16 hydroxyl group and a boat conformation of the D-ring. Furthermore, NOEs were observed between Hα-19 (δ1.82) and Hα-21 (δ4.23)/Hα-22 (δ2.25)/H-27 (δ1.38),

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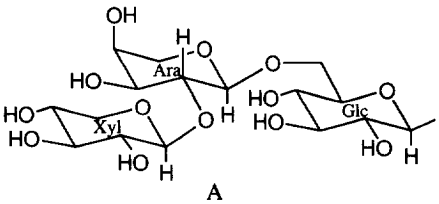
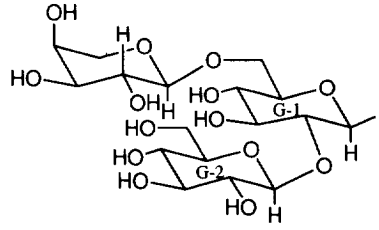


A



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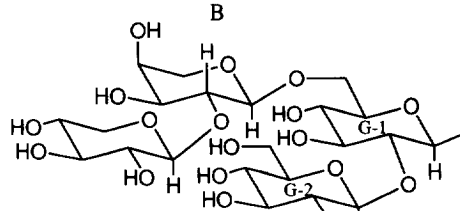
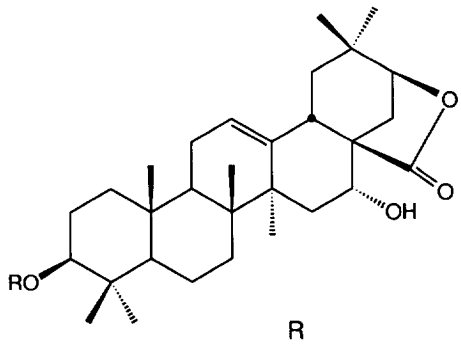


C



	R
1	A
2	B
3	C

suggesting a boat conformation of the E-ring. The absolute configuration at C-21 was determined to be *S* through the application of a Hudson–Klyne' lactone rule [9–11]. Hence, the aglycone of **1** was shown to be 3β,16α-dihydroxyolean-12-ene-28,21β-olide, namely, acacic acid lactone. The sugar sequence was determined as follows. The negative FAB-mass spectrum of **1** showed the fragment ion peaks *m/z* 763 $[M - C_5H_8O_4 - H]^-$ and *m/z* 631 $[M - 2C_5H_8O_4 - H]^-$, disclosing the sugar sequence to be Xyl-Ara-Glc-*O*- or Ara-Xyl-Glc-*O*-. In the ^{13}C NMR spectrum of **1**, the C-2 position of arabinose and C-6 position of glucose were shifted to δ80.7 and 69.6, respectively, by the glycosylation shifts [12, 13], showing that the sugar sequence was Xyl $\xrightarrow{2}$ Ara $\xrightarrow{6}$ Glc-*O*. In the HMBC experiment on **1**, long-range correlations were observed between H-1 (δ4.91) of the glucose and C-3 (δ88.5) of the aglycone, H-1 (δ5.18) of the arabinose and C-6 (δ69.6) of the glucose, and H-1 (δ5.00) of the xylose and C-2 (δ80.7) of the arabinose. Furthermore, NOEs were observed between H-1 (δ4.91) of the glucose and H-3 (δ3.52) of the aglycone, and H-1 (δ5.00) of the xylose and H-2 (δ4.55) of the arabinose. Hence, compound **1** was formulated as acacic acid lactone 3-*O*-β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside.

Comparisons of the ^{13}C NMR spectra of **2** and **3** with that of **1** showed that **2** and **3** were also glycosides of the same aglycone framework that varied structurally from **1** only in their saccharide moieties, and that these sugar units were also affixed to the C-3 position.

Albiziasaponin B (**2**), $[\alpha]_D$ − 40.0°, was obtained as needles and deduced to have the molecular formula $C_{47}H_{74}O_{18}$ from the observation of quasi-molecular ion at *m/z* 965 $[M + K]^+$ and 925 $[M - H]^-$ in the FAB-mass spectra. On acid hydrolysis, compound **2** afforded D-glucose and D-xylose in a ratio of 2:1, confirmed by specific rotation using chiral detection in HPLC. The ^1H and ^{13}C NMR spectra of **2** indicated the presence of one α-arabinopyranosyl unit [H-1: δ4.92 (*d*, *J* = 6.5 Hz), C-1: δ105.3], two β-glucopyranosyl units [H-1: δ4.83 (*d*, *J* = 8.0 Hz), C-1: δ105.1; H-1: δ5.33 (*d*, *J* = 7.3 Hz), C-1: δ106.1]. The negative FAB-mass spectrum of **2** showed the fragment ion peaks at *m/z* 793 $[M - C_5H_8O_4 - H]^-$ and 763 $[M - C_6H_{10}O_5 - H]^-$, disclosing the branched sugar. In the ^{13}C NMR spectrum of **2**, the C-2 and C-6 positions of glucose were shifted to δ83.2 and 69.7 respectively, establishing the site of glycosylation in **2**. In the HMBC experiment on **2**, long-range correlations were observed between H-1 (δ4.83) of the glucose (G-1) and C-3 (δ89.0) of the aglycone, H-1 (δ4.92) of the arabinose and C-6 (δ69.7) of the glucose (Glc-1), and H-1 (δ5.33) of the glucose (Glc-2) and C-2 (δ83.2) of the glucose (Glc-1). Hence, compound **2** was formulated as acacic acid lactone 3-*O*-β-D-glucopyranosyl (1 → 2)-*O*-[α-L-arabinopyranosyl-(1 → 6)] β-D-glucopyranoside.

Albiziasaponin C (**3**), $[\alpha]_D$ − 23.5°, was obtained as needles. The negative FAB-mass spectrum of **3** showed ion peaks at *m/z* 1057 $[M - H]^-$, 925 $[M - C_5H_8O_4 - H]^-$, 895 $[M - C_6H_{10}O_5 - H]^-$ and 763 $[M - C_5H_8O_4 - C_6H_{10}O_5 - H]^-$, i.e. 162 mass units higher than that of **1**, suggesting the molecular formula $C_{52}H_{82}O_{22}$. The acid hydrolysis of **3** afforded L-arabinose, D-glucose and D-xylose in a ratio of 1:2:1 confirmed by specific rotation using chiral detection in HPLC. The ^1H and ^{13}C NMR spectra of **3** indicated the presence of one α-arabinopyranosyl unit [H-1: δ5.14 (*d*, *J* = 5.1 Hz), C-1: δ102.5], two β-glucopyranosyl units [H-1: δ4.88 (*d*, *J* = 7.3 Hz), C-1: δ105.1 (Glc-1); H-1: δ5.39 (*d*, *J* = 7.6 Hz),

Table 1. ^1H and ^{13}C NMR data for **1–3** (pyridine-d_5, δ-values)

		1*			2†	3*		
	C	δ_C	Long-range C–H connectivities (H)	ROESY (H)	δ_C	δ_C	Long-range C–H connectivities (H)	ROESY (H)
	1	38.7	25	3, 5, 9	38.6	38.7	25	3, 5, 9
	2	26.8		24, 25	26.6	26.9		24, 25
	3	88.5	1 of Glc-1, 23, 24	1, 5, 23	89.0	88.6	1 of Glc-1, 23, 24	1, 5, 23
	4	39.6	23, 24		39.5	39.6	23, 24	
	5	56.0	23, 24, 25	1, 3, 7, 9	55.8	56.0	23, 24, 25	1, 3, 7, 9
	6	18.5		23, 24, 25, 26	18.4	18.5		23, 24, 25, 26
	7	32.6	26	5, 9, 15, 26, 27	32.5	32.6	26	5, 9, 15, 26, 27
	8	40.4	26, 27		40.3	40.4	26, 27	
	9	47.3	12, 25, 26	1, 5, 7, 27	47.2	47.3	12, 25, 26	1, 5, 7, 27
	10	37.0	25		36.9	37.0	25	
	11	23.8		1, 25, 26	23.7	23.8		1, 25, 26
	12	124.6		18	124.6	124.6		18
	13	140.1	27		140.1	140.1	27	
	14	43.4	12, 18, 26, 27		43.3	43.4	12, 18, 26, 27	
	15	38.3	27	7, 26, 22, 27	38.2	38.2	27	7, 26, 22, 27
	16	66.8	16	15, 26	66.7	66.8	16	15, 26
	17	50.0	16, 18, 21		50.0	50.0	16, 18, 21	
	18	41.8	12	12, 30	41.7	41.8	12	12, 30
	19	43.0	29, 30	21, 22, 27, 29	42.9	43.0	29, 30	21, 22, 27, 29
	20	34.2	29, 30		34.2	34.2	29, 30	
	21	83.5	21, 29, 30	19, 29	83.4	83.5	21, 29, 30	19, 29
	22	27.2	18	15, 19	26.7	27.2	18	15, 19
	23	28.2	24	3, 5, 6, 24	28.1	28.2	24	3, 5, 6, 24
	24	17.1	23	2, 6, 23, 25	16.8	16.8	23	2, 6, 23, 25
	25	15.8		2, 6, 11, 24, 26	15.7	15.8		2, 6, 11, 24, 26
	26	16.3		6, 7, 11, 16, 25	16.2	16.3		6, 7, 11, 16, 25
	27	28.9	15	7, 9, 15	28.7	28.9	15	7, 9, 15
	28	181.3			181.3	181.3		
	29	28.6	30	19, 21, 30	28.6	28.6	30	19, 21, 30
	30	24.3	29	18, 19, 30	24.3	24.3	29	18, 19, 30
Glc-1	1	106.8			105.1	105.1		
	2	75.7			83.2	83.2	1 of Glc-2	
	3	78.4			78.2	78.0		
	4	72.3			72.3	72.0		
	5	76.3			76.4	76.0		
	6	69.6	1 of Ara		69.7	69.3	1 of Ara	
Ara	1	102.4			105.3	102.5		
	2	80.7	1 of Xyl		71.6	80.8	1 of Xyl	
	3	72.7			74.3	72.7		
	4	67.4			69.1	67.4		
	5	64.4			66.5	64.4		
Xyl	1	106.4				106.5		
	2	75.5				75.6		
	3	77.9				78.0		
	4	70.9				70.9		
	5	67.5				67.5		
Glc-2	1				106.1	106.1		
	2				77.1	77.3		
	3				78.0	78.0		
	4				71.6	71.6		
	5				78.3	78.4		
	6				62.7	62.7		

*50 MHz.
†150 MHz.

C-1: δ106.1 (Glc-2)] and one β-xylopyranosyl unit [H-1: δ4.98 (*d*, *J* = 7.1 Hz), C-1: δ106.5]. The carbon signals due to the sugar moieties were superimposable on those of compound **2** isolated from same plant by Orsini *et al.* [5]. The sugar sequence of **3** was also confirmed by HMBC and ROESY experiments (Table 1). Hence, **3** was formulated as acacic acid actone 3-*O*-β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-*O*-[β-D-glucopyranosyl-(1 → 2)]-β-D-glucopyranoside.

EXPERIMENTAL

Mps were measured with a Yanagimoto micromelting point apparatus and were uncorr. Optical rotations were taken on a JASCO DIP-140 digital polarimeter, NMR spectra on Varian UNITY 200 and 600 spectrometers in pyridine-d_5 soln using TMS as an int. standard. NMR experiments included ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY, HMBC, TOCSY and ROESY. Coupling constants (*J* values) are given in Hz. The FAB-MS (Xe gun, 10 kV, triethylene glycol as the matrix) was measured on a JEOL JMS-PX303 mass spectrometer. For CC, Kiesel gel 60 (230–400 mesh, Merck), and for TLC, silica gel 60F-254 (Merck) were used. HPLC was carried out with a Waters ALC/GPC 244 instrument.

Plant material. Albizia lebbeck was collected on the campus of Indian Institute of Chemical Biology in June 1993 and was identified by Dr N. D. Paris, Department of Botany, University of Calcutta.

Extraction and isolation of compounds **1**–**3**. Air-dried and powdered bark (1.5 kg) of *A. lebbeck* was defatted with petrol and then extracted with MeOH. The MeOH soln was evapd to dryness *in vacuo*. The residue (21 g) was suspended in water, extracted successively with EtOAc and *n*-BuOH (3 × 300 ml each) and the solns were evapd to dryness *in vacuo* to provide EtOAc-soluble (5 g), *n*-BuOH-soluble (10 g) and water-soluble portions (4 g). The *n*-BuOH-soluble portion was subjected to Sephadex LH-20 CC eluting with MeOH to give a crude saponin fr. (7 g) that showed many spots on silica gel TLC with $CHCl_3$–MeOH–H_2O (13:7:2). This mixt. was subjected to CC on silica gel eluting with $CHCl_3$–MeOH (9:1) to yield fr. I (0.7 g); subsequent elution with $CHCl_3$–MeOH (4:1) afforded fr. II (1.5 g) and fr. III (2.1 g). Frs II and III were thereafter purified by repeated CC over silica gel eluting with $CHCl_3$–MeOH–H_2O (40:10:1) to give crude albiziasaponin A (0.05 g), and the mixture of albiziasaponins B and C (0.2 g), which were further purified by prep. HPLC (YMC ODS, 27–30% MeCN) furnishing albiziasaponin A (**1**, 30 mg) from fr. A. and albiziasaponins B (**2**, 20 mg) and C (**3**, 30 mg) from fr. B, respectively.

Albiziasaponin A (**1**). Needles, mp 200–202°, $[\alpha]_D$ − 22.0° (pyridine; *c* 3.0). FAB-MS *m/z*: 895 $[M - H]^-$, 763 $[M - Xyl - H]^-$, 631 $[M - Xyl - Ara - H]^-$. ^{1}H NMR (600 MHz): δ0.78 (3H, *s*, H_3-26), 0.82 (3H, *s*, H_3-25), 0.91 (3H, *s*, H_3-29), 0.99 (3H, *s*, H_3-30), 1.05 (3H, *s*, H_3-24), 1.32 (3H, *s*, H_3-23), 1.38 (3H, *s*, H_3-27), 1.36 (1H, *dd*, *J* = 13.3, 5.0 Hz, H_β-19), 1.44 (1H, *dd*, *J* = 14.6, 12.4 Hz, H_α-15), 1.82 (1H, *dd*, *J* = 13.3, 13.0 Hz, H_α-19), 2.25 (1H, *d*, *J* = 12.0 Hz, H_α-22), 2.30 (1H, *dd*, *J* = 14.6, 5.0 Hz, H_β-15), 2.76 (1H, *dd*, *J* = 12.0, 5.4 Hz, H_β-22), 3.52 (1H, *dd*, *J* = 11.7, 4.4 Hz, H-3), 4.23 (1H, *d*, *J* = 5.4 Hz, H-21), 4.52 (1H, *dd*, *J* = 12.4, 5.0 Hz, H-16), 5.30 (1H, *m*, H-12), 4.55 (1H, *dd*, *J* = 6.0, 5.1 Hz, H-2 of Ara), 4.91 (1H, *d*, *J* = 7.8 Hz, H-1 of Glc), 5.00 (1H, *d*, *J* = 6.8 Hz, H-1 of Xyl), 5.18 (1H, *d*, *J* = 5.1 Hz, H-1 of Ara). ^{13}C NMR: Table 1.

Albiziasaponin B (**2**). Needles, mp 260–262°, $[\alpha]_D$ − 40.0° (pyridine; *c* 2.1). Negative FAB-MS *m/z*: 925 $[M - H]^-$, 793 $[M - Ara - H]^-$, 763 $[M - Glc - H]^-$. Positive FAB-MS: *m/z* 965 $[M + K]^+$. ^{1}H NMR (200 MHz): δ0.77 (3H, *s*, H_3-26), 0.79 (3H, *s*, H_3-25), 0.96 (3H, *s*, H_3-29), 1.07 (3H, *s*, H_3-30), 1.10 (3H, *s*, H_3-24), 1.22 (3H, *s*, H_3-23), 1.31 (3H, *s*, H_3-27), 3.20 (1H, *dd*, *J* = 12.0, 5.5 Hz, H-3), 4.25 (1H, *d*, *J* = 4.0 Hz, H-21), *ca* 4.53 (1H, *m*, H-16), 5.32 (1H, *m*, H-12), 4.83 (1H, *d*, *J* = 8.0 Hz, H-1 of Glc), 4.92 (1H, *d*, *J* = 6.5 Hz, H-1 of Ara), 5.33 (1H, *d*, *J* = 7.3 Hz, H-1 of Glc). ^{13}C NMR: Table 1.

Albiziasaponin C (**3**). Needles, mp 198–200°, $[\alpha]_D$ − 23.5° (pyridine; *c* 3.2). Negative FAB-MS *m/z*: 1057 $[M - H]^-$, 925 $[M - Xyl - H]^-$, 895 $[M - Glc - H]^-$, 763 $[M - Xyl - Glc - H]^-$. ^{1}H NMR (600 MHz) (pyridine-d_5): δ0.79 (3H, *s*, H_3-26), 0.83 (3H, *s*, H_3-25), 0.91 (3H, *s*, H_3-29), 1.05 (3H, *s*, H_3-30), 1.11 (3H, *s*, H_3-24), 1.29 (3H, *s*, H_3-23), 1.37 (3H, *s*, H_3-27), 1.36 (1H, *dd*, *J* = 13.3, 4.5 Hz, H_β-19), 1.43 (1H, *dd*, *J* = 13.5, 12.5 Hz, H_α-15), 1.80 (1H, *dd*, *J* = 13.5, 13.0 Hz, H_α-19), 2.25 (1H, *d*, *J* = 12.0 Hz, H_α-22), 2.29 (1H, *dd*, *J* = 13.5, 4.5 Hz, H_β-15), 2.75 (1H, *dd*, *J* = 12.0, 5.3 Hz, H_β-22), 3.44 (1H, *dd*, *J* = 12.0, 5.5 Hz, H-3), 4.25 (1H, *d*, *J* = 5.3 Hz, H-21), 4.52 (1H, *dd*, *J* = 12.5, 4.5 Hz, H-16), 5.33 (1H, *m*, H-12), 4.17 (1H, *dd*, *J* = 8.0, 7.3 Hz, H-2 of Glc-1), 4.52 (1H, *dd*, *J* = 6.0, 5.1 Hz, H-2 of Ara), 4.88 (1H, *d*, *J* = 7.3 Hz, H-1 of Glc-1), 4.98 (1H, *d*, *J* = 7.1 Hz, H-1 of Xyl), 5.14 (1H, *d*, *J* = 5.1 Hz, H-1 of Ara), 5.39 (1H, *d*, *J* = 7.6 Hz, H-1 of Glc-2). ^{13}C NMR: Table 1.

Acid hydrolysis of albiziasaponins A (**1**), *B* (**2**) *and C* (**3**). A soln of each compound (3 mg) in 5% EtOH containing 5% H_2SO_4 was heated at 100° for 3 hr. The reaction mixt. was cooled and extracted with Et_2O. The aq. layer was neutralized with Amberlite IR-45 and evaporated *in vacuo* to dryness. Sugar was identified by using RI detection (Waters 410) and chiral detection (Shodex OR-1) in HPLC (Shodex RSpak DC-613, 75% MeCN, 1 ml min^{-1}, 70°) and comparison with authentic sugars (10 mM each of L-Ara, D-Glc and D-Xyl). The sugar part gave 3 peaks showing positive optical rotation at 5.75 min (D-Xyl, 5.73 min), 6.20 min (L-Ara, 6.18 min) and 7.38 min (D-Glc, 7.36 min).

REFERENCES

1. Watt, J. M. and Breyer-Brandwijk, M. G. (1962) *The Medicinal and Poisonous Plants of South and East Africa*, 2nd Edn, p. 556. Livingstone, Edinburgh.
2. Chadha, Y. R., (ed.) (1985) *The Wealth of India, Raw Materials*, Vol. **1**-A, p. 126. CSIR, New Delhi.

3. Chowdhury, A. R., Banerji, R., Misra, G. and Nigam, S. K. (1984) *J. Am. Oil Chem. Soc.* **61**, 1023.
4. Carpani, G., Orsini, F., Sisti, M. and Verotta, L. (1989) *Phytochemistry* **28**, 863.
5. Orsini, F., Pelizzoni, F. and Verotta, L. (1991) *Phytochemistry* **30**, 4111.
6. Anjaneyulu, A. S. R., Bapuji, M., Rao, M. G., Row, L. R., Sastry, P. C. S., Sree, A. and Subrahmanyam, C. (1977) *Indian J. Chem.* **15B**, 1.
7. Mahato, S. B., Pal, B. C. and Price, K. R. (1989) *Phytochemistry* **28**, 207.
8. Alegrio, L. V., Massiot, G., Lavaud, C., Le Men-Olivier, L. and Sevenet, T. (1993) *Plant Med. Phytother.* **26**, 101.
9. Hudson, C. S. (1910) *J. Am. Chem. Soc.* **32**, 338.
10. Hudson, C. S. (1939) *J. Am. Chem. Soc.* **61**, 1525.
11. Klyne, W. (1954) *Chem. Ind.* 1198.
12. Kasai, R., Okihara, M., Asakawa, J., Mizutani, K. and Tanaka, O. (1979) *Tetrahedron* **35**, 1427.
13. Tori, K., Yoshimura, Y., Arita, H. and Tomita, Y. (1979) *Tetrahedron Letters* 179.