Six New Triterpenoidal Glycosides Including Two New Sapogenols from Albizziae Cortex. V[1)]

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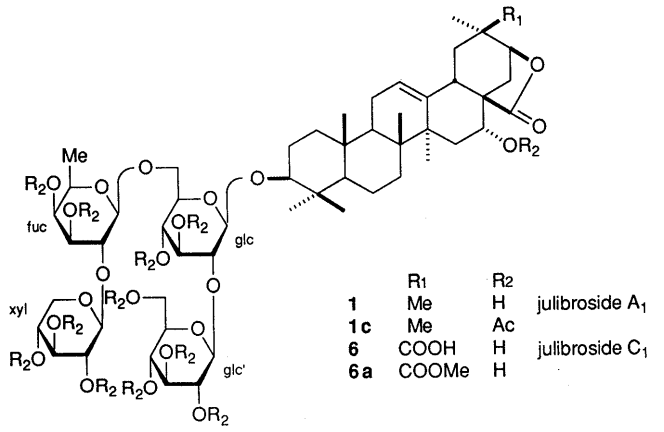
Six new triterpenoid glycosides called julibrosides A_1—A_4, B_1 and C_1 were isolated from Albizziae Cortex, the dried stem bark of *Albizzia julibrissin* DURAZZ. Their structures were determined based on spectral and chemical evidence. Julibrosides B_1 and C_1 had new sapogenols, designated julibrogenin B and C, respectively, while julibrosides A_3 included *N*-acetyl-D-glucosamine as a sugar component.

Keywords Albizziae Cortex; *Albizzia julibrissin*; Leguminosae; oleanene glycoside; oleanene sapogenol; julibrogenin; julibroside; *N*-acetyl-D-glucosamine

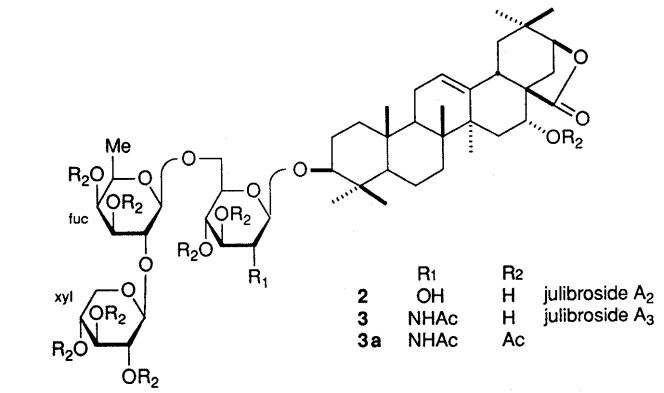
The dried stem bark of *Albizzia julibrissin* DURAZZ, Albizziae Cortex, is used as a tonic in China and Japan. During our studies on the constituents of leguminous plants,[1)] we have isolated fourteen glycosides[2)] including syringaresinol diglucoside which appears to be responsible for the pharmacological effect of a tonic.[3)]

Although earlier researchers found that the saponin fraction of this crude drug showed a strong uterotonic action, they reported the structure of sapogenins only from the acid hydrolysate of the fraction[4)]; there has been no report on the isolation of saponins. This paper deals with the isolation and structural elucidation of the genuine saponins (**1**—**6**) from this crude drug.

The crude saponin fraction obtained from Albizziae Cortex was chromatographed on reversed-phased silica gel (Bondapak C_{18}) column and divided into five fractions. Each fraction was repeatedly chromatographed on silica gel column to give triterpene glycosides, **1**—**6**.



	R1	R2	
1	Me	H	julibroside A_1
1c	Me	Ac	
6	COOH	H	julibroside C_1
6a	COOMe	H	



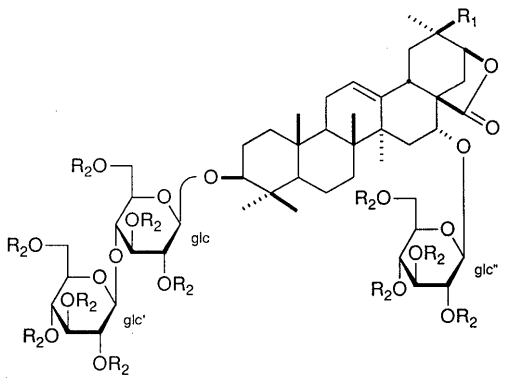
	R1	R2	
2	OH	H	julibroside A_2
3	NHAc	H	julibroside A_3
3a	NHAc	Ac	

Julibroside A_1 (**1**) was obtained as a white amorphous powder, $[\alpha]_D$ −12.6° (MeOH). The infrared (IR) spectrum of **1** featured absorptions of γ-lactone (1770 cm^{-1}) and hydroxy group. In the positive fast atom bombardment-mass spectrum (FAB-MS), **1** showed an $[M+Na]^+$ ion at *m/z* 1095. Fragment ion peaks at *m/z* 963 $[M+Na-pentose]^+$, 941 $[M+Na-hexose]^+$, 795 $[M+H-pentose-methylpentose]^+$ and 663 $[M+H-pentose-methylpentose-hexose]^+$ were also observed. The electron impact (EI)-MS of the acetate (**1c**) for **1** exhibited the characteristic terminal pentosyl and terminal hexosyl cation at *m/z* 259 and 331, respectively. In addition, the terminal

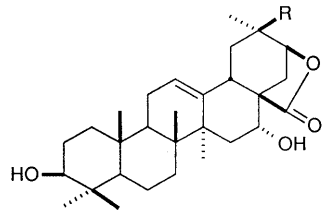
TABLE I. ^{13}C-NMR Data for Compounds **1**—**6a** (Aglycone Moieties), **1a**, **1b** and **5b**

	1a[a)]	1b	5b	1	2	3	4	5	6a
C- 1	38.5	39.0	39.0	38.6	38.6	38.5	38.4	38.1	38.6
C- 2	27.2	28.1	28.2	26.8	26.7	26.7	26.4	26.1	26.8
C- 3	78.9	78.1	78.1	88.1	87.9	88.1	88.9	88.7	88.2
C- 4	38.8	39.4	39.4	39.6	39.5	39.4	39.5	39.1	39.6
C- 5	55.5	56.0	56.0	56.0	55.8	55.9	55.9	55.6	55.9
C- 6	18.2	18.9	18.9	18.4	18.3	18.4	18.5	18.2	18.4
C- 7	32.1	33.6	33.6	32.5	32.4	32.6	32.5	32.2	32.5
C- 8	40.3	39.9	40.0	40.3	40.3	40.4	40.1	39.8	40.3
C- 9	47.0	47.3	47.3	47.3	47.2	47.2	47.2	46.9	47.2
C-10	37.0	37.5	37.5	36.9	36.9	37.0	37.0	36.7	37.0
C-11	23.5	23.9	23.9	23.8	23.7	23.7	23.7	23.5	23.9
C-12	125.0	122.7	123.1	124.5	124.4	124.5	123.5	123.2	124.9
C-13	139.2	144.5	144.3	140.1	140.0	140.1	140.0	139.5	139.4
C-14	43.3	42.1	42.2	43.3	43.2	43.3	42.6	42.3	43.1
C-15	26.5	35.9	35.9	38.2	38.1	38.2	33.4	32.9	37.5
C-16	67.6	74.4	74.4	66.7	66.6	66.6	77.0	76.5	66.4
C-17	49.7	51.8	51.9	49.9	49.8	50.0	49.8	50.0	49.4
C-18	40.5	41.1	40.7	41.7	41.6	41.7	41.7	41.3	40.6
C-19	43.7	48.6	44.4	42.8	42.7	42.8	37.9	33.2	37.0
C-20	33.8	36.7	40.3	34.1	34.0	34.1	34.1	38.9	45.4
C-21	83.7	73.5	75.3	83.4	83.3	83.4	84.4	81.3	78.9
C-22	36.2	41.9	42.2	27.1	27.0	27.1	29.1	28.6	29.0
C-23	28.8	28.8	28.8	28.5	28.4	28.5	28.1	27.9	28.2
C-24	15.6	15.7	15.7	15.8	15.6	15.7	15.5	15.2	15.7
C-25	15.6	16.6	16.6	16.3	16.1	16.3	16.4	16.1	16.3
C-26	16.0	17.6	17.6	16.8	16.9	17.0	16.9	16.6	16.8
C-27	28.1	27.2	27.4	28.0	28.0	28.0	27.1	26.8	28.0
C-28	181.0	179.4	179.0	181.2	181.2	181.2	181.2	180.9	181.1
C-29	29.0	30.1	25.5	28.9	28.9	28.8	28.9	27.4	22.4
C-30	23.8	18.4	65.5	24.2	24.1	24.2	26.1	66.6	176.0
OMe									52.2

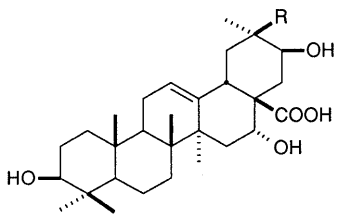
Chemical shifts (δ: ppm) were measured in pyridine-d_5 or *a*) in $CDCl_3$.



	R_1	R_2	
4	Me	H	julibroside A_4
4a	Me	Ac	
5	CH_2OH	H	julibroside B_1



	R	
1a	Me	acacic acid lactone
5a	CH_2OH	julibrogenin B
6b	COOMe	julibrogenin C methyl ester



	R	
1b	Me	acacic acid
5b	CH_2OH	

pentosyl-methylpentosyl cation was observed at *m/z* 489. The sapogenol obtained by acid hydrolysis of **1** was identified with acacic acid lactone (**1a**)[4] on thin layer chromatography (TLC). The ^{13}C-nuclear magnetic resonance (NMR) spectrum of **1** showed thirty signals due to sapogenol carbons (Table I) which were almost identical with those of **1a** except for C-3 signal with glycosylation shift,[5] indicating **1** was a 3-*O*-monodesmoside. The detailed analyses of the ^{13}C–^1H correlation spectroscopy (COSY) and ^1H–^1H COSY spectrum of **1** led to assignment of the glycosidic moiety as xylopyranosyl-(1→2)-fucopyranosyl-(1→6 or 1→2) [glucopyranosyl-(1→6 or 1→2)]-glucopyranoside (Table II). Investigation of the differential nuclear Overhauser effect (NOE) spectrum of **1** (Fig. 1) determined that the linkage of glycosidic moiety was acacic acid lactone 3-*O*-xylopyranosyl-(1→2)-fucopyranosyl-(1→6) [glucopyranosyl-(1→2)]-glucopyranoside. Since the absolute configurations of sugar species were identified according to the method reported by Hara *et al.*,[6] and the configurations of C-1 for the sugars were determined to be all *β* by ^1H-NMR spectrum, the structure of **1** was established as acacic acid lactone 3-*O*-*β*-D-xylopyranosyl-(1→2)-*β*-D-fucopyranosyl-(1→6) [*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucopyranoside.

Julibroside A_2 (**2**) was obtained as a white amorphous powder, $[\alpha]_D$ −15.2° (MeOH). An acidic hydrolysis of **2** gave acacic acid lactone (**1a**) as the sapogenol. In the FAB-MS of **2**, an $[M+Na]^+$ ion at *m/z* 933 appeared less than those of **1** by a hexosyl moiety. Since the fission patterns of sugar moiety at *m/z* 779 $[M+H-\text{pentose}]^+$, 633 $[M+H-\text{pentose}-\text{methylpentose}]^+$ were the same as those of **1**, the structure of **2** seemed to be a deshexosyl compound of **1**. In the ^{13}C-NMR spectrum of **2** (Tables I and II), the terminal glucosyl signals disappeared in contrast to those of **1**, and the remaining signals except for C-1—3 signals of the inner glucosyl moiety were identical with those of **1**.

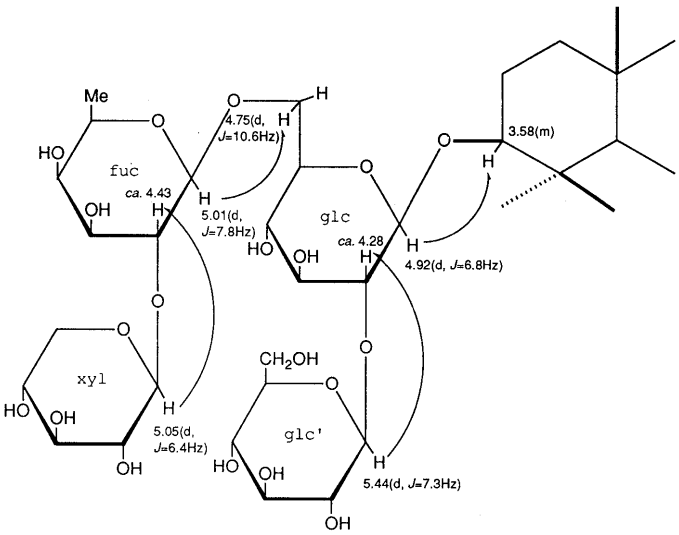


Fig. 1. The Differential NOE Experiment for **1**

Therefore, **2** was concluded to be the desglucosyl compound of **1**, that is, acacic acid lactone 3-*O*-*β*-D-xylopyranosyl-(1→2)-*β*-D-fucopyranosyl-(1→6)-*β*-D-glucopyranoside.

Julibroside A_3 (**3**) was obtained as a white amorphous powder, $[\alpha]_D$ −7.7° (MeOH) and gave acacic acid lactone (**1a**) on acid hydrolysis. The positive FAB-MS showed $[M+Na]^+$ ion at *m/z* 974, suggesting the molecular weight to be 951. In the EI-MS of the acetate (**3a**) of **3**, the peaks due to the terminal peracetylated pentosyl cation (*m/z* 259) and pentosyl-methylpentosyl cation (*m/z* 489) occurred similarly to those of **1c**, but the terminal peracetylated pentosyl-methylpentosyl-hexosyl cation was observed at one mass unit less (*m/z* 776), indicating the presence of an amino sugar moiety like glucosamine. Furthermore, an acetylamino group [*δ* 2.19 (3H, s, $NHCOC\underline{H}_3$), *δ* 8.96 (1H, d, J=9.2 Hz, $N\underline{H}COCH_3$)] appeared in the ^1H-NMR

TABLE II. ^{13}C-NMR Data for Compounds **1**—**6a** (Sugar Moieties) in Pyridine-d_5

	1	2	3	4	5	6a
glc-1	104.9	106.6		106.6	106.1	105.0
2	83.2	75.6		75.3	74.8	83.2
3	77.2	78.3		76.3	75.6	77.2
4	71.4	71.6		81.7	81.2	71.6
5	77.5	76.8		76.1	76.0	77.6
6	69.9	69.8		63.0	62.4	69.9
glcNAc-1			104.8			
2			58.0			
3			75.8			
4			72.5			
5			77.0			
6			69.9			
$NHCOCH_3$			170.0			
$NHCOCH_3$			23.7			
fuc-1	103.5	103.3	103.5			103.5
2	82.5	82.2	82.4			82.5
3	75.2	75.1	75.2			75.2
4	72.1	72.1	72.2			72.1
5	71.3	71.2	71.3			71.3
6	17.2	17.1	17.2			17.2
xyl-1	107.2	106.9	107.1			107.2
2	76.6	75.8	76.0			76.5
3	77.9	77.3	77.4			77.9
4	70.8	70.7	70.8			70.8
5	67.2	67.0	67.1			67.2
glc′-1	106.0			104.8	104.1	106.0
2	76.0			74.8	74.5	76.0
3	78.0			78.5	77.8	78.0
4	71.6			71.5	71.1	71.4
5	78.2			78.3	78.1	78.3
6	62.7			62.5	61.9	62.7
glc″-1				105.3	104.5	
2				75.0	74.6	
3				78.6	77.8	
4				71.7	71.2	
5				78.3	78.1	
6				62.5	62.0	

spectrum of **3**. By the ^{13}C-NMR (Table II) spectrum, the new sugar moiety of **3** was deduced to be *N*-acetylglucosamine.[7] Since the signals except for *N*-acetylglucosaminyl moiety were consistent with those of **2** and the C-6 signal of *N*-acetylglucosaminyl moiety was shifted to a lower field by glycosylation, the structure of **3** was determined to be acacic acid lactone 3-*O*-*β*-D-xylopyranosyl-(1→2)-*β*-D-fucopyranosyl-(1→6)-2-acetylamino-2-deoxy-*β*-D-glucopyranoside.

Julibroside A_4 (**4**) obtained as a white amorphous powder, $[\alpha]_D$ −16.4° (MeOH), gave acacic acid lactone (**1a**) on acid hydrolysis. The positive FAB-MS showed an $[M+Na]^+$ ion at *m/z* 979, indicating the molecular weight to be 956. Observation of fragment ion peaks at *m/z* 795 $[M+H-\text{hexose}]^+$ and 633 $[M+H-\text{hexose}-\text{hexose}]^+$ suggested **4** to be composed of **1a** and three moles of hexose. The ^{13}C-NMR spectrum of **4** revealed the occurrence of the glucopyranosyl-(1→4)-glucopyranosyl and the terminal glucopyranosyl moiety (Tables I and II). However, in the aglycone region, not only C-3 signal but also C-16 signal showed downfield shifts as compared with those of **1**, indicating **4** to be 3,16-*O*-bisdesmoside. In order to determine the linkage of sugar moieties, the EI-MS of the acetate (**4a**) of **4** was measured. Since the characteristic peak due to *retro* Diels–Alder fission[8] at *m/z* 592 [D/E ring+glc(Ac)$_4$] was observed, **4** was deduced to have 3-*O*-glucopyranosyl-(1→4)-glucopyranosyl and 16-*O*-glucopyranosyl residues. Moreover, the ^{1}H-NMR and gas liquid chromatography (GC) analysis showed that the sugar moiety was *β*-D-glucose. On the basis of these data, the structure of **4** was characterized as 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-glucopyranosyl-acacic acid lactone 16-*O*-*β*-D-glucopyranoside.

Julibroside B_1 (**5**) was obtained as a white amorphous powder, $[\alpha]_D$ −7.7° (MeOH). In the ^{13}C-NMR spectrum of **5**, the signals for the sugar region (Table II) were superimposable on those of **4**. However, in the aglycone region, a methyl group (*δ* 26.1) disappeared instead of a hydroxymethyl group appearing (*δ* 66.6). Since the signals except for C-19—21 were in good agreement with those of **4**, it was suggested that the hydroxymethyl attached to C-20. In order to determine the location of the hydroxymethyl group (C-29 or C-30), **5** was hydrolyzed to the sapogenol (**5a**) in an acid solution and then **5a** was saponified to **5b** by an alkaline solution. On the comparative analysis of the ^{13}C-NMR spectra of **5b** and **1b**, the C-30 signal of **5b** appeared at an extremely lower field than that of **1b** due to hydroxylation. On the contrary, the C-29 signal moved into a higher field by 4.6 ppm. Therefore, the structure of **5b** was concluded to be 3*β*,16*α*,21*β*,30-tetrahydroxyolean-12-en-28-oic acid. Since the aglycone (**5a**) of **5** was a new compound, **5a** was termed julibrogenin B. The structure of **5** was thus established as julibrogenin B 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-glucopyranosyl-16-*O*-*β*-D-glucopyranoside.

Julibroside C_1 (**6**) was obtained as a white amorphous powder, $[\alpha]_D$ −15.8° (MeOH). Since compound **6** had poor solubility in pyridine, it was converted to a methylate (**6a**) by etherial diazomethane. The ^{13}C-NMR signals of the sugar region (Table II) and the aglycone moiety except for C-19—21 (Table I) of **6a** showed a good coincidence with those of **1**. Although the fragmentation pattern of **6a** was similar to that of **1**, an $[M+Na]^+$ ion peak at *m/z* 1139 was higher by 44 mass units in the positive FAB-MS. In the aglycone region of the ^{13}C-NMR spectrum (Table I) of **6a**, a methoxy carbonyl group (*δ* 52.2 and 176.0) appeared instead of the disappearance of a methyl group (*δ* 24.2) in contrast to **1**. Since the aglycone (**6b**) of **6a** was reduced to **5a** with $NaBH_4$, the location of carbomethoxy group was concluded to be at C-30. Compound **6b** was a new aglycone, so we designated it julibrogenin C. Consequently, the structure of **6** was established as julibrogenin C 3-*O*-[*β*-D-xylopyranosyl-(1→2)-*β*-D-fucopyranosyl-(1→6)][*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucopyranoside.

Six new triterpenoidal glycosides including two new sapogenols were obtained from Albizziae Cortex. Moreover *N*-acetyl-D-glucosamine was found as a component sugar. A glycoside having *N*-acetyl-D-glucosamine is very rare as a plant constituent. Such compounds were mainly isolated from Leguminosae, for example, *Pithecellobium cubense*, *P. arboreum*,[7a] *Albizzia anthelmintica*,[7c] *A. lucida*[7d] and *Entada phaseoloides*.[7e] In addition, they have been known to show various activity, for instance, inhibition of leukotriene D_4,[7b] molluscicidal activity,[7c] and cytotoxic activity in a brine shrimp test.[7d] Since Albizziae Cortex is used not only as a tonic but also an antipyretic, anodyne, sedative and diuretic, it might be possible that these

glycosides clarify the pharmacological action of this crude drug. On the other hand, triterpene glycosides conjugating monoterpene acid at C-21 are also known to be contained in this plant.[4] In our series of studies on this plant, we plan to elucidate the conjugated saponins.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. The optical rotations were measured with a JASCO DIP-360 automatic digital polarimeter. IR spectra were recorded with a Hitachi IR spectrometer, model 270-30. ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-GX 400 NMR spectrometer and chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. The EI- and FAB-MS were measured with a JEOL DX-300 spectrometer. TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck). GC was performed by a Hewlett Packard HP5890A. The GC conditions were as follows: column, Ohio Valley OV-1 (0.5 μ film bonded, 0.32 × 30 m); column oven temperature, 230 °C; injection port temperature, 270 °C; detection temperature, 270 °C; carrier gas, He (2.2 kg/cm^2). Column chromatography was carried out on Kieselgel 60 (70—230 mesh, and 230—400 mesh, Merck), Sephadex LH-20 (Pharmacia), Bondapak C_{18} (Waters) and MCI gel CHP 20P (Mitsubishi Chemical, Ind.).

Extraction and Isolation Albizziae Cortex was purchased from Uchida Wakanyaku Co., Ltd., Tokyo and 2.0 kg was extracted with MeOH twice under reflux. The combined extract (126 g) was concentrated and partitioned with 1-BuOH and H_2O. The aqueous extract (51 g) was subjected to Bondapak C_{18} column chromatography using 0%→100% MeOH to give fractions 1 to 4. Fractions 4 was separated by MCI gel CHP 20P (0%→100% MeOH), Bondapak C_{18} (0%→100% MeOH) and silica gel ($CHCl_3$–MeOH–H_2O (8:2:0.2→7:3:0.5)) to provide compounds **1** (0.0008%), **2** (0.0002%), **3** (0.0006%), **4** (0.0015%), **5** (0.0011%) and **6** (0.0005%).

Compound 1 (Julibroside A_1) A white amorphous powder, $[\alpha]_D^{25}$ −12.6° (c=0.48, MeOH). IR (KBr): 3465 (ν_{O-H}), 1770 ($\nu_{C=O}$, γ-lactone) cm^{-1}. Positive FAB-MS m/z: 1095 $[M+Na]^+$, 1073 $[M+H]^+$, 963 $[M+Na-xyl]^+$, 941 $[M+H-xyl]^+$, 933 $[M+Na-glc]^+$, 833 $[M+Na-D/E\ ring]^+$, 817 $[M+Na-xyl-fuc]^+$, 795 $[M+H-xyl-fuc]^+$, 779 $[M+H-xyl-glc]^+$, 663 $[M+H-xyl-fuc-glc]^+$, 471 $[aglycone+H]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.81, 0.86, 0.89, 1.05, 1.15, 1.32, 1.42 (each 3H, s, *tert*-Me × 7), 1.51 (3H, d, J=6.6 Hz, fuc H-6), 3.58 (1H, m, H-3), 3.58 (1H, t, J=9.5 Hz, xyl H-5$_{ax}$), 3.78 (1H, q-like, J=6.6 Hz, fuc H-5), 4.23 (1H, d, J=5.4 Hz, H-21), 4.54 (1H, m, H-16), 4.75 (1H, d, J=10.6 Hz, glc H-6), 4.92 (d, J=6.8 Hz, glc H-1), 5.01 (d, J=7.8 Hz, fuc H-1), 5.05 (d, J=6.4 Hz, xyl H-1), 5.44 (d, J=7.3 Hz, glc′ H-1), 5.30 (1H, br s, H-12). NOE: Fig. 1. ^{13}C-NMR: Tables I and II.

Characterization of Sapogenol and Sugars for 1 The glycoside of **1** (5 mg) was dissolved in 1 N HCl/H_2O (2 ml) and heated at 90 °C for 2 h. After filtration of the mixture, the precipitate was identified with acacic acid lactone (**1a**) by TLC. Rf, 0.22 ($CHCl_3$–MeOH (19:1)), 0.42 (n-hexane–acetone (2:1)) while the filtrate was evaporated under N_2 stream. After addition of water, the acidic solution was evaporated to again remove HCl. This procedure was repeated until a neutral solution was obtained, which was, finally, evaporated and dried *in vacuo*. After the residue (3 mg) was dissolved in pyridine (0.3 ml), the mixture was added to a pyridine solution (1 ml) of L-cysteine methyl ester hydrochloride (0.06 mol/l) and warmed at 60 °C for 1 h. The mixture was evaporated under N_2 stream and dried *in vacuo*. The obtained syrup was trimethylsilylated with N-trimethylsilylimidazole (0.2 ml) at 60 °C for 1 h. After addition of n-hexane (2 ml) and H_2O (2 ml), the n-hexane layer was taken off and checked by GC. The retention time (t_R) of peaks was at 16.66 min (D-glucose, 16.55 min), 11.70 min (D-fucose, 11.59 min), and 9.33 min (D-xylose, 9.35 min).

Acetylation of 1 A solution of **1** in Ac_2O–pyridine (1:1) was heated at 80 °C on a block heater for 2 h. The reaction mixture was evaporated under a N_2 gas and then chromatographed on a silica gel to give **1c**, a white amorphous powder, EI-MS m/z: 259 $[(xyl)Ac_3]$, 331 $[(glc)Ac_4]$, 489 $[(xyl+fuc)Ac_5]$, ^{1}H-NMR (in $CDCl_3$) δ: 0.81, 0.91, 0.98, 1.01, 1.04, 1.05, 1.24 (each 3H, s, *tert*-Me × 7), 1.16 (3H, d, J=6.2 Hz, fuc H-6), 3.14 (1H, dd, J=11.6, 4.6 Hz, H-3), 4.22 (1H, d, J=5.9 Hz, H-21), 5.44 (1H, br s, H-12), 1.99, 2.00, 2.01, 2.02, 2.06, 2.12, 2.13 (s, OAc × 12).

Compound 2 (Julibroside A_2) A white amorphous powder, $[\alpha]_D^{25}$ −15.2° (c=0.48, MeOH). IR (KBr): 3430 (ν_{O-H}), 1765 ($\nu_{C=O}$, γ-lactone) cm^{-1}. Positive FAB-MS m/z: 933 $[M+Na]^+$, 911 $[M+H]^+$, 779 $[M+H-xyl]^+$, 633 $[M+H-xyl-fuc]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.82, 0.85, 0.90, 1.04, 1.05, 1.30, 1.42 (each 3H, s, *tert*-Me × 7), 1.50 (3H, d, J=6.2 Hz, fuc H-6), 3.59 (1H, t, J=9.9 Hz, xyl H-5$_{ax}$), 3.67 (1H, dd, J=11.9, 4.6 Hz, H-3), 3.77 (1H, q-like, J=6.6 Hz, fuc H-5), 4.24 (1H, d, J=5.9 Hz, H-21), 4.80 (1H, d, J=11.0 Hz, glc H-6), 4.92 (d, J=8.1 Hz, glc H-1), 4.97 (d, J=7.7 Hz, fuc H-1), 5.02 (d, J=7.0 Hz, xyl H-1), 5.31 (1H, br s, H-12). ^{13}C-NMR: Tables I and II.

Characterization of Sapogenol and Sugars for 2 A sample of **2** was hydrolyzed in the same manner as above. The precipitate was identified with acacic acid lactone (**1a**) by TLC. The filtrate was followed in the same manner as above and analyzed by GC. t_R (min) 16.59 (D-glucose), 11.65 (D-fucose), 9.30 (D-xylose).

Compound 3 (Julibroside A_3) A white amorphous powder, $[\alpha]_D^{25}$ −10.6° (c=0.32, MeOH). IR (KBr): 3430 (ν_{O-H}), 1775 ($\nu_{C=O}$, γ-lactone) cm^{-1}. Positive FAB-MS m/z: 974 $[M+Na]^+$, 952 $[M+H]^+$, 820 $[M+H-xyl]^+$, 674 $[M+H-xyl-fuc]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.81, 0.83, 0.89, 1.04, 1.06, 1.24, 1.42 (each 3H, s, *tert*-Me × 7), 1.50 (3H, d, J=6.6 Hz, fuc H-6), 2.19 (3H, s, NHCOC$\underline{H}_3$), 3.57 (1H, dd, J=11.5, 9.3 Hz, H-3), 5.28 (1H, br s, H-12), 8.96 (1H, d, J=9.2 Hz, N$\underline{H}$COCH$_3$). ^{13}C-NMR: Tables I and II.

Acetylation of 3 A solution of **3** in Ac_2O–pyridine (1:1) was heated at 80 °C on a block heater for 2 h. The reaction mixture was worked up in the manner descrived above to give **3a**, a white amorphous powder. EI-MS m/z: 259 $[(xyl)Ac_3]^+$, 489 $[(xyl+fuc)Ac_5]^+$, 776 $[(xyl+fuc+glcNAc)Ac_7]^+$, 984 $[A/B\ ring+(sugar)Ac_7]^+$, 1287 $[M]^+$. ^{1}H-NMR (in $CDCl_3$) δ: 0.78, 0.91, 0.93, 0.97, 1.01, 1.04, 1.23 (each 3H, s, *tert*-Me × 7), 1.17 (3H, d, J=6.2 Hz, fuc H-6), 3.18 (1H, dd, J=11.6, 4.6 Hz, H-3), 5.45 (1H, br s, H-12), 1.91, 1.99, 2.00, 2.01, 2.03, 2.07, 2.13 (s, OAc × 9).

Characterization of Sapogenol and Sugars for 3 A sample of **3** was hydrolyzed in the manner above. The precipitate was identified with acacic acid lactone (**1a**) by TLC. The filtrate was followed as above and analyzed by GC. t_R (min) 20.18 (N-acetyl-D-glucosamine), 11.45 (D-fucose), 9.12 (D-xylose).

Compound 4 (Julibroside A_4) A white amorphous powder, $[\alpha]_D^{25}$ −16.4° (c=0.48, MeOH). IR (KBr): 3450 (ν_{O-H}), 1765 ($\nu_{C=O}$, γ-lactone) cm^{-1}. Positive FAB-MS m/z: 979 $[M+Na]^+$, 957 $[M+H]^+$, 795 $[M+H-glc]^+$, 633 $[M+H-glc-glc]^+$, 555 $[M+Na-D/E\ ring]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.78, 0.80, 0.97, 1.00, 1.02, 1.32, 1.33 (each 3H, s, *tert*-Me × 7), 3.35 (1H, dd, J=12.1, 4.5 Hz, H-3), 4.24 (1H, d, J=4.8 Hz, H-21), 4.79 (1H, t-like, J=7.1 Hz, H-16), 4.89 (1H, d, J=7.3 Hz, glc H-1), 5.04 (1H, d, J=8.1 Hz, glc′ H-1), 5.15 (1H, d, J=7.7 Hz, glc″ H-1), 5.46 (1H, br s, H-12). ^{13}C-NMR: Tables I and II.

Acetylation of 4 A solution of **4** in Ac_2O–pyridine (1:1) was heated and the reaction mixture was worked up as described above to give **4a**, a white amorphous powder. EI-MS m/z: 331 $[(glc)Ac_4]^+$, 495 $[A/B\ ring+(glc)Ac_3]^+$, 592 $[D/E\ ring+(glc)Ac_4]^+$, 619 $[(glc+glc)Ac_7]^+$. ^{1}H-NMR (in $CDCl_3$) δ: 0.73, 0.77, 0.88, 0.91, 0.99, 1.00, 1.12 (each 3H, s, *tert*-Me × 7), 3.06 (1H, dd, J=11.7, 4.4 Hz, H-3), 5.49 (1H, br s, H-12), 1.98, 2.00, 2.01, 2.02, 2.03, 2.06, 2.09, 2.11 (s, OAc × 9).

Characterization of Sapogenol and Sugars for 4 A sample of **4** was hydrolyzed as above. The precipitate was identified with acacic acid lactone (**1a**) by TLC. The filtrate was followed in the above described manner and analyzed by GC. t_R (min), 16.78 (D-glucose).

Compound 5 (Julibroside B_1) A white amorphous powder, $[\alpha]_D^{25}$ −7.7° (c=0.48, MeOH). IR (KBr): 3740 (ν_{O-H}), 1765 ($\nu_{C=O}$, γ-lactone) cm^{-1}. Positive FAB-MS m/z: 995 $[M+Na]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.73, 0.81, 1.03, 1.23, 1.33, 1.36 (each 3H, s, *tert*-Me × 6), 3.32 (1H, dd, J=11.7, 7.3 Hz, H-3), 4.87 (1H, d, J=7.7 Hz, glc H-1), 5.05 (1H, d, J=8.1 Hz, glc′ H-1), 5.20 (1H, d, J=8.1 Hz, glc″ H-1), 5.48 (1H, br s, H-12). ^{13}C-NMR: Tables I and II.

Characterization of Sapogenol and Sugars for 5 A sample of **5** was hydrolyzed in the manner above. The precipitate was separated by silica gel to give julibrogenin B (**5a**), a white amorphous powder, $[\alpha]_D^{25}$ +18.1° (c=0.17, MeOH). IR (KBr): 3450 (ν_{O-H}), 1740 ($\nu_{C=O}$, γ-lactone) cm^{-1}. EI-MS m/z: 486 $[M]^+$. ^{1}H-NMR (in $CDCl_3$) δ: 0.79, 0.89, 0.92, 0.99, 1.03, 1.24 (each 3H, s, *tert*-Me × 6), 3.19 (1H, dd, J=10.8, 7.0 Hz, H-3), 3.29, 3.65 (each 1H, ABq, J=11.2 Hz, H_2-30), 4.47 (1H, d, J=5.5 Hz, H-21), 5.40 (1H, br s, H-12). The filtrate was followed as above and analyzed by GC. t_R (min), 16.80 (D-glucose).

Saponification of 5a A sample of **5a** was saponified in 3% KOH/MeOH for 1 h at 60 °C. After neutralization with 1 N HCl/MeOH, the mixture was separated by silica gel to give **5b**, a white amorphous powder, $[\alpha]_D^{25}$ +2.0° (c=0.14, pyridine). Positive FAB-MS m/z: 505 $[M+H]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.94, 1.05, 1.08, 1.25, 1.68, 1.90

(each 3H, s, *tert*-Me × 6), 3.48 (1H, m, H-3), 3.81 (1H, br d, J = 12 Hz, H-21), 4.30, 4.91 (each 1H, ABq, J = 10.5 Hz, H_2-30), 5.76 (1H, br s, H-12). ^{13}C-NMR: Table I.

Compound 6 (Julibroside C_1) A white amorphous powder, $[\alpha]_D^{25}$ −15.8° (c = 0.48, MeOH). IR (KBr): 3450 (ν_{O-H}), 1760 ($\nu_{C=O}$, γ-lactone) cm^{-1}. Positive FAB-MS m/z: 1125 $[M+Na]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.80, 0.83, 1.12, 1.26, 1.42, 1.62 (each 3H, s, *tert*-Me × 6), 1.50 (3H, d, J = 6.6 Hz, fuc H-6), 3.56 (1H, m, H-3), 5.58 (1H, br s, H-12).

Methylation of 6 The methanolic solution of **6** was methylated by etherial CH_2N_2. The mixture was subjected to silica gel to give julibroside C_1 methylester (**6a**), a white amorphous powder, $[\alpha]_D^{25}$ −16.9° (c = 0.66, MeOH). IR (KBr): 3450 (ν_{O-H}), 1775 ($\nu_{C=O}$, γ-lactone) cm^{-1}. Positive FAB-MS m/z: 1139 $[M+Na]^+$, 1117 $[M+H]^+$, 985 $[M+H-xyl]^+$, 839 $[M+H-xyl-fuc]^+$, 677 $[M+H-xyl-fuc-glc]^+$, 515 [aglycone + H]$^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.78, 0.86, 1.14, 1.30, 1.40, 1.40 (each 3H, s, *tert*-Me × 6), 1.51 (3H, d, J = 6.2 Hz, fuc H-6), 3.53 (1H, dd, J = 11.8, 4.4 Hz, H-3), 3.69 (3H, s, 30-COOMe), 4.23 (1H, d, J = 5.5 Hz, H-21), 4.75 (1H, d, J = 11.0 Hz, glc H-6), 4.91 (d, J = 7.0 Hz, glc H-1), 4.99 (d, J = 7.7 Hz, fuc H-1), 5.04 (d, J = 6.6 Hz, xyl H-1), 5.42 (d, J = 7.3 Hz, glc′ H-1), 5.43 (1H, br s, H-12). ^{13}C-NMR: Tables I and II.

Characterization of Sugars for 6a The glycoside of **6a** was dissolved into 1 N HCl/H_2O and heated at 90 °C for 2 h. After filtration of the mixture, the precipitate was separated by silica gel to give julibrogenin C methyl ester (**6a**), a white amorphous powder, $[\alpha]_D^{25}$ +8.3° (c = 0.87, MeOH). ^{1}H-NMR (in $CDCl_3$) δ: 0.79, 0.87, 0.91, 0.99, 1.22, 1.30 (each 3H, s, *tert*-Me × 6), 3.19 (1H, m, H-3), 3.74 (3H, s, 30-COOC$\underline{H}_3$), 4.01 (1H, m, H-16), 4.88 (1H, d, J = 5.5 Hz, H-21), 5.46 (1H, br s, H-12). The filtrate was followed in the same manner as above and analyzed by GC. t_R (min), 16.48 (D-glucose), 11.59 (D-fucose), 9.28 (D-xylose).

$NaBH_4$ Reduction of 6b Methanolic solution of **6b** was reduced with $NaBH_4$ overnight at rt. The reduction product of **6b** was identified as **5a** by TLC. *Rf*, 0.36 ($CHCl_3$–MeOH–H_2O (9 : 1 : 0.1)), 0.39 (*n*-hexane–acetone (1 : 1)).

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