

Indonesian Medicinal Plants. I. Chemical Structures of Calotroposides A and B, Two New Oxy pregnane-Oligoglycosides from the Root of *Calotropis gigantea* (Asclepiadaceae)

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Two new oxy pregnane-oligoglycosides named calotroposides A (1) and B (2) have been isolated from the root of *Calotropis gigantea* (Asclepiadaceae), an Indonesian medicinal plant, and their chemical structures have been elucidated by chemical and spectroscopic methods as 12-*O*-benzoyllineolon 3-*O*- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranoside and 12-*O*-benzoyldeacetylmetaplexigenin 3-*O*- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranoside, respectively.

Keywords Indonesian medicinal plant; *Calotropis gigantea*; Asclepiadaceae; oxy pregnane-oligoglycoside; calotroposide; cymarose; oleandrose

Indonesia is one of the richest countries in the world in natural resources. In particular the variety of plant species is enormous, so that Indonesian medicinal plants are very important from the viewpoint of finding new naturally occurring drug materials. Since 1985, we have made several scientific expeditions to examine Indonesian medicinal plants as well as traditional folk-medicines, called "jamu."¹⁾ All the plant materials collected by us in Indonesia have been botanically identified at the Herbarium Bogoriense, Research and Development Centre for Biology-LIPI, Indonesia.¹⁾ Since 1986, we have been engaged in chemical investigations of the medicinal plants collected during the surveys. In this and the following papers, the chemical and biological findings will be presented.

The root of *Calotropis gigantea* DRYAND. (Asclepiadaceae), which is called "Koreng susu" in Timor Island or

"Biduri" in Java Island, has been traditionally used as an antidote for snake-bite and as an anti-scabetic. As for the chemical constituents isolated from the plant, a protein, calotropin,²⁾ and several triterpenes (*i.e.* α -, β -amyriins, lupeol, 24-methylenecycloartenol, and taraxasterol),³⁾ have so far been reported. As a part of our continuing chemical study of Indonesian medicinal plants,⁴⁾ we have investigated the glycosidic constituents of the root of *Calotropis gigantea* collected in Timor Island and have isolated seven new oxy pregnane-oligoglycosides, named calotroposides A (1), B (2), C, D, E, F, and G. Here we present a full account of the structure elucidation of calotroposides A (1) and B (2).

The methanol extract of the root was partitioned into an *n*-hexane–water mixture. Separation of the *n*-hexane-soluble portion by silica gel column chromatography and subse-

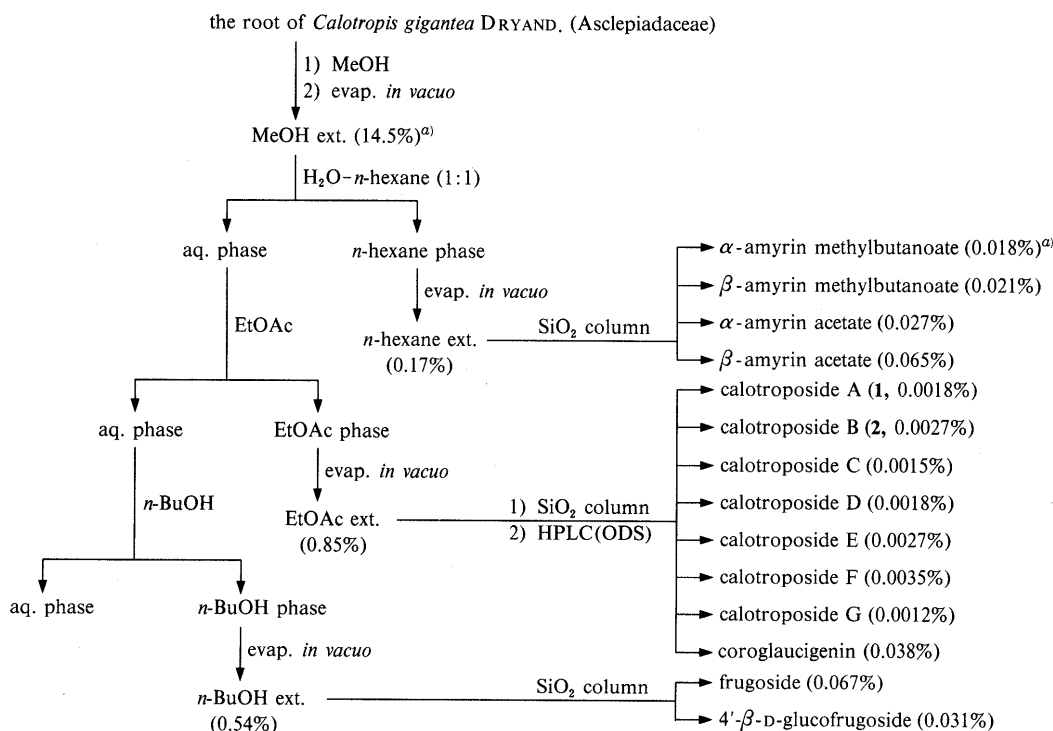


Fig. 1

^{a)} The % yield from the air-dried root.

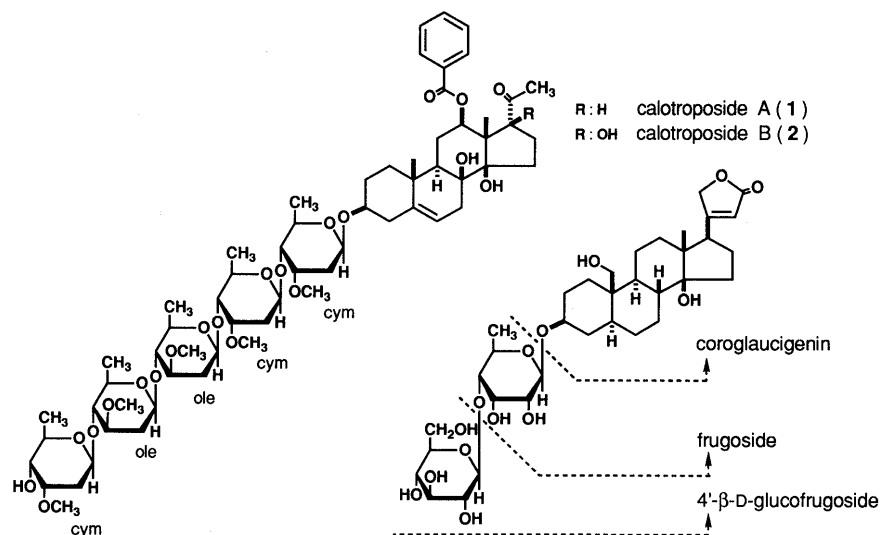


Fig. 2

quent high-performance liquid chromatography (HPLC) on reversed-phase adsorbent provided α -amyirin methylbutanoate,³⁾ β -amyirin methylbutanoate,³⁾ α -amyirin acetate³⁾ and β -amyirin acetate.³⁾ The water-soluble portion was further partitioned into a mixture of ethyl acetate and water. After purification by silica gel column chromatography and reversed-phase HPLC, the ethyl acetate-soluble portion gave calotroposides A (**1**, 0.0018% from the root), B (**2**, 0.0027%), C (0.0015%), D (0.0018%), E (0.0027%), F (0.0035%), and G (0.0012%) together with coroglaucigenin^{5,6)} (0.038%) (Fig. 1). On the other hand, separation of the *n*-butanol-soluble portion, which was obtained by an *n*-butanol–water partition of the water-soluble portion, by silica gel column chromatography afforded two known cardenolides, frugoside (0.067%) and 4'- β -D-glucofrugoside (0.031%), which were previously isolated from some asclepiadaceous plants.^{6,7)} We have undertaken the structure elucidation of **1** and **2** as described below.

Calotroposide A (1) Calotroposide A (**1**) showed a negative fast atom bombardment (FAB) ion at m/z 1187 for $(M-H)^-$, indicating its molecular weight to be 1188, and absorption bands due to a hydroxyl (3540 cm^{-1}) and a carbonyl (1710 cm^{-1}) group in the infrared (IR) spectrum.

The proton and carbon-13 nuclear magnetic resonance (^1H - and ^{13}C -NMR) spectra of **1** exhibited signals characteristic of an oxypregnane-oligoglycoside containing oleandrose and cymarose moieties⁸⁾ (Table I). Five anomeric proton signals were observed in the ^1H -NMR spectrum of **1** at δ 4.70, 4.92 (1H each, both dd, $J=9.8, 1.8\text{ Hz}$) and at δ 4.97, 5.12, 5.26 (1H each, all dd, $J=9.5, 1.8\text{ Hz}$), which indicated that **1** possesses five monosaccharide moieties and all the glycosidic linkages are of β -configuration as judged from the coupling constants.⁸⁾ Also in the ^{13}C -NMR spectrum of **1**, five anomeric carbon signals were observed at δ_c 96.3 (C-1'), 100.0 (C-1''), 100.4 (C-1'''), 101.9 (C-1'''), 98.5 (C-1''').

On methanolysis with 9% HCl–MeOH, calotroposide A (**1**) liberated the aglycone **3** and two methyl glycosides, which were identified as methyl oleandroside (**a**) and methyl cymaroside (**b**) by comparison of the ^{13}C -NMR data

with those reported.⁹⁾ Both methyl glycosides (**a**, **b**) were hydrolyzed further with 5% aqueous HCl to yield D-oleandrose ($[\alpha]_D -17.3^\circ$ in H_2O) and D-cymarose ($[\alpha]_D +54.2^\circ$ in H_2O), respectively.

The mass spectrum (MS) of the aglycone **3** showed its molecular ion peak at m/z 468 as well as fragmentation ion peaks which were similar to those of 12-*O*-benzoylisolineolone.¹⁰⁾ The ^1H -NMR spectrum of **3** suggested the presence of a benzoyl group [signals at δ 7.42 (2H, dd, $J=7.6\text{ Hz}$), 7.53 (1H, t, $J=7.6\text{ Hz}$), 8.27 (2H, d, $J=7.6\text{ Hz}$)]. Furthermore, the circular dichroism (CD) spectrum of **3** showed a negative maximum ($[\theta]_{247} -3.30 \times 10^4$)¹¹⁾ ascribable to the C-20 carbonyl moiety in the 17α -side chain of a lineolone-type compound.¹²⁾ In the ^{13}C -NMR of **3**, esterification shifts¹³⁾ were observed for the signals assignable to C-11 (-4.2 ppm), C-12 ($+4.8\text{ ppm}$), and C-13 (-1.8 ppm) as compared with those of lineolone¹²⁾ (**4**), which was prepared by alkaline hydrolysis of **3** with 10% aqueous KOH. Consequently, the aglycone **3** has been determined to be 12-*O*-benzoyllineolone, the 17-epimer of 12-*O*-benzoylisolineolone,¹⁰⁾ which was previously isolated from *Cynanchum boerhaviaefolium* (Asclepiadaceae).

The location of the carbohydrate moiety attached to the C-3 hydroxyl group of the aglycone has been determined from the fact that glycosylation shifts^{13,14)} were observed in the ^{13}C -NMR spectrum of **1** for the C-2 (-2.2 ppm), C-3 ($+6.1\text{ ppm}$), and C-4 (-4.3 ppm) signals as compared with those of the aglycone **3**.

Acidic hydrolysis of calotroposide A (**1**) with 5% aqueous HCl gave the aglycone **3** and a mixture of oleandrose and cymarose, whose ratio was determined to be 2:3 by gas-liquid chromatographic (GLC) analysis. In order to determine the monosaccharide sequence in the oligosaccharide moiety, **1** was first acetylated with acetic anhydride and pyridine to furnish a monoacetate **5**. The ^1H -NMR spectrum of **5** showed a characteristic signal at δ 4.52 (1H, dd, $J=9.8, 2.9\text{ Hz}$, 4''''-H), which was assignable to the acetoxymethine proton of the terminal sugar. The coupling constant of this particular signal indicated that the proton was adjacent to one axial (5''''-) and one equatorial (3''''-) protons, so that the terminal sugar must be cymarose. On partial hydrolysis with 0.5% aqueous H_2SO_4 at 50°C and

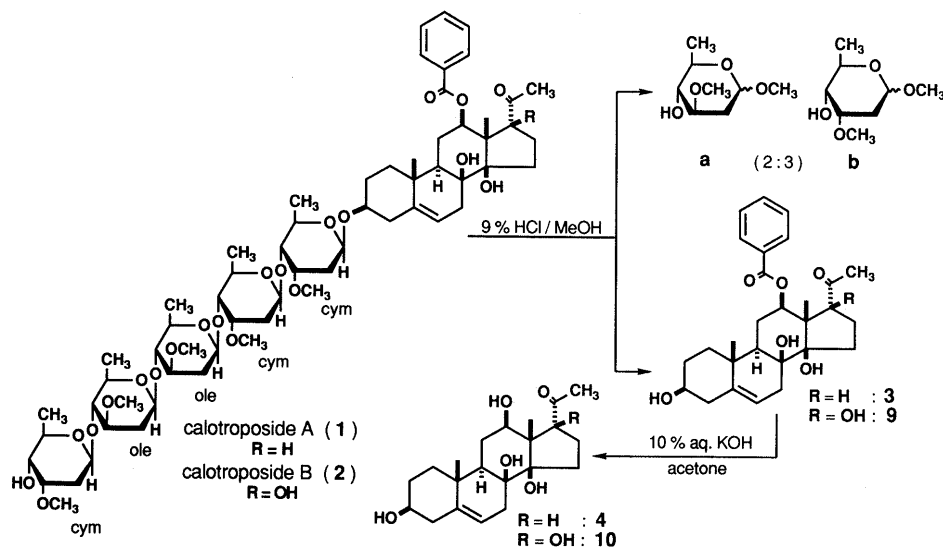


Chart 1

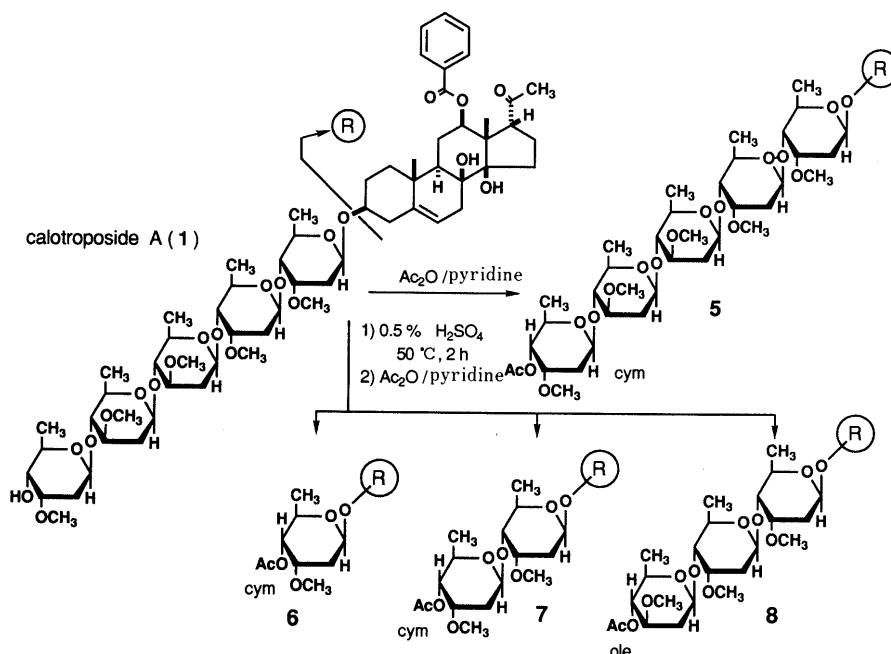


Chart 2

subsequent acetylation, **1** gave three products (**6**, **7**, and **8**). The ^1H -NMR spectra of **6**, **7**, and **8** exhibited signals assignable to acetoxymethine protons in the individual terminal sugars at δ 4.54 (1H, dd, $J=9.8$, 2.9 Hz, 4'-H), 4.52 (1H, dd, $J=9.8$, 3.0 Hz, 4''-H), and 4.65 (1H, dd, $J=9.3$, 9.3 Hz, 4'''-H), so that the terminal sugar were elucidated to be cymarose in **6** and **7** and oleandrose in **8**.

Based on the foregoing evidence, the structure of calotroposide A (**1**) has been concluded to be 12-*O*-benzoyl-lineolon 3-*O*- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranoside.

Calotroposide B (2) Calotroposide B (**2**) showed a negative FAB ion at m/z 1203 for $(\text{M}-\text{H})^-$, 16 mass units larger than that of calotroposide A (**1**). The IR and ultraviolet (UV) spectra of **2** showed similar absorption patterns to those of **1**. The ^{13}C -NMR spectrum of **2** was

also quite similar to that of **1** except for the chemical shifts of C-16 (+11.1 ppm), C-17 (+32.2 ppm), and C-18 (-5.0 ppm) in the aglycone moiety. These findings suggested that the structure of the aglycone part of **2** may be a 17-hydroxyl derivative of benzoyllineolon (**3**).

On methanolysis with 9% HCl-MeOH, **2** gave the aglycone **9**, methyl oleandroside (**a**), and methyl cymaroside (**b**). The methyl glycosides (**a**, **b**) were further hydrolyzed with 5% aqueous HCl to yield D-oleandrose and D-cymarose, respectively, as indicated by their optical rotations. The mass spectrum of **9** showed a molecular ion (M^+) peak at m/z 484, which was 16 mass unit larger than that of benzoyllineolon (**3**). Furthermore, alkaline treatment of **9** provided deacetylmetaplexigenin (**10**).¹⁵⁾ In the ^{13}C -NMR spectrum of **9**, esterification shifts¹³⁾ of the carbon signals were observed for C-11 (-4.7 ppm), C-12 (+5.2 ppm), and C-13 (-1.9 ppm) as compared with those

of **10**, so that the benzoyl group is linked to the C-12 hydroxyl group of **10**. Thus, the structure of the aglycone **9** has been established as 12-*O*-benzoyldeacetylmetaplexigenin,¹⁵⁾ which is known as the aglycone of wilfosides

TABLE I. ¹³C-NMR Chemical Shifts for **1** and **2** in *d*₅-Pyridine (δ in ppm)

	1	2		1	2
C-1	39.2	39.2	cym C-1'	96.3	96.4
C-2	29.8	29.8	C-2'	36.9	37.0
C-3	77.7	77.8	C-3'	77.6	77.6
C-4	38.9	38.9	C-4'	82.7	82.8
C-5	139.4	139.4	C-5'	69.0	69.0
C-6	119.1	119.1	C-6'	18.6	18.6
C-7	34.2	33.8	C-3'-OMe	58.9	58.9
C-8	74.5	74.3	cym C-1''	100.0	100.1
C-9	44.6	44.4	C-2''	37.1	37.2
C-10	37.7	37.8	C-3''	78.0	78.0
C-11	24.9	25.0	C-4''	82.9	82.9
C-12	73.7	74.2	C-5''	68.8	68.9
C-13	56.1	58.3	C-6''	18.7	18.7
C-14	87.5	89.5	C-3''-OMe	58.9	58.9
C-15	35.1 ^{a)}	34.7 ^{a)}	ole C-1'''	100.4	100.4
C-16	22.1	33.2 ^{a)}	C-2'''	37.4	37.4
C-17	60.3	92.5	C-3'''	78.9	79.0
C-18	15.8	10.8	C-4'''	83.1	83.2
C-19	18.1	18.1	C-5'''	71.6	71.6
C-20	209.5	210.1	C-6'''	18.5	18.6
C-21	32.1	27.8	C-3'''-OMe	57.3	57.4
-CO-Ph	165.4	165.3	ole C-1''''	101.9	101.9
Phenyl			C-2''''	37.4	37.6
(C-1)	131.3	131.2	C-3''''	79.1	79.1
(C-2)	128.8	128.9	C-4''''	83.3	83.4
(C-3)	129.9	129.9	C-5''''	71.8	71.8
(C-4)	133.2	133.2	C-6''''	18.4	18.6
(C-5)	129.9	129.9	C-3''''-OMe	57.3	57.4
(C-6)	128.8	128.9	cym C-1'''''	98.5	98.5
			C-2'''''	35.8	35.8
			C-3'''''	79.0	79.0
			C-4'''''	74.1	74.0
			C-5'''''	71.1	71.2
			C-6'''''	19.0	19.0
			C-3'''''-OMe	57.9	57.9

a) Indicated assignments in each column may be interchangeable.

isolated from *Cynanchum wilfordi* (Asclepiadaceae).

From a comparison of the ¹H- and ¹³C-NMR spectra of calotroposide B (**2**) with those of calotroposide A (**1**), it was presumed that **2** possesses the same sugar sequence in the oligosaccharide moiety as that of **1**, which was attached to the C-3 hydroxyl group of **9**. Namely, in the ¹H-NMR spectrum of **2**, five anomeric proton signals were observed at δ 4.70, 4.91 (1H each, both dd, *J*=9.5, 1.8 Hz) and δ

TABLE II. ¹³C-NMR Chemical Shifts for **3**, **4**, **9** and **10** in *d*₅-Pyridine (δ in ppm)

	3	4	9	10
C-1	39.2	39.2	39.2	39.2
C-2	32.0	32.1	32.1 ^{a)}	32.1 ^{a)}
C-3	71.6	71.6	71.6	71.6
C-4	43.2	43.3	43.3	43.2
C-5	140.5	140.4	140.4	140.2
C-6	118.4	118.5	118.4	118.6
C-7	34.2 ^{a)}	34.2 ^{a)}	33.9 ^{b)}	34.1 ^{b)}
C-8	74.7	74.6	74.5	74.6
C-9	44.8	45.1	44.5	44.9
C-10	37.5	37.4	37.4	37.2
C-11	25.0	29.2	25.1	29.8
C-12	73.8	69.0	74.1	68.9
C-13	56.1	57.9	58.4	60.3
C-14	87.5	87.4	89.6	89.2
C-15	35.2 ^{a)}	35.3 ^{a)}	34.8 ^{b)}	35.0 ^{b)}
C-16	22.2	22.1	33.3 ^{a)}	32.0 ^{a)}
C-17	60.4	61.3	92.5	92.4
C-18	15.8	14.6	10.8	9.2
C-19	18.4	18.5	18.4	18.4
C-20	209.4	210.6	210.0	210.5
C-21	32.1	32.0	27.8	27.7
-CO-Ph	165.5		165.3	
Phenyl				
(C-1)	131.4		131.3	
(C-2)	128.8		128.9	
(C-3)	129.9		129.9	
(C-4)	133.2		133.2	
(C-5)	129.9		129.9	
(C-6)	128.8		128.9	

a, b) The assignments in each column may be interchangeable.

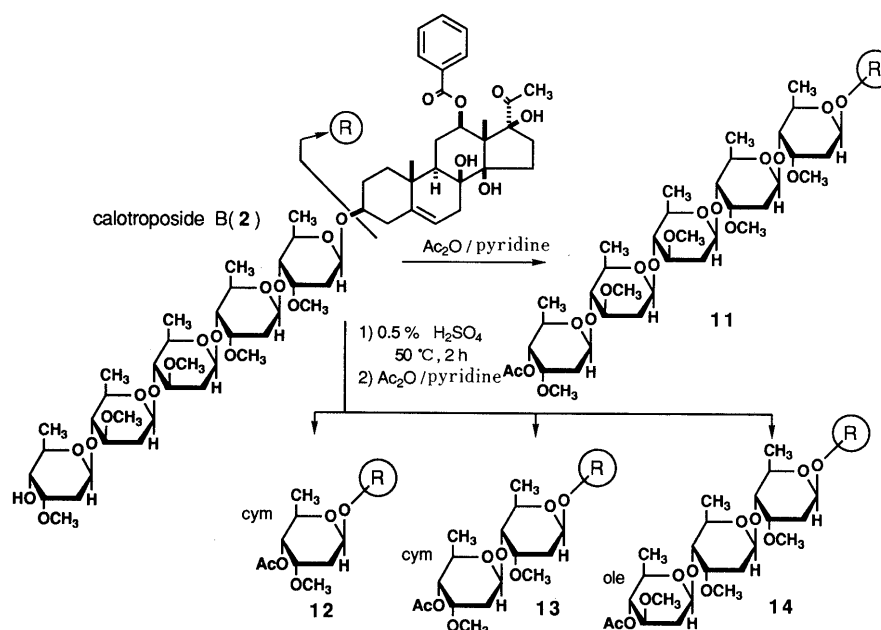


Chart 3

4.98, 5.12, 5.26 (1H each, all dd, $J=9.8, 1.8$ Hz), whose coupling constants indicated the β orientation for all glycosidic linkages.

Upon acetylation, calotroposide B (**2**) afforded a monoacetate (**11**), which showed a characteristic signal assignable to one acetoxymethine proton at δ 4.52 (1H, dd, $J=9.8, 2.9$ Hz) in the $^1\text{H-NMR}$ spectrum. Accordingly, it was determined that cymarose is the terminal sugar. Partial hydrolysis of **2** with 0.5% aqueous H_2SO_4 followed by acetylation yielded three hydrolysates **12**, **13**, and **14**. The $^1\text{H-NMR}$ spectra of **12**, **13**, and **14** exhibited acetoxymethine signals at δ 4.54 (dd, $J=9.5, 2.7$ Hz), 4.52 (dd, $J=9.8, 2.7$ Hz), and 4.61 (dd, $J=9.5, 9.5$ Hz), respectively, which indicated that the terminal sugar was a cymarose for **12** and **13** and an oleandrose for **14**.

Therefore, the structure of calotroposide B (**2**) has been concluded to be 12-*O*-benzoyldeacetylmetaplexigenin 3-*O*- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-oleandropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranosyl(1 $\rightarrow$ 4)- β -D-cymaropyranoside.

Furthermore, it should be noted that, among the constituents isolated here from *Calotropis gigantea*, coroglaucigenin showed an anticholine activity (ED_{50} 10 $\mu\text{g/ml}$) while both frugoside and 4'- β -D-glucifrugoside showed spasmogenic activity (ED_{50} 0.4 $\mu\text{g/ml}$).

The elucidation of chemical structures of calotroposides C, D, E, F, and G will be reported elsewhere.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. UV spectra were obtained with a Hitachi 330 spectrophotometer. Optical rotations were measured with a JASCO DIP-370 digital polarimeter in a 0.5 dm tube. CD spectra were measured on a JASCO J-500A spectropolarimeter equipped with a 501N data processor. Electron impact-mass spectra (EI-MS) were taken on a JEOL JMS-D300 spectrometer. FAB-MS were taken on a JEOL SX102 spectrometer. $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra were measured with a JEOL GX-500 spectrometers. IR spectra were taken with a Hitachi 260-30 spectrometer. For GLC and HPLC, a Hitachi 663-50 gas chromatograph and a Shimadzu LC-6A were used. Column chromatography was carried out using Kieselgel 60 (70–230 mesh, Merck) and Cosmosil 75 C_{18} -OPN (Nakarai Tesque). Thin-layer chromatography (TLC) was conducted on precoated Kieselgel 60F₂₅₄ plates (0.2 mm, Merck). Detection of the spots was carried out by spraying 10% $\text{Ce}(\text{SO}_4)_2/\text{H}_2\text{SO}_4$ on the TLC plates, followed by heating at 110°C.

Isolation of Calotroposides Dried root (3.5 kg) of *Calotropis gigantea* DRYAND. (Asclepiadaceae), which was collected at Kupang, Timor Island, Indonesia in 1988, was extracted with MeOH under reflux and the solvent was evaporated off under reduced pressure to give the MeOH extract (500 g). The MeOH extract was partitioned into *n*-hexane– H_2O (1:1). The *n*-hexane phase was taken and concentrated under reduced pressure to give the *n*-hexane extract (26.6 g), while the water phase was shaken with EtOAc. The EtOAc phase was evaporated under reduced pressure to afford the EtOAc extract (29.7 g). The water-soluble portion was again treated with *n*-BuOH and the *n*-BuOH phase was taken and concentrated under reduced pressure to give the *n*-BuOH extract (19.0 g). The *n*-hexane extract (12.5 g) was subjected to repeated column chromatography [1] SiO_2 1 kg, *n*-hexane:EtOAc = 50:1; 2) SiO_2 1 kg, *n*-hexane:EtOAc = 3:1] to afford α -amyrin methylbutanoate (303 mg, 0.018%), β -amyrin methylbutanoate (345 mg, 0.021%), α -amyrin acetate (444 mg, 0.027%), and β -amyrin acetate (1.07 g, 0.065%). The physical data for these triterpenoidal constituents were identical with those reported.³⁾ The *n*-BuOH extract (9.0 g) was purified by column chromatography (SiO_2 900 g, CHCl_3 :MeOH: H_2O = 10:3:1, lower phase) to afford frugoside (1.1 g, 0.067%) and 4'- β -D-glucifrugoside (514 mg, 0.031%). Physical data for both cardenolides were identical with those reported.^{6,7)} The EtOAc extract (29.8 g) was separated by column chromatography (SiO_2 2.5 kg, CHCl_3 :MeOH = 40:1 $\rightarrow$ 5:1) and reversed-phase HPLC (Shim-pack PREP-ODS, 0.25 m $\times$ 20 mm, MeOH: H_2O = 9:1) to afford calotroposides

A (**1**, 62 mg, 0.0018%), B (**2**, 95 mg, 0.0027%), C (51 mg, 0.0015%), D (62 mg, 0.0018%), E (95 mg, 0.0027%), F (121 mg, 0.0035%), and G (41 mg, 0.0012%), together with coroglaucigenin (1.33 g, 0.038%), whose physical data were identical with those reported.^{4,6)}

Calotroposide A (1): A white amorphous solid. $[\alpha]_D +2.3^\circ$ ($c=1.0$, in CHCl_3 at 22°C). IR (CHCl_3) cm^{-1} : 3540, 1710, 1600, 1450, 1270, 1100. UV (MeOH) nm (log ϵ): 230 (4.06), 273 (3.16), 280 (3.09). $^1\text{H-NMR}$ (d_5 -pyridine) δ : 1.33 (3H, s, 18- H_3), 1.39, 1.40, 1.55 (3H each, all d, $J=6.1$ Hz), 1.45 (3H, d, $J=5.8$ Hz), 1.48 (3H, d, $J=5.5$ Hz) ($\text{CH}_3 \times 5$ in sugar moiety), 2.04 (3H, s, 19- H_3), 2.11 (3H, s, 21- H_3), 3.47 (3H, s, OCH_3), 3.51 (6H, s, $\text{OCH}_3 \times 2$), 3.56, 3.58 (3H each, both s, $\text{OCH}_3 \times 2$), 3.86 (1H, m, 3-H), 4.70, 4.92 (1H each, both dd, $J=9.8, 1.8$ Hz, two anomeric protons), 4.97, 5.12, 5.26 (1H each, all dd, $J=9.5, 1.8$ Hz, three anomeric protons), 5.31 (1H, t-like, 6-H), 5.34 (1H, dd, $J=11.7, 4.1$ Hz, 12-H), 7.47 (2H, dd, $J=7.5, 7.5$ Hz), 7.55 (1H, t, $J=7.5$ Hz), 8.29 (2H, d, $J=7.5$ Hz) (benzoyl moiety). $^{13}\text{C-NMR}$: as given in Table I. FAB-MS (negative) m/z : 1187 ($\text{M}-\text{H}$)⁻. High resolution FAB-MS m/z : Calcd for $\text{C}_{63}\text{H}_{96}\text{O}_{21} + \text{Na}$: 1211.6340. Found: 1211.6290 ($\text{M} + \text{Na}$)⁺.

Calotroposide B (2): A white amorphous solid. $[\alpha]_D +12.2^\circ$ ($c=0.9$, in CHCl_3 at 22°C). IR (CHCl_3) cm^{-1} : 3530, 1710, 1600, 1450, 1275, 1100. UV (MeOH) nm (log ϵ): 230 (4.05), 273 (3.15), 280 (3.09). $^1\text{H-NMR}$ (d_5 -pyridine) δ : 1.33 (3H, s, 18- H_3), 1.39, 1.40, 1.55 (3H each, all d, $J=6.1$ Hz, $\text{CH}_3 \times 3$ in sugar moiety), 1.45, 1.48 (3H each, both d, $J=6.4$ Hz, $\text{CH}_3 \times 2$ in sugar moiety), 2.07 (3H, s, 19- H_3), 2.36 (3H, s, 21- H_3), 3.47, 3.52, 3.56, 3.58, 3.63 (3H each, all s, $\text{OCH}_3 \times 5$), 3.86 (1H, m, 3-H), 4.70, 4.91 (1H each, both dd, $J=9.5, 1.8$ Hz, two anomeric protons), 4.98, 5.12, 5.26 (1H each, all dd, $J=9.8, 1.8$ Hz, three anomeric protons), 5.31 (1H, t-like, 6-H), 5.34 (1H, dd, $J=11.7, 4.6$ Hz, 12-H), 7.47 (2H, dd, $J=7.6, 7.6$ Hz), 7.55 (1H, t, $J=7.6$ Hz), 8.29 (2H, d, $J=7.6$ Hz) (benzoyl moiety). $^{13}\text{C-NMR}$: as given in Table I. FAB-MS m/z : 1203 ($\text{M}-\text{H}$)⁻. High resolution FAB-MS m/z : Calcd for $\text{C}_{63}\text{H}_{96}\text{O}_{22} + \text{Na}$: 1227.6290. Found: 1227.6270 ($\text{M} + \text{Na}$)⁺.

Methanolysis of 1 Giving 3 A solution of **1** (35 mg) in 9% HCl–MeOH (1.5 ml) was heated under reflux for 2 h. After cooling, the reaction mixture was neutralized with Ag_2CO_3 powder and the precipitate was removed by filtration. The solvent was evaporated off under reduced pressure from the filtrate to give a product (22 mg). Purification of the product by column chromatography (SiO_2 10 g, benzene:acetone = 7:1) afforded **3** (15 mg), methyl oleandroside (a mixture of α -a and β -a, 4 mg) and methyl cymaroside (a mixture of α -b and β -b, 5 mg).

3: Colorless needles, mp 243–245°C (MeOH). $[\alpha]_D -57.2^\circ$ ($c=0.5$, in CHCl_3 at 25°C). IR (CHCl_3) cm^{-1} : 3540, 1710, 1600, 1450, 1280, 1110. UV (EtOH) nm (log ϵ): 230 (4.18), 273 (3.15), 280 (3.09). CD ($c=4.98 \times 10^{-2}$, MeOH): $[\theta]_{247} -3.30 \times 10^4$ (negative max.). $^1\text{H-NMR}$ (d_5 -pyridine) δ : 1.39 (3H, s, 18- H_3), 2.04 (3H, s, 19- H_3), 2.12 (3H, s, 21- H_3), 3.87 (1H, m, 3-H), 5.34 (1H, t-like, 6-H), 7.42 (2H, dd, $J=7.6, 7.6$ Hz), 7.53 (1H, t, $J=7.6$ Hz), 8.27 (2H, d, $J=7.6$ Hz) (benzoyl moiety). $^{13}\text{C-NMR}$: as given in Table II. EI-MS m/z (%): 468 (M^+ , 2), 346 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COOH}$, 52), 328 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COOH} - \text{H}_2\text{O}$, 14), 105 (COC_6H_5 , 100). High resolution EI-MS m/z : Calcd for $\text{C}_{28}\text{H}_{36}\text{O}_6$: 468.2500. Found: 468.2510 (M^+).

Methyl Oleandroside (a): $^{13}\text{C-NMR}$ (d_5 -pyridine) δ : 18.5 (C-6), 36.7 (C-2), 56.0 (C-1- OCH_3), 56.9 (C-3- OCH_3), 72.8 (C-5), 76.3 (C-4), 81.4 (C-3), 101.1 (C-1) for β -a; 18.5 (C-6), 35.2 (C-2), 54.3 (C-1- OCH_3), 57.0 (C-3- OCH_3), 68.6 (C-5), 76.7 (C-4), 79.1 (C-3), 98.7 (C-1) for α -a.

Methyl Cymaroside (b): $^{13}\text{C-NMR}$ (d_5 -pyridine) δ : 18.9 (C-6), 35.2 (C-2), 55.9 (C-1- OCH_3), 57.8 (C-3- OCH_3), 71.1 (C-5), 74.1 (C-4), 78.6 (C-3), 99.5 (C-1) for β -b; 18.5 (C-6), 31.8 (C-2), 54.8 (C-1- OCH_3), 56.7 (C-3- OCH_3), 65.2 (C-5), 73.3 (C-4), 76.5 (C-3), 97.7 (C-1) for α -b. These $^{13}\text{C-NMR}$ data for **a** and **b** were identical with those reported.⁹⁾

Acidic Hydrolysis of Methyl Oleandroside and Methyl Cymaroside Methyl oleandroside (**a**, 15 mg) was treated with 5% aqueous HCl (1 ml) at room temperature for 1 h. The reaction mixture was neutralized with Ag_2CO_3 powder and the precipitate was removed by filtration. The solvent was evaporated off under reduced pressure from the filtrate to give a product, which was purified by column chromatography (SiO_2 1 g, benzene:acetone = 5:2) to afford D-oleandrose (8.4 mg), $[\alpha]_D -17.3^\circ$ ($c=0.50$, 24 h after dissolution in H_2O , at 25°C). D-Cymarose {8.4 mg, $[\alpha]_D +54.2^\circ$ ($c=0.62$, 24 h after dissolution in H_2O , at 25°C)} was obtained from methyl cymaroside (**b**, 17 mg) through the same procedure as described for D-oleandrose from methyl oleandroside (**a**).

Alkaline Hydrolysis of 3 Giving 4 A mixture of **3** (8 mg) in acetone (0.5 ml) and 10% aqueous KOH (0.5 ml), was heated under reflux for 2 h. After cooling, the reaction mixture was neutralized with Dowex 50W $\times$ 8 (H^+ form) and the resin was filtered off. The solvent was evaporated off

under reduced pressure from the filtrate to give a product (8 mg). Purification of the product by column chromatography (SiO₂ 5 g, *n*-hexane:benzene:acetone=1:2:1) afforded **4** (=lineolon,¹² 5 mg).

4: Colorless needles, mp 238–242 °C (acetone). $[\alpha]_D^{25} +19.8^\circ$ ($c=0.3$, in MeOH at 25 °C). IR (CHCl₃) cm^{-1} : 3460, 2920, 1710, 1450, 1270, 1105. CD ($c=1.07 \times 10^{-2}$, MeOH): $[\theta]_{245}^{25} -2.18 \times 10^4$ (negative max.). ¹H-NMR (*d*₅-pyridine) δ : 1.45 (3H, s, 18-H₃), 1.98 (3H, s, 19-H₃), 2.11 (3H, s, 21-H₃), 3.86 (1H, m, 3-H), 3.94 (1H, dd, $J=11.8, 4.2$ Hz, 12-H), 5.36 (1H, t-like, 6-H). ¹³C-NMR: as given in Table II. EI-MS m/z (%): 364 (M^+ , 2), 346 ($M^+ - H_2O$, 14), 55 (100). High-resolution EI-MS m/z : Calcd for C₂₁H₃₂O₅: 364.2250. Found: 364.2237 (M^+).

Acidic Hydrolysis of 1 for Analysis of Sugar Moiety Calotroposide A (**1**, 5 mg) was treated with 5% aqueous HCl (2 ml) at 80 °C for 2 h. After cooling, the reaction mixture was neutralized with Ag₂CO₃ powder. The precipitate was removed by filtration. The solvent was evaporated off under reduced pressure from the filtrate to give a product (4 mg). The product was then treated with bis(trimethylsilyl)trifluoroacetamide (0.2 ml) and pyridine (0.1 ml) at room temperature for 10 min. The mixture was subjected to GLC analysis to determine the sugar components as TMS-oleandrose and TMS-cymarose in 2:3 ratio by comparison with authentic samples, which were prepared from methyl glycosides (**a**, **b**) by treatment with 5% aqueous HCl and trimethylsilylation. GLC conditions: column, 2% OV-17 on Chromosorb WAWDMCS (80–100 mesh), 3 mm $\times$ 2 m; column temperature, 80 °C, carrier gas, N₂; flow-rate, 35 ml/min. TMS-oleandrose: t_R 38.4, 42.4 min; TMS-cymarose: t_R 49.2, 56.4 min.

Acetylation of 1 Giving 5 Calotroposide A (**1**, 14 mg) was treated with Ac₂O (0.5 ml) and pyridine (0.5 ml) at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with EtOAc. The EtOAc extract was washed with 5% aqueous HCl, aqueous saturated NaHCO₃, and brine, then dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (13 mg). Purification of the product by column chromatography (SiO₂ 5 g, benzene:acetone=4:1) afforded **5** (11 mg).

5: A white amorphous solid. $[\alpha]_D^{25} +2.2^\circ$ ($c=0.7$, in CHCl₃ at 23 °C). IR (CHCl₃) cm^{-1} : 3530, 1730, 1710, 1600, 1450, 1270, 1100. UV (MeOH) nm (log ϵ): 230 (4.12), 272 (3.12), 280 (3.05). ¹H-NMR (CDCl₃) δ : 1.12 (3H, s, 18-H₃), 1.20 (3H, d, $J=6.1$ Hz), 1.21 (3H, d, $J=5.2$ Hz), 1.22, 1.29, 1.31 (3H each, all d, $J=6.1$ Hz) (CH₃ $\times$ 5 in sugar moiety), 1.59 (3H, s, 19-H₃), 2.03 (3H, s, 21-H₃), 2.11 (3H, s, OCOCH₃), 3.39 (6H, s, OCH₃ $\times$ 2), 3.43, 3.44, 3.45 (3H each, all s, OCH₃ $\times$ 3), 3.56 (1H, m, 3-H), 4.44, 4.66 (1H each, both dd, $J=9.8, 1.8$ Hz, two anomeric protons), 4.52 (1H, dd, $J=9.8, 2.9$ Hz, 4''-H), 4.75, 4.85, 4.97 (1H each, all dd, $J=9.5, 1.8$ Hz, three anomeric protons), 4.98 (1H, dd, $J=11.6, 4.3$ Hz, 12-H), 5.38 (1H, t-like, 6-H), 7.44 (2H, dd, $J=7.6, 7.6$ Hz), 7.66 (1H, t, $J=7.6$ Hz), 7.96 (2H, d, $J=7.6$ Hz) (benzoyl moiety). FAB-MS m/z : 1253 ($M+Na$)⁺. High-resolution FAB-MS m/z : Calcd for C₆₅H₉₈O₂₂ + Na: 1253.6470. Found: 1253.6447 ($M+Na$)⁺.

Partial Hydrolysis of 1 Followed by Acetylation A solution of **1** (25 mg) in MeOH (1.2 ml) was treated with 0.5% aqueous H₂SO₄ (0.4 ml) and the whole mixture was heated with stirring at 50 °C for 2 h. After cooling, the reaction mixture was neutralized with aqueous saturated Ba(OH)₂ and the precipitate was filtered off. The solvent from the filtrate was removed under reduced pressure to give a product (20 mg). The product was treated with Ac₂O (0.5 ml) and pyridine (0.5 ml) at room temperature for 12 h. Work-up of the reaction mixture in a usual manner gave a product (20 mg). Purification of this product by HPLC (Shim pack PREP-ODS, 0.25 m $\times$ 20 mm, MeOH:H₂O=10:1) afforded **6** (2.5 mg), **7** (5.1 mg), and **8** (5.2 mg).

6: A white amorphous solid. $[\alpha]_D^{25} -9.8^\circ$ ($c=0.4$, CHCl₃ at 24 °C). IR (KBr) cm^{-1} : 3500, 1740, 1720, 1600, 1450, 1270, 1100. ¹H-NMR (CDCl₃) δ : 1.13 (3H, s, 18-H₃), 1.20 (3H, d, $J=6.4$ Hz, 5'-CH₃), 1.56 (3H, s, 19-H₃), 2.03 (3H, s, 21-H₃), 2.12 (3H, s, OCOCH₃), 3.41 (3H, s, OCH₃), 3.56 (1H, m, 3-H), 4.54 (1H, dd, $J=9.8, 2.9$ Hz, 4'-H), 4.89 (1H, dd, $J=9.5, 1.8$ Hz, 1'-H), 4.95 (1H, dd, $J=11.5, 4.3$ Hz, 12-H), 5.38 (1H, t-like, 6-H), 7.43 (2H, dd, $J=7.7, 7.7$ Hz), 7.54 (1H, t, $J=7.7$ Hz), 7.96 (2H, d, $J=7.7$ Hz) (benzoyl moiety). FAB-MS m/z : 677 ($M+Na$)⁺. High-resolution FAB-MS m/z : Calcd for C₃₇H₅₀O₁₀ + Na: 677.3302. Found: 677.3273 ($M+Na$)⁺.

7: A white amorphous solid. $[\alpha]_D^{25} -7.4^\circ$ ($c=0.4$, CHCl₃ at 24 °C). IR (KBr) cm^{-1} : 3500, 1740, 1720, 1600, 1460, 1270, 1100. ¹H-NMR (CDCl₃) δ : 1.12 (3H, s, 18-H₃), 1.23, 1.29 (3H each, both d, $J=6.5$ Hz, CH₃ $\times$ 2 in sugar moiety), 1.56 (3H, s, 19-H₃), 2.03 (3H, s, 21-H₃), 2.11 (3H, s, OCOCH₃), 3.40, 3.46 (3H each, both s, OCH₃ $\times$ 2), 3.56 (1H, m, 3-H), 4.52 (1H, dd, $J=9.8, 3.0$ Hz, 4''-H), 4.78, 4.85 (1H each, both dd, $J=9.8, 1.8$ Hz, two anomeric protons), 4.95 (1H, dd, $J=11.6, 4.6$ Hz, 12-H), 5.38

(1H, t-like, 6-H), 7.42 (2H, dd, $J=7.7, 7.7$ Hz), 7.52 (1H, t, $J=7.7$ Hz), 7.96 (2H, d, $J=7.7$ Hz) (benzoyl moiety). FAB-MS m/z : 821 ($M+Na$)⁺. High resolution FAB-MS m/z : Calcd for C₄₄H₆₂O₁₃ + Na: 821.4088. Found: 821.4033 ($M+Na$)⁺.

8: A white amorphous solid. $[\alpha]_D^{25} -16.8^\circ$ ($c=0.6$, CHCl₃ at 24 °C). IR (KBr) cm^{-1} : 3500, 1740, 1720, 1600, 1450, 1270, 1100. ¹H-NMR (CDCl₃) δ : 1.12 (3H, s, 18-H₃), 1.19 (3H, d, $J=6.4$ Hz), 1.22 (6H, d, $J=6.4$ Hz), (CH₃ $\times$ 3 in sugar moiety), 1.56 (3H, s, 19-H₃), 2.03 (3H, s, 21-H₃), 2.09 (3H, s, OCOCH₃), 3.32 (3H, s, OCH₃), 3.45 (6H, s, OCH₃ $\times$ 2), 3.56 (1H, m, 3-H), 4.51 (1H, dd, $J=9.8, 2.0$ Hz, one anomeric proton), 4.65 (1H, dd, $J=9.3, 9.3$ Hz, 4'''-H), 4.76, 4.85 (1H each, both dd, $J=9.5, 1.8$ Hz, two anomeric protons), 4.95 (1H, dd, $J=11.6, 4.6$ Hz, 12-H), 5.37 (1H, t-like, 6-H), 7.47 (2H, dd, $J=7.6, 7.6$ Hz), 7.54 (1H, t, $J=7.6$ Hz), 7.96 (2H, d, $J=7.6$ Hz) (benzoyl moiety). FAB-MS m/z : 965 ($M+Na$)⁺. High resolution FAB-MS m/z : Calcd for C₅₁H₇₄O₁₆ + Na: 965.4875. Found: 965.4920 ($M+Na$)⁺.

Methanolysis of 2 A solution of **2** (30 mg) in 9% HCl-MeOH (2.0 ml) was heated under reflux for 2 h. After cooling, the reaction mixture was neutralized with Ag₂CO₃ powder and the precipitate was removed by filtration. The solvent was evaporated off under reduced pressure from the filtrate to give a product (20 mg). Purification of the product by column chromatography (SiO₂ 10 g, benzene:acetone=7:1) afforded **9** (=12-*O*-benzoyldeacetylmetaplexigenin,¹⁵ 12 mg), methyl oleandroside (**a**, 4 mg) and methyl cymaroside (**b**, 4 mg).

9: Colorless needles, mp 247 °C (MeOH). $[\alpha]_D^{25} -20.6^\circ$ ($c=0.8$, in CHCl₃ at 24 °C). IR (CHCl₃) cm^{-1} : 3460, 2920, 1710, 1600, 1450, 1270, 1180. UV (EtOH) nm (log ϵ): 282 (4.12), 273 (3.04), 280 (2.95). ¹H-NMR (CDCl₃) δ : 1.15 (3H, s, 18-H₃), 1.54 (3H, s, 19-H₃), 2.07 (3H, s, 21-H₃), 3.58 (1H, m, 3-H), 4.86 (1H, dd, $J=11.7, 4.6$ Hz, 12-H), 5.39 (1H, t-like, 6-H), 7.44 (2H, dd, $J=7.6, 7.3$ Hz), 7.55 (1H, t, $J=7.3$ Hz), 7.94 (2H, d, $J=7.6$ Hz) (benzoyl moiety); (*d*₅-pyridine) δ : 1.40 (3H, s, 18-H₃), 2.07 (3H, s, 19-H₃), 2.35 (3H, s, 21-H₃), 3.86 (1H, m, 3-H), 5.35 (1H, t-like, 6-H), 5.37 (1H, dd, $J=11.7, 4.6$ Hz, 12-H), 7.48 (2H, dd, $J=7.7, 7.7$ Hz), 7.53 (1H, t, $J=7.7$ Hz), 8.28 (2H, d, $J=7.7$ Hz) (benzoyl moiety). ¹³C-NMR: as given in Table II. EI-MS m/z (%): 484 (M^+ , 0.2), 441 ($M^+ - COCH_3$, 18), 319 ($M^+ - C_6H_5COOH - COCH_3$, 54), 301 (41), 283 (42), 105 (COC₆H₅, 100). High-resolution EI-MS m/z : Calcd for C₂₈H₃₆O₇: 484.2463. Found: 484.2461 (M^+).

Alkaline Hydrolysis of 9 Giving 10 A mixture of **9** (10 mg) in acetone (0.5 ml) and 10% aqueous KOH (0.5 ml) was heated under reflux for 2 h. After cooling, the reaction mixture was neutralized with Dowex 50W $\times$ 8 (H⁺ form) and the resin was filtered off. The solvent was evaporated off under reduced pressure from the filtrate to give a product (9 mg). Purification of the product by column chromatography (SiO₂ 5 g, *n*-hexane:benzene:acetone=1:2:1) afforded **10** (=deacetylmetaplexigenin,¹⁵ 7 mg).

10: Colorless needles, mp. 192–195 °C (EtOAc). $[\alpha]_D^{25} +30.5^\circ$ ($c=0.45$, in MeOH at 25 °C). IR (CHCl₃) cm^{-1} : 3460, 2930, 1700. ¹H-NMR (CDCl₃) δ : 1.17 (3H, s, 18-H₃), 1.26 (3H, s, 19-H₃), 2.35 (3H, s, 21-H₃), 3.57 (1H, m, 3-H), 3.68 (1H, dd, $J=11.7, 4.5$ Hz, 12-H), 5.37 (1H, t-like, 6-H). ¹³C-NMR: as given in Table II. FAB-MS m/z : 381 ($M+H$)⁺. High-resolution FAB-MS m/z : Calcd for C₂₁H₃₃O₆: 381.2277. Found: 381.2291 ($M+H$)⁺.

Acidic Hydrolysis of 2 for Analysis of Sugar Moiety Calotroposide B (**2**, 6 mg) was treated with 5% aqueous HCl (2 ml) at 80 °C for 2 h. After cooling, the reaction mixture was neutralized with Ag₂CO₃ powder. The precipitate was removed by filtration. The solvent was evaporated off under reduced pressure from the filtrate to give a product (4 mg). The product was then treated with bis(trimethylsilyl)trifluoroacetamide (0.2 ml) and pyridine (0.1 ml) at room temperature for 10 min. The mixture was subjected to GLC analysis to determine that the sugar components were cymarose and oleandrose by comparison with authentic samples prepared from methyl oleandroside (**a**) and methyl cymaroside (**b**). GLC conditions: the same as for analysis of sugars from calotroposide A (**1**) described above.

Acetylation of 2 Giving 11 Calotroposide B (**2**, 12 mg) was treated with Ac₂O (0.5 ml) and pyridine (0.5 ml) at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with EtOAc. The EtOAc extract was washed with 5% aqueous HCl, aqueous saturated NaHCO₃, and brine, then dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (13 mg). Purification of the product by column chromatography (SiO₂ 5 g, benzene:acetone=4:1) afforded **11** (10 mg).

11: A white amorphous solid. $[\alpha]_D^{25} +19.4^\circ$ ($c=0.5$, in CHCl₃ at 22 °C). IR (CHCl₃) cm^{-1} : 3530, 1730, 1710, 1600, 1450, 1270, 1100. UV (EtOH) nm (log ϵ): 230 (4.12), 272 (3.11), 280 (3.05). ¹H-NMR (CDCl₃) δ : 1.13 (3H,

s, 18-H₃), 1.20 (3H, d, $J=6.1$ Hz), 1.21 (3H, d, $J=5.5$ Hz), 1.22, 1.29, 1.31 (3H each, all d, $J=6.1$ Hz) (CH₃ × 5 in sugar moiety), 1.54 (3H, s, 19-H₃), 2.07 (3H, s, 21-H₃), 2.11 (3H, s, OCOCH₃), 3.39, 3.40, 3.43, 3.46, 3.47 (3H each, all s, OCH₃ × 5), 3.56 (1H, m, 3-H), 4.44, 4.67 (1H each, both dd, $J=9.8$, 1.8 Hz, two anomeric protons), 4.52 (1H, dd, $J=9.8$, 2.9 Hz, 4''''-H), 4.57, 4.85, 4.97 (1H each, all dd, $J=9.5$, 1.8 Hz, three anomeric protons), 4.96 (1H, dd, $J=11.4$, 4.6 Hz, 12-H), 5.38 (1H, t-like, 6-H), 7.44 (2H, dd, $J=7.6$, 7.6 Hz), 7.54 (1H, t, $J=7.6$ Hz), 7.94 (2H, d, $J=7.6$ Hz) (benzoyl moiety). FAB-MS m/z : 1269 (M+Na)⁺. High-resolution FAB-MS m/z : Calcd for C₆₅H₉₈O₂₃+Na: 1269.6460. Found: 1269.6397 (M+Na)⁺.

Partial Hydrolysis of 2 Followed by Acetylation A solution of **2** (25 mg) in MeOH (1.5 ml) was treated with 0.5% aqueous H₂SO₄ (0.5 ml) and the whole mixture was heated with stirring at 50 °C for 2 h. After cooling, the reaction mixture was neutralized with aqueous saturated Ba(OH)₂ and the precipitate was filtered off. The solvent from the filtrate was removed under reduced pressure to give a product (20 mg). The product was treated with Ac₂O (0.5 ml) and pyridine (0.5 ml) at room temperature for 12 h. Work-up of the reaction mixture in a usual manner gave a product (20 mg). Purification of this product by HPLC (Shim-pack PREP-ODS, 0.25 m × 20 mm, MeOH:H₂O=10:1) afforded **12** (2.5 mg), **13** (2.3 mg), and **14** (2.5 mg).

12: A white amorphous solid. $[\alpha]_D^{25} +5.8^\circ$ ($c=0.4$, in CHCl₃ at 24 °C). IR (KBr) cm⁻¹: 3450, 1740, 1720, 1600, 1450, 1270, 1100. ¹H-NMR (CDCl₃) δ : 1.13 (3H, s, 18-H₃), 1.20 (3H, d, $J=6.4$ Hz, 6'-H₃), 1.56 (3H, s, 19-H₃), 2.07 (3H, s, 21-H₃), 2.11 (3H, s, OCOCH₃), 3.42 (3H, s, OCH₃), 3.56 (1H, m, 3-H), 4.54 (1H, dd, $J=9.5$, 2.7 Hz, 4'-H), 4.88 (1H, dd, $J=9.5$, 2.0 Hz, 1'-H), 4.96 (1H, dd, $J=11.4$, 4.5 Hz, 12-H), 5.37 (1H, t-like, 6-H), 7.44 (2H, dd, $J=7.3$, 7.3 Hz), 7.56 (1H, t, $J=7.3$ Hz), 7.95 (2H, d, $J=7.3$ Hz) (benzoyl moiety). FAB-MS m/z : 693 (M+Na)⁺. High resolution FAB-MS m/z : Calcd for C₃₇H₅₀O₁₁+Na: 693.3251. Found: 693.3248 (M+Na)⁺.

13: A white amorphous solid. $[\alpha]_D^{25} +3.9^\circ$ ($c=0.3$, in CHCl₃ at 25 °C). IR (KBr) cm⁻¹: 3500, 1740, 1720, 1600, 1450, 1270, 1100. ¹H-NMR (CDCl₃) δ : 1.13 (3H, s, 18-H₃), 1.18 (3H, d, $J=6.4$ Hz), 1.23 (3H, d, $J=6.0$ Hz), (CH₃ × 2 in sugar moiety), 1.56 (3H, s, 19-H₃), 2.07 (3H, s, 21-H₃), 2.11 (3H, s, OCOCH₃), 3.40, 3.46 (3H each, both s, OCH₃ × 2), 3.56 (1H, m, 3-H), 4.52 (1H, dd, $J=9.8$, 2.7 Hz, 4''-H), 4.78 (1H, dd, $J=9.4$, 2.0 Hz), 4.85 (1H, dd, $J=9.8$, 1.8 Hz) (two anomeric protons), 4.86 (1H, dd, $J=11.6$, 4.5 Hz, 12-H), 5.38 (1H, t-like, 6-H), 7.45 (2H, dd, $J=7.6$, 7.6 Hz), 7.56 (1H, t, $J=7.6$ Hz), 7.94 (2H, d, $J=7.6$ Hz) (benzoyl moiety). FAB-MS m/z : 837 (M+Na)⁺. High resolution FAB-MS m/z : Calcd for C₄₄H₆₂O₁₄+Na: 837.4037. Found: 837.3981 (M+Na)⁺.

14: A white amorphous solid. $[\alpha]_D^{25} +2.9^\circ$ ($c=0.4$, in CHCl₃ at 24 °C). IR (KBr) cm⁻¹: 3470, 1740, 1720, 1600, 1450, 1270, 1100. ¹H-NMR (CDCl₃) δ : 1.13 (3H, s, 18-H₃), 1.19 (3H, d, $J=6.1$ Hz), 1.22 (6H, d, $J=6.1$ Hz) (CH₃ × 3 in sugar moiety), 1.56 (3H, s, 19-H₃), 2.07 (3H, s, 21-H₃), 2.10 (3H, s, OCOCH₃), 3.32 (3H, s), 3.45 (6H, s) (OCH₃ × 3), 3.56 (1H, m, 3-H), 4.51 (1H, dd, $J=9.8$, 2.1 Hz, one anomeric proton), 4.61

(1H, dd, $J=9.5$, 9.5 Hz, 4'''-H), 4.76, 4.85 (1H each, both dd, $J=9.8$, 1.8 Hz, two anomeric protons), 4.87 (1H, dd, $J=11.5$, 4.3 Hz, 12-H), 5.39 (1H, t-like, 6-H), 7.44 (2H, dd, $J=7.6$, 7.6 Hz), 7.56 (1H, t, $J=7.6$ Hz), 7.94 (2H, d, $J=7.6$ Hz) (benzoyl moiety). FAB-MS m/z : 981 (M+Na)⁺. High resolution FAB-MS m/z : Calcd for C₅₁H₇₄O₁₇+Na: 981.4824. Found: 981.4868 (M+Na)⁺.

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