Indonesian Medicinal Plants. V.[1] Chemical Structures of Calotroposides C, D, E, F, and G, Five Additional New Oxypregnane-Oligoglycosides from the Root of *Calotropis gigantea* (Asclepiadaceae)

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Following the chemical characterization of calotroposides A (1) and B (2), five related oxypregnane-oligoglycosides named calotroposides C (3), D (4), E (5), F (6), and G (7) have been additionally isolated from the root of *Calotropis gigantea* (Asclepiadaceae), an Indonesian medicinal plant. The chemical structures of the new calotroposides have been elucidated on the basis of chemical and physicochemical properties as 12-*O*-benzoyldeacetylmetaplexigenin 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside for 3, 12-*O*-benzoyllineolon 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside for 4, 12-*O*-benzoyldeacetylmetaplexigenin 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside for 5, 12-*O*-benzoyllineolon 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside for 6, and 12-*O*-benzoyllineolon 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside for 7.

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

The root of *Calotropis gigantea* DRYAND. (Asclepiadaceae) is a traditional folk medicine and has been used as an antidote for snake-bite and as an anti-scabetic in Timor Island, Indonesia.[2] As a part of our chemical characterization studies of Indonesian medicinal plants,[3] we have been engaged in chemical investigations on the constituents of the root and have isolated seven new oxypregnane-oligoglycosides named calotroposides A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), F (**6**), and G (**7**).[3e] The chemical structure elucidation of calotroposides A (**1**) and B (**2**) was reported in our previous paper.[3e] We deal herein with the structure elucidation of the remaining five oxypregnane-oligoglycosides, calotroposides C (**3**), D (**4**), E (**5**), F (**6**), and G (**7**).

Calotroposide G (**7**) showed a negative ion peak at *m/z* 899 for $(M-H)^-$ in its fast atom bombardment (FAB) mass spectrum (MS), thus indicating the molecular weight to be 900. The infrared (IR) spectrum of **7** showed absorption bands due to hydroxyl (3565 cm^{-1}) and carbonyl (1715 cm^{-1}) groups, whereas the ultraviolet (UV) spectrum of **7** suggested the presence of a benzoyl group (absorption maxima at 230, 270, and 280 nm).

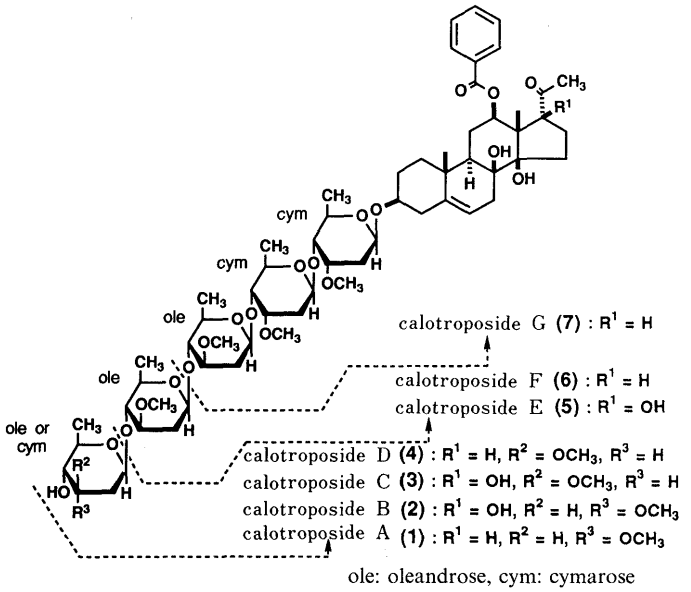

Fig. 1

The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **7** exhibited the signals characteristic of an oxypregnane-oligoglycoside containing one oleandrose and two cymarose moieties[4] (Tables I and II). Three anomeric proton signals were observed in the proton (^1H) NMR spectrum of **7** at δ 4.78 (1H, dd, J=9.8, 1.5 Hz); δ 4.97 and 5.14 (1H both, dd, J=9.5, 1.8 Hz), which indicated that **7** possesses three monosaccharide moieties all with a β-glycosidic linkage as judged from the coupling constants.[4]

On methanolysis with 9% methanolic hydrogen chloride, calotroposide G (**7**) liberated 12-*O*-benzoyllineolon (**8**),[5] which is the aglycone of the previously reported calotroposide A (**1**),[3e] 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.[6] Both methyl glycosides (**a**, **b**) were hydrolyzed further with 5% aqueous hydrochloric acid to yield D-oleandrose and D-cymarose, respectively, as substantiated by their optical rotations.

The location of the carbohydrate moiety on the C-3 hydroxyl group of the aglycone **8** was determined from the fact that glycosylation shifts[7] were observed in the ^{13}C-NMR spectrum of **7** for the signals of C-2 (−2.3 ppm), C-3 (+6.3 ppm), and C-4 (−4.3 ppm) as compared with those signals of the aglycone **8** (Table I).

Acidic hydrolysis of calotroposide G (**7**) with 5% aqueous hydrochloric acid yielded a mixture of oleandrose and cymarose in 1:2 ratio as determined by gas liquid chromatographic (GLC) analysis. Finally, a monoacetate (**9**), prepared from **7**, was shown to be identical with a trisaccharide monoacetate, one of the acetolysis products of calotroposide A (**1**).[3e] Thus, the structure of calotroposide G (**7**) has been concluded to be 12-*O*-benzoyllineolon 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside.

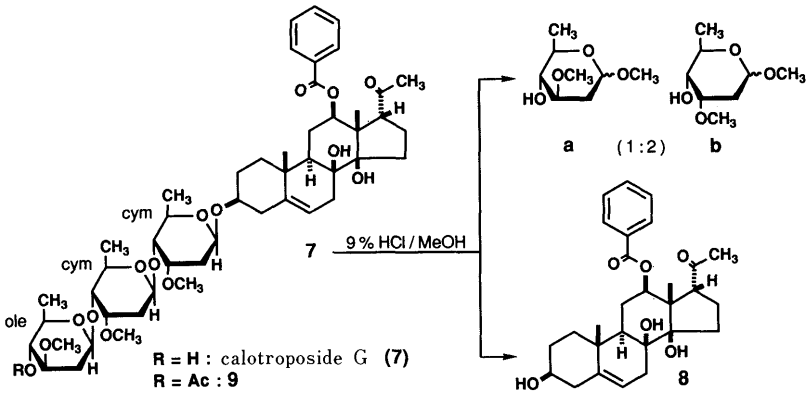

Chart 1

TABLE I. ^{13}C-NMR Data for the Aglycone Parts of Calotroposides C (3), D (4), E (5), F (6), and G (7), and for 8 and 11 (in C_5D_5N)

	3	4	5	6	7	8	11
C-1	39.3	39.2	39.3	39.0	39.2	39.2	39.2
C-2	29.8	29.7	29.8	29.6	29.7	32.0	32.1
C-3	77.7	77.7	77.8	77.8	77.9	71.6	71.6
C-4	38.9	38.8	38.9	38.7	38.9	43.2	43.3
C-5	139.5	139.5	139.5	139.2	139.4	140.5	140.4
C-6	119.1	118.9	119.0	119.0	119.1	118.4	118.4
C-7	33.9[a]	33.8[a]	33.8[a]	34.0[a]	34.1[a]	34.2[a]	33.9[a]
C-8	74.2	74.2	74.3	74.3	74.5	74.7	74.5
C-9	44.5	44.4	44.4	44.4	44.6	44.8	44.5
C-10	37.6	37.6	37.4	37.4	37.5	37.5	37.4
C-11	25.0	24.9	25.0	24.8	24.9	25.0	25.1
C-12	74.1	73.9	74.0	73.5	73.7	73.8	74.1
C-13	58.4	56.0	58.3	55.9	56.0	56.1	58.4
C-14	89.5	87.4	89.5	87.3	87.4	87.5	89.6
C-15	34.8[a]	35.1[a]	34.8[a]	34.9[a]	35.1[a]	35.2[a]	34.8[a]
C-16	33.2[a]	22.0	33.1[a]	21.9	22.1	22.2	33.3[a]
C-17	92.5	60.2	92.4	60.1	60.2	60.4	92.5
C-18	10.7	15.7	10.7	15.7	15.8	15.8	10.8
C-19	18.2	18.2	18.2	18.0	18.1	18.4	18.4
C-20	209.9	209.3	209.9	209.4	209.5	209.4	210.1
C-21	27.7	32.0	27.7	32.0	32.1	32.1	27.8
CO-Ph	165.3	165.4	165.3	165.3	165.4	165.5	165.3
Phenyl							
(C-1)	131.3	131.2	131.2	131.0	131.2	131.4	131.3
(C-2)	128.9	128.7	128.8	128.7	128.8	128.8	128.9
(C-3)	129.9	129.8	129.8	129.7	129.8	129.9	129.9
(C-4)	133.2	133.1	133.2	133.1	133.2	133.2	133.2
(C-5)	129.9	129.8	129.8	129.7	129.8	129.9	129.9
(C-6)	128.9	128.7	128.8	128.7	128.8	128.8	128.9

a) The assignments in each column may be interchangeable.

TABLE II. ^{13}C-NMR Data for Sugar Moieties of Calotroposides C (3), D (4), E (5), F (6), and G (7) (in C_5D_5N)

		3	4	5	6	7
cym	C-1′	96.4	96.3	96.4	96.2	96.3
	C-2′	37.0[a]	37.1[a]	37.0[a]	37.3[a]	37.2[a]
	C-3′	77.7[b]	77.7[b]	77.8[b]	77.7[b]	77.7[b]
	C-4′	83.2[c]	83.2[c]	83.2[c]	83.1[c]	83.3[c]
	C-5′	69.1[d]	68.9[d]	69.0[d]	68.7[d]	69.0[d]
	C-6′	18.7[e]	18.6[e]	18.6[e]	18.5[e]	18.5[e]
	C-3′-OMe	58.8[f]	58.7[f]	58.8[f]	58.7[f]	58.8[f]
cym	C-1″	100.1	100.0	100.2	100.1	100.4
	C-2″	37.3[a]	37.2[a]	37.2[a]	37.3[a]	37.3[a]
	C-3″	77.8[b]	77.9[b]	77.7[b]	77.5[b]	77.6[b]
	C-4″	83.4[c]	83.1[c]	82.6[c]	82.9[c]	83.1[c]
	C-5″	69.0[d]	69.0[d]	68.9[d]	68.8[d]	69.0[d]
	C-6″	18.8[e]	18.7[e]	18.7[e]	18.5[e]	18.5[e]
	C-3″-OMe	58.9[f]	58.8[f]	58.9[f]	58.8[f]	58.7[f]
ole	C-1‴	100.3	100.2	100.4	100.2	102.0
	C-2‴	37.3[a]	37.4[a]	37.3[a]	36.9[a]	36.9[a]
	C-3‴	79.1	79.0	79.0	78.8	81.1
	C-4‴	82.9[c]	82.9[c]	82.6[c]	82.5[c]	75.8
	C-5‴	71.7	71.5	71.7	71.4	73.1
	C-6‴	18.5[e]	18.5[e]	18.4[e]	18.3[e]	18.6[e]
	C-3‴-OMe	57.3	57.2	57.2	57.1	57.1
ole	C-1⁗	100.4	100.3	101.7	101.9	
	C-2⁗	37.4[a]	37.4[a]	37.3[a]	37.4[a]	
	C-3⁗	79.3	79.2	81.6	81.3	
	C-4⁗	82.8[c]	82.8[c]	76.3	76.1	
	C-5⁗	71.8	71.6	72.9	72.8	
	C-6⁗	18.6[e]	18.6[e]	18.5[e]	18.4[e]	
	C-3⁗-OMe	57.3	57.2	57.0	57.0	
ole	C-1⁗′	102.0	101.8			
	C-2⁗′	37.4[a]	37.6[a]			
	C-3⁗′	81.6	81.4			
	C-4⁗′	77.7	77.7			
	C-5⁗′	73.0	72.8			
	C-6⁗′	18.6[e]	18.7[e]			
	C-3⁗′-OMe	57.0	57.0			

a—*f*) The assignments in each column may be interchangeable.

Calotroposide F (**6**) showed a negative FAB-MS ion at *m/z* 1043 $(M-H)^-$, which demonstrated the molecular weight to be 1044. The IR and UV spectra of **6** showed very similar absorption patterns to those of calotroposide G (**7**).

On methanolysis with 9% methanolic hydrogen chloride, calotroposide F (**6**) afforded 12-*O*-benzoyllineolon (**8**),[5] methyl oleandroside (**a**), and methyl cymaroside (**b**). The methyl glycosides (**a**, **b**) were further hydrolyzed with 5% aqueous hydrochloric acid to yield D-oleandrose and D-cymarose, respectively. Furthermore, treatment of **6** with 5% aqueous hydrochloric acid provided a mixture of **a** and **b** in 1 : 1 ratio as determined by GLC analysis.

In the ^{1}H-NMR spectrum of calotroposide F (**6**), four anomeric proton signals were observed at δ 4.70 (1H, dd, J=9.8, 1.5 Hz), δ 4.97, (1H, dd, J=9.8, 1.8 Hz), δ 5.12 and 5.26 (1H both, dd, J=9.5, 1.8 Hz), which indicated all the glycosidic linkages to have β-orientation.[4] Acetylation of **6** afforded a monoacetate (**10**) which, in its ^{1}H-NMR spectrum, showed a characteristic signal at δ 4.66 (1H, dd, J=9.3, 9.3 Hz, 4⁗-H) assignable to one acetoxymethine proton, thus indicating the terminal sugar of **6** to be oleandrose. Partial hydrolysis of **6** with 0.5% aqueous sulfuric acid furnished calotroposide G (**7**) in good yield.

Furthermore, the location of the carbohydrate moiety

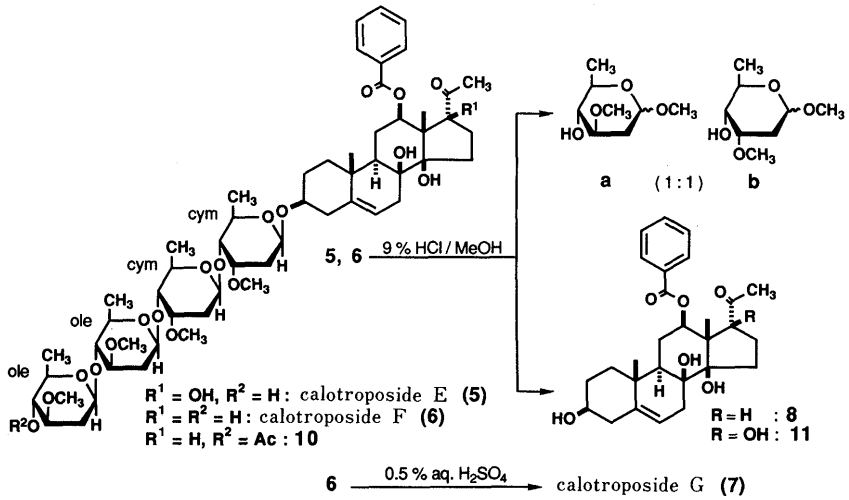

Chart 2

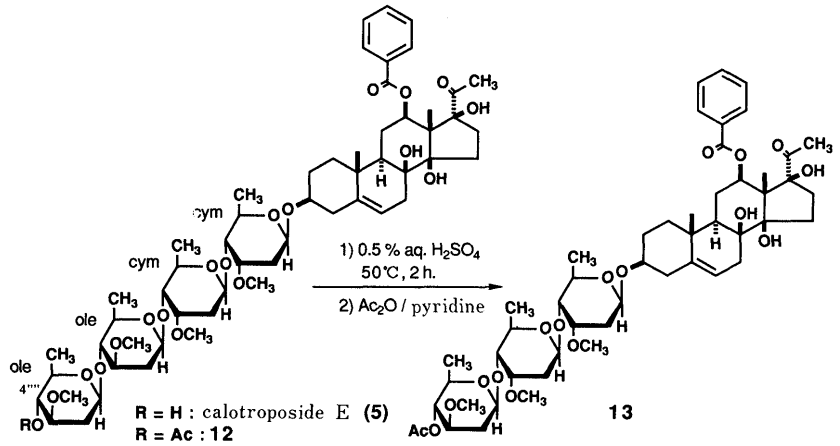

Chart 3

attached to the C-3 hydroxyl group of the aglycone **8** was confirmed from the glycosylation shifts[7] observed in the ^{13}C-NMR spectrum of **6** for the signals due to C-2 (−2.4 ppm), C-3 (+6.2 ppm), and C-4 (−4.5 ppm) as compared with those of the aglycone **8** (Table I). Consequently, the structure of calotroposide F (**6**) has been concluded to be 12-*O*-benzoyllineolon 3-*O*-*β*-D-oleandropyranosyl(1→4)-*β*-D-oleandropyranosyl(1→4)-*β*-D-cymaropyranosyl(1→4)-*β*-D-cymaropyranoside.

Calotroposide E (**5**) provided a negative FAB-MS ion at *m/z* 1056 due to $(M-H)^-$. The ^{13}C-NMR spectrum of **5** was very similar to that of calotroposide F (**6**) except for the signals assignable to C-16 (+11.2 ppm in the case of **5**), C-17 (+32.3 ppm), and C-18 (−5.0 ppm) of the aglycone moiety (Table I).

Treatment of calotroposide E (**5**) with 9% methanolic hydrogen chloride liberated 12-*O*-benzoyldeacetylmetaplexigenin (**11**),[8] methyl oleandroside (**a**), and methyl cymaroside (**b**). By comparison of the ^{1}H- and ^{13}C-NMR data for **5** with those for **6**, we concluded that **5** possesses the same sugar sequence in its oligosaccharide moiety as that of calotroposide F (**6**), which carries its sugar moiety on the C-3 hydroxyl group of the aglycone. Namely, in the ^{1}H-NMR spectrum of **5**, four anomeric proton signals were observed at *δ* 4.70 (1H, dd, *J*=9.8, 1.5 Hz), *δ* 4.97 (1H, dd, *J*=9.8, 1.8 Hz), and *δ* 5.11 and 5.25 (1H both, dd, *J*=9.5, 1.8 Hz).

A monoacetate (**12**), prepared by ordinary acetylation of calotroposide E (**5**), showed, in its ^{1}H-NMR spectrum, a signal at *δ* 4.66 (dd, *J*=9.5, 9.5 Hz) which was characteristically assignable to 4''''-H of the terminal oleandrose. Furthermore, mild hydrolysis of **5** with 0.5% aqueous sulfuric acid followed by acetylation yielded a partial hydrolysate monoacetate (**13**), which was identical with one of the acetolysis products[3e] obtained from calotroposide B (**2**) by partial acidic hydrolysis and subsequent acetylation.

Based on the foregoing findings, the structure of calotroposide E (**5**) has been concluded to be 12-*O*-benzoyldeacetylmetaplexigenin 3-*O*-*β*-D-oleandropyranosyl(1→4)-*β*-D-oleandropyranosyl(1→4)-*β*-D-cymaropyranosyl(1→4)-*β*-D-cymaropyranoside.

Calotroposide D (**4**) showed a negative FAB-MS ion at *m/z* 1187 assignable to $(M-H)^-$. By comparison of the ^{1}H- and ^{13}C-NMR spectra of **4** with those of calotroposides F (**6**) and G (**7**), we considered that **4** is an oligoglycoside of 12-*O*-benzoyllineolon (**8**)[5] having oleandrose and cymarose moieties attached to the C-3 hydroxyl group of **8**.

On methanolysis, calotroposide D (**4**) gave the aglycone **8**, methyl oleandroside (**a**), and methyl cymaroside (**b**). Both methyl glycosides (**a**, **b**) were further hydrolyzed to furnish D-oleandrose and D-cymarose, respectively. On the other

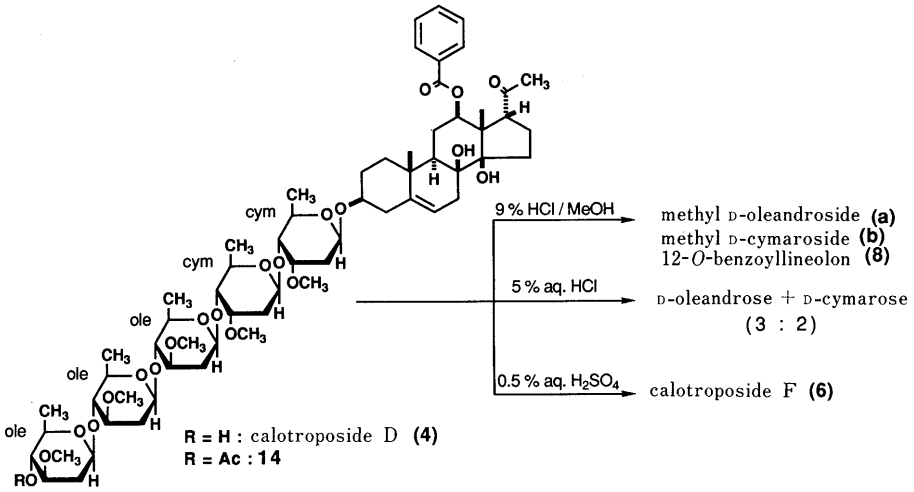

Chart 4

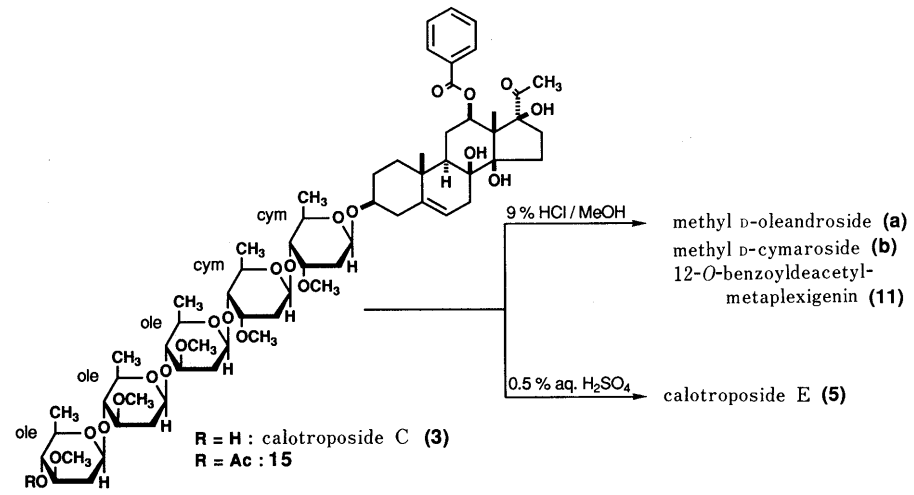

Chart 5

hand, hydrolysis of **4** with 5% aqueous hydrochloric acid afforded a mixture of oleandrose and cymarose in 3:2 ratio as shown by GLC analysis. The ^{1}H-NMR spectrum of **4** showed five anomeric proton signals at δ 4.72 (1H, dd, J=9.8, 1.5 Hz), δ 4.91 and 4.97 (1H both, dd, J=9.8, 1.8 Hz), and δ 5.12 and 5.27 (1H both, dd, J=9.5, 1.8 Hz). These coupling patterns indicated all glycosidic linkages to have β-configuration.[4]

Upon acetylation with acetic anhydride and pyridine, calotroposide D (**4**) furnished a monoacetate (**14**), which, in its ^{1}H-NMR spectrum, showed a signal at δ 4.67 (1H, dd, J=9.3, 9.3 Hz, 4''''-H) characteristically assignable to the acetoxymethine proton of the terminal oleandrose moiety. Furthermore, treatment of **4** with 0.5% aqueous sulfuric acid provided a partial hydrolysate, which was identical with calotroposide F (**6**).

Consequently, the structure of calotroposide D (**4**) has been determined to be 12-*O*-benzoyllineolon 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside.

Finally, in the negative FAB-MS of calotroposide C (**3**), an $(M-H)^-$ ion was observed at m/z 1203, which was 16 mass units larger than the $(M-H)^-$ ion of calotroposide D (**4**). The IR and UV spectra of **3** showed similar absorption patterns to those of calotroposide D (**4**). The ^{1}H- and ^{13}C-NMR spectra of **3** indicated that the oligosaccharide moiety of **3** is identical with that of **4** and is attached to the C-3 hydroxyl group of the aglycone. The ^{1}H-NMR spectrum of **3** showed five anomeric proton signals at δ 4.72 (1H, dd, J=9.8, 1.5 Hz), δ 4.91 and 4.97 (1H both, dd, J=9.8, 1.8 Hz), and δ 5.12 and 5.23 (1H both, dd, J=9.5, 1.8 Hz), and these coupling constants show all the glycosidic linkages to have β-orientation.[4]

Methanolysis of calotroposide C (**3**) with 9% methanolic hydrogen chloride afforded 12-*O*-benzoyldeacetylmetaplexigenin (**11**),[8] methyl oleandroside (**a**), and methyl cymaroside (**b**). Acetylation of **3** afforded a monoacetate (**15**) which again showed a signal characteristically assignable to 4''''-H of the terminal oleandrose. Mild hydrolysis of **3** with 0.5% aqueous sulfuric acid furnished a hydrolysate which was identical with calotroposide E (**5**), a tetraglycoside.

Thus, the structure of calotroposide C (**3**) has been elucidated to be 12-*O*-benzoyldeacetylmetaplexigenin 3-*O*-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-oleandropyranosyl(1→4)-β-D-cymaropyranosyl(1→4)-β-D-cymaropyranoside.

In conclusion, we have isolated seven new oxypregnane-oligoglycosides, having a linear oligosaccharide moiety containing oleandrose and cymarose, named calotroposides A (**1**),[3e] B (**2**),[3e] C (**3**), D (**4**), E (**5**), F (**6**) and G (**7**), from the root of *Calotropis gigantea* (Asclepiadaceae), an Indonesian medicinal plant.

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in our previous paper.[3e] The isolation procedures for calotroposides C (**3**), D (**4**), E (**5**), F (**6**), and G (**7**) were also described in the previous paper.[3e]

Calotroposide C (**3**): A white amorphous solid, $[\alpha]_D$ −1.9° (c=1.2, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3485, 1710, 1600, 1450, 1270, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.16), 272 (3.15), 280 (3.10). ^{1}H-NMR (d_5-pyridine) δ: 1.32 (3H, s, 18-H_3), 1.39, 1.40 (3H both d, J=6.1 Hz, $CH_3\times2$ in sugar moiety), 1.45, 1.49 (3H both d, J=5.5 Hz, $CH_3\times2$ in sugar moiety), 1.58 (3H, d, J=6.1 Hz, CH_3 in sugar moiety), 2.05 (3H, s, 19-H_3), 2.33 (3H, s, 21-H_3), 3.48, 3.51, 3.54, 3.58, 3.62 (3H each, all s, $OCH_3\times5$), 3.86 (1H, m, 3-H), 4.72 (1H, dd, J=9.8, 1.5 Hz), 4.91, 4.97 (1H both dd, J=9.8, 1.8 Hz), 5.12, 5.23 (1H both dd, J=9.5, 1.8 Hz) (five anomeric protons), 5.31 (1H, t-like, 6-H), 5.33 (1H, dd, J=11.8, 4.0 Hz, 12-H), 7.46 (2H, dd, J=7.5, 7.5 Hz), 7.56 (1H, t, J=7.5 Hz), 8.26 (2H, d, J=7.5 Hz) (benzoyl moiety). ^{13}C-NMR: as given in Tables I and II. FAB-MS (negative) m/z: 1203 $(M-H)^-$. High-resolution FAB-MS m/z: Calcd for $C_{63}H_{96}O_{22}$+Na: 1227.6290. Found: 1227.6260 $(M+Na)^+$.

Calotroposide D (**4**): A white amorphous solid, $[\alpha]_D$ −17.6° (c=1.1, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3485, 1710, 1600, 1450, 1275, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.15), 270 (3.15), 280 (3.08). ^{1}H-NMR (d_5-pyridine) δ: 1.32 (3H, s, 18-H_3), 1.38, 1.40 (3H both d, J=6.1 Hz, $CH_3\times2$ in sugar moiety), 1.45, 1.49 (3H both d, J=5.5 Hz, $CH_3\times2$ in sugar moiety), 1.58 (3H, d, J=6.1 Hz, CH_3 in sugar moiety), 2.02 (3H, s, 19-H_3), 2.11 (3H, s, 21-H_3), 3.48, 3.51, 3.53, 3.58, 3.62 (3H each, all s, $OCH_3\times5$), 3.86 (1H, m, 3-H), 4.72 (1H, dd, J=9.8, 1.5 Hz), 4.91, 4.97 (1H both dd, J=9.8, 1.8 Hz), 5.12, 5.27 (1H both dd, J=9.5, 1.8 Hz) (five anomeric protons), 5.31 (1H, t-like, 6-H), 5.40 (1H, dd, J=11.8, 4.2 Hz, 12-H), 7.45 (2H, dd, J=7.6, 7.6 Hz), 7.56 (1H, t, J=7.6 Hz), 8.26 (2H, d, J=7.6 Hz) (benzoyl moiety). ^{13}C-NMR: as given in Tables I and II. FAB-MS (negative) m/z: 1187 $(M-H)^-$. High-resolution FAB-MS m/z: Calcd for $C_{63}H_{96}O_{21}$+Na: 1211.6340. Found: 1211.6320 $(M+Na)^+$.

Calotroposide E (**5**): A white amorphous solid, $[\alpha]_D$ −1.6° (c=1.4, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3475, 1710, 1600, 1450, 1275, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.12), 270 (3.15), 280 (3.05). ^{1}H-NMR (d_5-pyridine) δ: 1.32 (3H, s, 18-H_3), 1.39 (6H, d, J=6.1 Hz, $CH_3\times2$ in sugar moiety), 1.46 (3H, d, J=5.5 Hz, CH_3 in sugar moiety), 1.58 (3H, d, J=6.1 Hz, CH_3 in sugar moiety), 2.04 (3H, s, 19-H_3), 2.30 (3H, s, 21-H_3), 3.48, 3.51, 3.58, 3.62 (3H each, all s, $OCH_3\times4$), 3.86 (1H, m, 3-H), 4.70 (1H, dd, J=9.8, 1.5 Hz), 4.97 (1H, dd, J=9.8, 1.5 Hz), 5.11, 5.25 (1H both dd, J=9.5, 1.8 Hz) (four anomeric protons), 5.31 (1H, t-like, 6-H), 5.36 (1H, dd, J=11.9, 4.3 Hz, 12-H), 7.45 (2H, dd, J=7.5, 7.5, Hz), 7.55 (1H, t, J=7.5 Hz), 8.27 (2H, d, J=7.5 Hz) (benzoyl moiety). ^{13}C-NMR: as given in Tables I and II. FAB-MS (negative) m/z: 1059 $(M-H)^-$. High-resolution FAB-MS m/z: Calcd for $C_{56}H_{84}O_{19}$+Na: 1083.5504. Found: 1083.5440 $(M+Na)^+$.

Calotroposide F (**6**): A white amorphous solid, $[\alpha]_D$ −15.6° (c=1.5, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3515, 1710, 1600, 1450, 1275, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.06), 270 (3.10), 280 (3.05). ^{1}H-NMR (d_5-pyridine) δ: 1.32 (3H, s, 18-H_3), 1.38, 1.39 (3H both d, J=6.1 Hz, $CH_3\times2$ in sugar moiety), 1.46 (3H, d, J=5.5 Hz, CH_3 in sugar moiety), 1.58 (3H, d, J=6.1 Hz, CH_3 in sugar moiety), 2.05 (3H, s, 19-H_3), 2.11 (3H, s, 21-H_3), 3.48, 3.52, 3.58, 3.62 (3H each, all s, $OCH_3\times4$), 3.84 (1H, m, 3-H), 4.70 (1H, dd, J=9.8, 1.5 Hz), 4.97 (1H, dd, J=9.8, 1.8 Hz), 5.12, 5.26 (1H both dd, J=9.5, 1.8 Hz) (four anomeric protons), 5.31 (1H, t-like, 6-H), 5.40 (1H, dd, J=12.2, 4.2 Hz, 12-H), 7.46 (2H, dd, J=7.5, 7.5 Hz), 7.54 (1H, t, J=7.5 Hz), 8.26 (2H, d, J=7.5 Hz) (benzoyl moiety). ^{13}C-NMR: as given in Tables I and II. FAB-MS (negative) m/z: 1043 $(M-H)^-$. High-resolution FAB-MS m/z: Calcd for $C_{56}H_{84}O_{18}$+Na: 1067.5554. Found: 1067.5530 $(M+Na)^+$.

Calotroposide G (**7**): A white amorphous solid, $[\alpha]_D$ −17.4° (c=0.94, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3565, 1715, 1600, 1450, 1275, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.12), 270 (3.12), 280 (3.05). ^{1}H-NMR (d_5-pyridine) δ: 1.34 (3H, s, 18-H_3), 1.41 (3H, d, J=6.4 Hz, CH_3 in sugar moiety), 1.43, 1.59 (3H both d, J=6.1 Hz, $CH_3\times2$ in sugar moiety), 2.05 (3H, s, 19-H_3), 2.12 (3H, s, 21-H_3), 3.47, 3.59, 3.63 (3H each, all s, $OCH_3\times3$), 3.86 (1H, m, 3-H), 4.78 (1H, dd, J=9.8, 1.5 Hz), 4.97, 5.14 (1H both dd, J=9.5, 1.8 Hz) (three anomeric protons), 5.30 (1H, t-like, 6-H), 5.42 (1H, dd, J=11.9, 4.0 Hz, 12-H), 7.47 (2H, dd, J=7.4, 7.4 Hz), 7.55 (1H, t, J=7.4 Hz), 8.28 (2H, d, J=7.4 Hz) (benzoyl moiety). ^{13}C-NMR: as given in Tables I and II. FAB-MS (negative) m/z: 899 $(M-H)^-$. High-resolution FAB-MS m/z: Calcd for $C_{49}H_{72}O_{15}$+Na: 923.4767. Found: 923.4836 $(M+Na)^+$.

Methanolysis of Calotroposide G (7) A solution of calotroposide G (**7**, 32 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 yield a product. Purification of the product by column chromatography (SiO_2 10 g, benzene : acetone = 7 : 1) afforded the aglycone (**8**, 13 mg), methyl oleandroside (**a**, 4 mg) and methyl cymaroside (**b**, 4 mg). The aglycone **8** was identical with an authentic sample of 12-*O*-benzoyllineolon[3e,5] on the basis of comparisons of IR, ^{1}H- and ^{13}C-NMR data. The ^{13}C-NMR data for methyl oleandroside (**a**) and methyl cymaroside (**b**) were identical with those reported in the literature.[3e,6]

Methyl oleandroside (**a**, 4 mg) was treated with 5% aqueous HCl 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 afford D-oleandrose (2.1 mg), $[\alpha]_D$ −12.8° (c=0.18, 24 h after dissolving in H_2O, at 22 °C). D-Cymarose {1.9 mg, $[\alpha]_D$ +52.6° (c=0.15, 24 h after dissolving in H_2O, at 22 °C)} was obtained from methyl cymaroside (**b**, 4 mg) through the same procedure as that for D-oleandrose from methyl oleandroside (**a**).

Acidic Hydrolysis of Calotroposide G (7) Calotroposide G (**7**, 5 mg) was treated with 5% aqueous HCl (2 ml) at 80 °C 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 (3 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 compositions as TMS–oleandrose and TMS–cymarose in 1 : 2 ratio by comparison with authentic samples, which were prepared respectively from methyl oleandroside (**a**) and methyl cymaroside (**b**) by treatment with 5% aqueous HCl and subsequent trimethylsilylation. GLC conditions: column, 2% OV-17 on Chromosorb WAWDMCS (80—100 mesh), i.d. 3 mm × 2 m; column temperature, 80 °C; carrier gas N_2; flow-rate, 35 ml/min. TMS–oleandrose: t_R 38.6, 42.7 min; TMS–cymarose: t_R 50.0, 58.4 min.

Acetylation of Calotroposide G (7) Giving 9 Calotroposide G (**7**, 5 mg) was treated with Ac_2O (1 ml) and pyridine (1 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 $NaHCO_3$, and brine, then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product. Purification of the product by column chromatography (SiO_2 2 g, benzene : acetone = 4 : 1) afforded a monoacetate (**9**, 3.5 mg). The monoacetate (**9**) was identical with an authentic sample, which was prepared from calotroposide A (**1**) by treatment with 0.5% aqueous H_2SO_4 and subsequent acetylation,[3e] by comparison of the physical data (IR and ^{1}H-NMR) and by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9 : 2).

Methanolysis of Calotroposide F (6) 12-*O*-Benzoyllineolon (**8**, 13 mg), methyl oleandroside (**a**, 4 mg) and methyl cymaroside (**b**, 4 mg) were obtained from calotroposide F (**6**, 28 mg) through a procedure similar to that for obtaining **8** from calotroposide G (**7**). Acidic hydrolysis of methyl oleandroside (**a**) or methyl cymaroside (**b**) with 5% aqueous HCl was carried out to afford D-oleandrose {$[\alpha]_D$ −11.2° (c=0.20, 24 h after dissolving in H_2O, at 23 °C)} or D-cymarose {$[\alpha]_D$ +52.9° (c=0.17, 24 h after dissolving in H_2O, at 23 °C)}.

Acidic Hydrolysis of Calotroposide F (6) Calotroposide F (**6**, 3 mg) was treated with 5% aqueous HCl (1 ml) at 80 °C for 2 h. The reaction mixture was worked up through the same procedure as described for acidic hydrolysis of calotroposide G (**7**), to give a mixture of oleandrose and cymarose. The GLC analysis of TMS–oleandrose and TMS–cymarose, which were prepared from oleandrose and cymarose by trimethylsilylation, was carried out under the same conditions as described above, and their ratio was determined as 1 : 1.

Acetylation of Calotroposide F (6) Giving 10 Calotroposide F (**6**, 16 mg) was treated with acetic anhydride (1 ml) and pyridine (1 ml) at room temperature for 12 h. The reaction mixture was worked up in a usual manner to give a product, which was purified by column chromatography

(SiO_2 5 g, benzene : acetone = 4 : 1) to afford **10** (15 mg).

10: A white amorphous solid, $[\alpha]_D$ −14.4° (c = 1.3, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3510, 1730, 1710, 1600, 1450, 1270, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.15), 273 (3.12), 280 (3.06). ^{1}H-NMR ($CDCl_3$) δ: 1.12 (3H, s, 18-H_3), 1.21 (6H, d, J = 6.1 Hz, CH_3 × 2 in sugar moiety), 1.29, 1.59 (3H both d, J = 6.1 Hz, CH_3 × 2 in sugar moiety), 1.55 (3H, s, 19-H_3), 2.03 (3H, s, 21-H_3), 2.09 (3H, s, $OCOCH_3$), 3.34, 3.40, 3.44, 3.45 (3H each, all s, OCH_3 × 4), 3.56 (1H, m, 3-H), 4.45, 4.71 (1H both dd, J = 9.5, 1.5 Hz), 4.74, 4.84 (1H both dd, J = 9.8, 1.8 Hz) (four anomeric protons), 4.66 (1H, dd, J = 9.3, 9.3 Hz, 4''''-H), 4.95 (1H, dd, J = 11.4, 4.4 Hz, 12-H), 5.37 (1H, t-like, 6-H), 7.43 (2H, dd, J = 7.5, 7.5 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.96 (2H, d, J = 7.5 Hz) (benzoyl moiety). FAB-MS m/z: 1109 $(M+Na)^+$. High-resolution FAB-MS m/z: Calcd for $C_{58}H_{86}O_{19}$ + Na: 1109.5660. Found: 1109.5610 $(M+Na)^+$.

Partial Hydrolysis of Calotroposide F (6) Giving 7 A solution of calotroposide F (**6**, 10 mg) in acetone (0.5 ml) was treated with 0.5% aqueous H_2SO_4 (0.5 ml) at room temperature for 1 h. 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. Purification of the product by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9:2) afforded a hydrolysate (6 mg), which was identical with calotroposide G (**7**) by comparisons of IR, ^{1}H- and ^{13}C-NMR data and by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9 : 2).

Methanolysis of Calotroposide E (5) A solution of **5** (20 mg) in 9% HCl–MeOH (1 ml) was heated under reflux for 2 h. After cooling, the reaction mixture was neturalized 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. Purification of the product by column chromatography (SiO_2 10 g, benzene : acetone = 7 : 1) afforded the aglycone (**11**, 7 mg), methyl oleandroside (**a**, 3 mg) and methyl cymaroside (**b**, 3 mg). The aglycone **11** was identical with the authentic sample of 12-*O*-benzoyldeacetylmetaplexigenin[3e,8] by comparisons of IR, ^{1}H- and ^{13}C-NMR data. Acidic hydrolysis of methyl oleandroside (**a**) and methyl cymaroside (**b**) with 5% aqueous HCl was carried out to afford D-oleandrose {$[\alpha]_D$ −12.1° (c = 0.09, 24 h after dissolving in H_2O, at 23 °C)} and D-cymarose {$[\alpha]_D$ +49.5° (c = 0.10, 24 h after dissolving in H_2O, at 23 °C)}.

Acidic Hydrolysis of Calotroposide E (5) Calotroposide E (**5**, 3 mg) was treated with 5% aqueous HCl (1 ml) at 80 °C for 2 h. The reaction mixture was worked up through the same procedure as described for acidic hydrolysis of calotroposide G (**7**), to give a mixture of oleandrose and cymarose. The GLC analysis of TMS-oleandrose and TMS–cymarose, which were prepared from oleandrose and cymarose by trimethylsilylation, was carried out under the same conditions as described above, to determine the sugar composition ratio as 1 : 1.

Acetylation of Calotroposide E (5) Giving 12 Calotroposide E (**5**, 15 mg) was treated with acetic anhydride (1 ml) and pyridine (1 ml) at room temperature for 12 h. The reaction mixture was worked up in a usual manner to give a product. Purification of the product by column chromatography (SiO_2 5 g, benzene : acetone = 4 : 1) afforded **12** (14 mg).

12: A white amorphous solid, $[\alpha]_D$ +1.5° (c = 0.71, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3500, 1730, 1710, 1600, 1450, 1275, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.12), 270 (3.10), 280 (3.05). ^{1}H-NMR ($CDCl_3$) δ: 1.13 (3H, s, 18-H_3), 1.21, 1.22 (3H both d, J = 6.4 Hz, CH_3 × 2 in sugar moiety), 1.30, 1.61 (3H each, d, J = 6.1 Hz, CH_3 × 2 in sugar moiety), 1.55 (3H, s, 19-H_3), 2.06 (3H, s, 21-H_3), 2.09 (3H, s, $OCOCH_3$), 3.34, 3.40, 3.44, 3.45 (3H each, all s, OCH_3 × 4), 3.56 (1H, m, 3-H), 4.45, 4.71 (1H both dd, J = 9.5, 1.5 Hz), 4.76, 4.84 (1H both dd, J = 9.8, 1.8 Hz) (four anomeric protons), 4.66 (1H, dd, J = 9.5, 9.5 Hz, 4''''-H), 4.86 (1H, dd, J = 11.6, 4.6 Hz, 12-H), 5.39 (1H, t-like, 6-H), 7.44 (2H, dd, J = 7.4, 7.4 Hz), 7.56 (1H, t, J = 7.4 Hz), 7.94 (2H, d, J = 7.4 Hz) (benzoyl moiety). FAB-MS m/z: 1125 $(M+Na)^+$. High-resolution FAB-MS m/z: Calcd for $C_{58}H_{86}O_{20}$ + Na: 1125.5617. Found: 1125.5670 $(M+Na)^+$.

Partial Hydrolysis of Calotroposide E (5) Followed by Acetylation A solution of calotroposide E (**5**, 30 mg) in MeOH (1.5 ml) was treated with 0.5% aqueous H_2SO_4 (0.5 ml) 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 was removed under reduced pressure from the filtrate to give a product. Purification of the product by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9 : 2) afforded a hydrolysate (8 mg), which was treated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) at room temperature for 12 h. The reaction mixture was worked up in a usual manner to give a product. Purification of the product by column chromatography (SiO_2 5 g, benzene : acetone = 4 : 1) afforded **13** (7 mg), which was identical with a derivative of calotroposide B (**2**)[3e] prepared by partial hydrolysis and subsequent acetylation of **2**, by comparisons of IR and ^{1}H-NMR data.

Methanolysis of Calotroposide D (4) 12-*O*-Benzoyllineolon (**8**, 14 mg), methyl oleandroside (**a**, 4 mg) and methyl cymaroside (**b**, 4 mg) were obtained from calotroposide D (**4**, 29 mg) through a procedure similar to that for obtaining **8** from calotroposide G (**7**). Acidic hydrolysis of thus obtained methyl oleandroside (**a**) and methyl cymaroside (**b**) with 5% aqueous HCl was carried out to afford D-oleandrose {$[\alpha]_D$ −11.5° (c = 0.16, 24 h after dissolving in H_2O, at 23 °C} and D-cymarose {$[\alpha]_D$ +51.6° (c = 0.14, 24 h after dissolving in H_2O, at 23 °C)}.

Acidic Hydrolysis of Calotroposide D (4) Calotroposide D (**4**, 3 mg) was treated with 5% aqueous HCl (1 ml) at 80 °C for 2 h. The reaction mixture was worked up through the same procedure as described for acidic hydrolysis of calotroposide G (**7**), to give a mixture of oleandrose and cymarose. The GLC analysis of TMS–oleandrose and TMS–cymarose, which were prepared from oleandrose and cymarose by trimethylsilylation, was carried out under the same conditions as described above to determine the sugar composition ratio as 3 : 2.

Acetylation of Calotroposide D (4) Giving 14 Calotroposide D (**4**, 15 mg) was treated with acetic anhydride (1 ml) and pyridine (1 ml) at room temperature for 12 h. The reaction mixture was worked up in a usual manner to give a product, which was purified by column chromatography (SiO_2 5 g, benzene : acetone = 4 : 1) to afford **14** (10 mg).

14: A white amorphous solid, $[\alpha]_D$ −12.4° (c = 1.0, in $CHCl_3$ at 23 °C). IR ($CHCl_3$) cm^{-1}: 3520, 1730, 1710, 1600, 1450, 1275, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.10), 272 (3.12), 280 (3.06). ^{1}H-NMR ($CDCl_3$) δ: 1.13 (3H, s, 18-H_3), 1.18 (3H, d, J = 6.1 Hz, CH_3 in sugar moiety), 1.28 (6H, d, J = 6.1 Hz, CH_3 × 2 in sugar moiety), 1.31 (3H, d, J = 6.1 Hz, CH_3 in sugar moiety), 1.54 (3H, s, 19-H_3), 1.60 (3H, d, J = 5.5 Hz, CH_3 in sugar moiety), 2.03 (3H, s, 21-H_3), 2.09 (3H, s, $OCOCH_3$), 3.33, 3.39, 3.41, 3.44, 3.45 (1H each, all s, OCH_3 × 5), 3.56 (1H, m, 3-H), 4.43 (1H, dd, J = 9.5, 1.6 Hz), 4.66, 4.70 (1H both dd, J = 9.5, 1.8 Hz), 4.73, 4.85 (1H both dd, J = 9.5, 1.6 Hz) (five anomeric protons), 4.67 (1H, dd, J = 9.3, 9.3 Hz, 4''''-H), 4.86 (1H, dd, J = 11.6, 4.6 Hz, 12-H), 5.39 (1H, t-like, 6-H), 7.42 (2H, dd, J = 7.5, 7.5 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.96 (2H, d, J = 7.5 Hz) (benzoyl moiety). FAB-MS m/z: 1253 $(M+Na)^+$. High-resolution FAB-MS m/z: Calcd for $C_{65}H_{98}O_{22}$ + Na: 1253.6467. Found: 1253.6520 $(M+Na)^+$.

Partial Hydrolysis of Calotroposide D (4) Giving 6 A solution of calotroposide D (**4**, 6 mg) in acetone (0.5 ml) was treated with 0.5% aqueous H_2SO_4 (0.5 ml) at room temperature for 1 h. The reaction mixture was neutralized with aqueous saturated $Ba(OH)_2$ and the precipitate was removed by filtration. The solvent was evaporated off under reduced pressure from the filtrate to give a product. Purification of the product by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9 : 2) afforded a hydrolysate (2 mg), which was identical with calotroposide F (**6**) on the basis of comparisons of IR, ^{1}H-, and ^{13}C-NMR data and by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9 : 2).

Methanolysis of Calotroposide C (3) A solution of **3** (20 mg) in 9% HCl–MeOH (1.0 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. Purification of the product by column chromatography (SiO_2 10 g, benzene : acetone = 7 : 1) afforded the aglycone (**11**, 5 mg), methyl oleandroside (**a**, 3 mg) and methyl cymaroside (**b**, 3 mg). The aglycone **11** was identical with 12-*O*-benzoyldeacetylmetaplexigenin[3e,8] on the basis of comparisons of IR, ^{1}H-, and ^{13}C-NMR data. Acidic hydrolysis of thus obtained methyl oleandroside (**a**) and methyl cymaroside (**b**) with 5% aqueous HCl was carried out to afford D-oleandrose {$[\alpha]_D$ −12.5° (c = 0.11, 24 h after dissolving in H_2O, at 23 °C)} and D-cymarose {$[\alpha]_D$ +48.8° (c = 0.09, 24 h after dissolving in H_2O, at 23 °C)}.

Acidic Hydrolysis of Calotroposide C (3) Calotroposide C (**3**, 3 mg) was treated with 5% aqueous HCl (1 ml) at 80 °C for 2 h. The reaction mixture was worked up through the same procedure as described for acidic hydrolysis of calotroposide G (**7**), to give a mixture of oleandrose and cymarose. The GLC analysis of TMS–oleandrose and TMS–cymarose, which were prepared from oleandrose and cymarose by trimethylsilylation, was carried out under the same conditions as described above to determine the sugar composition ratio as 2 : 3.

Acetylation of Calotroposide C (3) Giving 15 Calotroposide C (**3**, 13 mg) was treated with acetic anhydride (1 ml) and pyridine (1 ml) at room temperature for 12 h. The reaction mixture was worked up in a usual manner to give a product, which was purified by column chromatography

(SiO_2 5 g, benzene : acetone = 4 : 1) to afford **15** (12 mg).

15: A white amorphous solid, $[\alpha]_D$ +0.4° (c = 1.1, in $CHCl_3$ at 24 °C). IR ($CHCl_3$) cm^{-1}: 3510, 1730, 1710, 1600, 1450, 1270, 1100. UV (MeOH) λ_{max} nm (log ε): 230 (4.12), 273 (3.10), 280 (3.05). ^{1}H-NMR ($CDCl_3$) δ: 1.13 (3H, s, 18-H_3), 1.19 (3H, d, J = 6.1 Hz, CH_3 in sugar moiety), 1.29 (6H, d, J = 6.1 Hz, CH_3 × 2 in sugar moiety), 1.32 (3H, d, J = 6.1 Hz, CH_3 in sugar moiety), 1.55 (3H, s, 19-H_3), 1.59 (3H, d, J = 5.5 Hz, CH_3 in sugar moiety), 2.06 (3H, s, 21-H_3), 2.09 (3H, s, $OCOCH_3$), 3.33, 3.39, 3.41, 3.44, 3.45 (3H each, all s, OCH_3 × 5), 3.57 (1H, m, 3-H), 4.43 (1H, dd, J = 9.5, 1.6 Hz), 4.66 (1H, dd, J = 9.5, 1.8 Hz), 4.70 (1H, dd, J = 9.5, 1.6 Hz), 4.75 (1H, dd, J = 9.5, 1.8 Hz), 4.85 (1H, dd, J = 9.5, 1.6 Hz) (five anomeric protons), 4.65 (1H, dd, J = 9.5, 9.5 Hz, 4''''-H), 4.86 (1H, dd, J = 11.6, 4.6 Hz, 12-H), 5.39 (1H, t-like, 6-H), 7.43 (2H, dd, J = 7.5, 7.5 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.94 (2H, d, J = 7.5 Hz) (benzoyl moiety). FAB-MS m/z: 1269 $(M+Na)^+$. High-resolution FAB-MS m/z: Calcd for $C_{65}H_{98}O_{23}$ + Na: 1269.6397. Found: 1269.6470 $(M+Na)^+$.

Partial Hydrolysis of Calotroposide C (3) Giving 5 A solution of calotroposide C (**3**, 7 mg) in acetone (1.0 ml) was treated with 0.5% aqueous H_2SO_4 (1.0 ml) at room temperature for 1 h. The reaction mixture was neutralized with aqueous saturated $Ba(OH)_2$ and the precipitate was removed by filtration. The solvent was evaporated off under reduced pressure from the filtrate to give a product. Purification of the product by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9 : 2) afforded a hydrolysate (4 mg), which was identical with calotroposide E (**5**) on the basis of comparisons of IR, ^{1}H- and ^{13}C-NMR data and by HPLC (Shim-Pack CLC-ODS, MeOH : H_2O = 9 : 2).

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