Five New Steroidal Glycosides from *Caralluma dalzielii*

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Five new pregnane glycosides, caradalzielosides A–E (**1**–**5**), were isolated from the aerial parts of *Caralluma dalzielii*. Their structures were elucidated by extensive 1D- and 2D-NMR spectroscopic analysis as well as by HR-FAB-MS experiments.

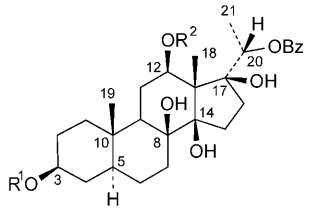
Introduction. – As a part of our studies on Nigerian folkloric medicinal plants [1][2], we have investigated the chemical constituents of *Caralluma dalzielii* N. E. BROWN, which has been used as a tonic, aphrodisiac, analgesic, and antiemetic [3]. The plant is a perennial succulent with quadrangular branches belonging to the family of Asclepiadaceae, which is still treated as an independent family. However, modern molecular and genetic studies suggest that it should be incorporated into the Apocynaceae family [4][5]. On the basis of the new taxonomy, the genus *Caralluma* is classified into the subfamily Asclepiadoideae, tribe Ceropegieae [4].

In previous studies on *C. dalzielii*, tomentogenin (=3,12,14,17,20-pentahydroxypregnane) esters [6] and their glycosides [7] were identified. Herein, we report the isolation and structure elucidation of five new steroidal glycosides named caradalzielosides A–E (**1**–**5**), resp. from this plant. They consist of 5,6-dihydrosarcostins (=3,8,12,14,17,20-hexahydroxypregnanes) with acetyl (Ac) and/or benzoyl (Bz) groups as aglycones and oligosaccharide chains originating from two to four sugar units.

Results and Discussion. – Compounds **1**–**5** were isolated from the $CHCl_3$/MeOH 1:1 extract of the aerial parts of *C. dalzielii* by column chromatography and centrifugal liquid–liquid-partition chromatography.

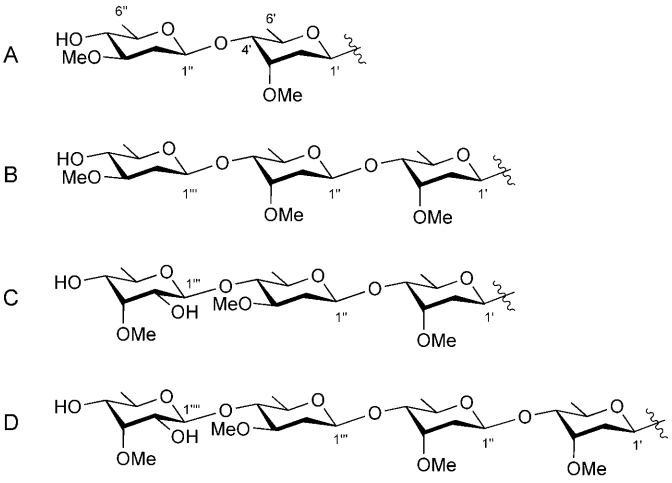
Caradalzieloside A (**1**) was obtained as a colorless, amorphous solid. It exhibited a UV absorption at 229 nm, and its specific rotation $[\alpha]_D^{25}$ was +19. The molecular formula was established as $C_{44}H_{66}O_{14}$ by HR-FAB-MS, showing the $[M-H]^-$ ion peak at *m*/*z* 817.4368. Three Me groups at δ(H) 0.92 (*s*, 3 H), 1.33 (*d*, *J*=6.2 Hz, 3 H), and 1.47 (*s*, 3 H) were observed in the ^{1}H-NMR spectrum (*Table 1*), which, in combination with the ^{13}C-NMR data, indicated a C_{21} steroidal skeleton for its aglycone moiety. The presence of an Ac and a Bz group was deduced by the HMBC correlations between the Me H-atoms at δ(H) 1.88 (*s*) and a C=O function at δ(C) 171.2, and between the aromatic resonances at δ(H) 8.01 (*d*, *J*=7.4 Hz, 2 H) and a second C=O group at δ(C) 164.8, respectively. The ^{13}C,^{1}H-COSY, HMBC, and NOESY spectra allowed us to unambiguously assign all resonances of the aglycone of **1** (*Table 1*). The location of

the ester moieties were confirmed by correlations between H–C(12) [δ(H) 4.61 (*dd*, J = 11.1, 4.3 Hz)] and the AcO C=O group at δ(C) 171.2, and between H–C(20) [δ(H) 4.83 (*q*, J = 6.2 Hz)] and the BzO C=O group at δ(C) 164.8. The ^{13}C-NMR data of the aglycone were in agreement with those of stalagmoside II isolated from *C. stalagmifera* [8]. Therefore, the structure of the aglycone of **1** was determined as '(5α)-5,6-dihydrosarcostin 12-acetate 20-benzoate' (= (3β,5α,12β,14β,17α,20*S*)-12-acetoxy-3,8,14,17-tetrahydroxypregnan-20-yl benzoate).



	R^1	R^2
1	A	Ac
2	B	Ac
3	B	Bz
4	C	Ac
5	D	Bz

Ac = acetyl
Bz = benzoyl



The ^{1}H-NMR spectroscopic data of the sugar moiety of **1** (*Table 2*) showed two Me groups [δ(H) 1.24 (*d*, J = 6.3 Hz, 3 H); 1.32 (*d*, J = 6.1 Hz, 3 H)] and two MeO functions [δ(H) 3.45 (*s*, 3 H); 3.39 (*s*, 3 H)], as well as two anomeric H-atoms [δ(H) 4.86 (*dd*, J = 9.7, 1.9 Hz, 1 H); 4.50 (*dd*, J = 9.9, 2.2 Hz, 1 H)]. The ^{1}H,^{1}H- and ^{13}C,^{1}H-COSY spectra suggested that **1** comprised two 2,6-dideoxy sugars. From the coupling constants in the ^{1}H-NMR spectrum and the NOEs in the NOESY spectrum, they were identified as β-cymaropyranose and β-oleandropyranose[1]). Long-range correlations were observed between H–C(3) at δ(H) 3.57–3.66 (*m*) of the aglycone and C(1′) at δ(C) 95.5 of the sugar, as well as between H–C(4′) at δ(H) 3.23 (*dd*, J = 9.6, 2.8 Hz) and C(1″) at δ(C) 101.4 in the HMBC spectrum. Thus, the interlinkage of the sugar chain was indi-

[1]) Cymaropyranose (Cym) = 2,6-dideoxy-3-*O*-methyl-*ribo*-hexopyranose; oleandropyranose (Ole) = 2,6-dideoxy-3-*O*-methyl-*arabino*-hexopyranose.

Table 1. *^{1}H- and ^{13}C-NMR Spectroscopic Data of the Aglycones of* **1**, **2**, *and* **4**. At 400/100 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz. Assignments are based on ^{1}H,^{13}C-COSY and HMBC experiments.

Position	**1**		**2**		**4**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
CH_2(1)	0.95–1.01 (*m*, H_α)	37.8	0.95–1.02 (*m*, H_α)	37.7	0.95–1.01 (*m*, H_α)	37.7
	1.66–1.70 (*m*, H_β)		1.66–1.70 (*m*, H_β)		1.67–1.72 (*m*, H_β)	
CH_2(2)	1.81–1.85 (*m*, H_α)	28.7	1.80–1.85 (*m*, H_α)	28.6	1.80–1.85 (*m*, H_α)	28.7
	1.51–1.55 (*m*, H_β)		1.51–1.54 (*m*, H_β)		1.50–1.56 (*m*, H_β)	
H–C(3)	3.57–3.66 (*m*, H_α)	76.9	3.57–3.66 (*m*, H_α)	76.8	3.59–3.64 (*m*, H_α)	76.9
CH_2(4)	1.82–1.86 (*m*, H_α)	34.0	1.83–1.87 (*m*, H_α)	33.9	1.83–1.89 (*m*, H_α)	33.9
	1.27–1.33 (*m*, H_β)		1.28–1.36 (*m*, H_β)		1.30–1.36 (*m*, H_β)	
H–C(5)	1.01–1.06 (*m*)	45.2	1.01–1.06 (*m*, H_α)	45.1	1.01–1.06 (*m*, H_α)	45.1
CH_2(6)	1.18–1.22 (*m*, H_α)	24.5	1.17–1.23 (*m*, H_α)	24.4	1.17–1.23 (*m*, H_α)	24.5
	1.54–1.59 (*m*, H_β)		1.56–1.60 (*m*, H_β)		1.57–1.62 (*m*, H_β)	
CH_2(7)	1.26–1.30 (*m*, H_α)	33.9	1.24–1.32 (*m*, H_α)	33.8	1.26–1.31 (*m*, H_α)	33.8
	1.59–1.66 (*m*, H_β)		1.60–1.66 (*m*, H_β)		1.62–1.68 (*m*, H_β)	
C(8)		75.4		75.7		75.7
H–C(9)	1.14 (br. *d*, J=12.7)	46.2	1.14 (br. *d*, J=12.1)	46.2	1.11–1.17 (*m*)	46.2
C(10)		36.1		36.1		36.1
CH_2(11)	1.59–1.66 (*m*, H_α)	23.7	1.60 – 1.66 (*m*, H_α)	23.6	1.62–1.68 (*m*, H_α)	23.6
	1.75–1.79 (*m*, H_β)		1.75 – 1.79 (*m*, H_β)		1.75–1.79 (*m*, H_β)	
H–C(12)	4.61	74.2	4.61	74.1	4.61	74.1
	(*dd*, J=11.1, 4.3)		(*dd*, J=11.1, 4.3)		(*dd*, J=11.1, 4.3)	
C(13)		56.5		56.5		56.5
C(14)		87.8		87.8		87.8
CH_2(15)	1.92–1.98 (*m*, 2 H)	32.8	1.91–1.95 (*m*)	32.7	1.91–1.95 (*m*)	32.8
			2.00–2.04 (*m*)		2.00–2.04 (*m*)	
CH_2(16)	1.88–1.92 (*m*)	31.9	1.94–2.00 (*m*, 2 H)	31.9	1.94–2.00 (*m*, 2 H)	31.9
	1.98–2.02 (*m*)					
C(17)		88.1		88.0		88.1
Me(18)	1.47 (*s*)	10.8	1.47 (*s*)	10.8	1.47 (*s*)	10.8
Me(19)	0.92 (*s*)	12.4	0.92 (*s*)	12.4	0.92 (*s*)	12.4
H–C(20)	4.83 (*q*, J=6.2)	74.7	4.83 (*q*, J=6.2)	74.7	4.85 (*q*, J=6.3)	74.7
Me(21)	1.33 (*d*, J=6.2)	15.1	1.33 (*d*, J=6.2)	15.1	1.33 (*d*, J=6.3)	15.1
8-OH	2.43 (*s*)		2.44 (*s*)		2.43 (*s*)	
14-OH	4.66 (*s*)		4.67 (*s*)		4.66 (*s*)	
17-OH	3.17 (*s*)		3.21 (*s*)		3.17 (*s*)	
12-AcO:						
C=O		171.2		171.2		171.2
Me	1.88 (*s*)	21.7	1.88 (*s*)	21.7	1.88 (*s*)	21.7
20-BzO:						
C=O		164.8		164.8		164.8
C(1)		130.1		130.1		130.1
H–C(2,6)	8.01 (*d*, J=7.4)	129.5	8.02 (*d*, J=7.7)	129.5	8.02 (*d*, J=7.7)	129.5
H–C(3,5)	7.47 (*t*, J=7.4)	128.6	7.47 (*t*, J=7.7)	128.6	7.47 (*t*, J=7.7)	128.6
H–C(4)	7.60 (*t*, J=7.4)	133.2	7.60 (*t*, J=7.7)	133.2	7.59 (*t*, J=7.7)	133.2

cated as β-oleandropyranosyl-(1 → 4)-β-cymaropyranosyl. The same side chain has been found in a pregnane glycoside isolated from *C. retrospiciens* [9], and its ^{13}C-NMR spectroscopic data assured the structure of the oligosaccharide moiety.

Table 2. *^{1}H- and ^{13}C-NMR Spectroscopic Data of the Sugar Moieties of* **1** – **3**. At 400/100 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz. Assignments are based on ^{1}H,^{13}C-COSY and HMBC experiments. Cym and Ole refer to cymaropyranosyl and oleandropyranosyl, resp.

Position	**1**		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
Cym:						
H–C(1′)	4.86 (*dd*, *J* = 9.7, 1.9)	95.5	4.85 (*dd*, *J* = 9.5, 1.8)	95.4	4.85 (*dd*, *J* = 9.5, 1.8)	95.5
H_α–C(2′)	1.57–1.62 (*m*)	35.7	1.55–1.59 (*m*)	35.43	1.54–1.60 (*m*)	35.50
H_β–C(2′)	2.08 (*ddd*, *J* = 14.0, 3.9, 1.9)		2.04–2.10 (*m*)		2.04–2.08 (*m*)	
H–C(3′)	3.79–3.82 (*m*)	77.0	3.78–3.82 (*m*)	76.9	3.78–3.82 (*m*)	77.0
H–C(4′)	3.23 (*dd*, *J* = 9.6, 2.8)	82.8	3.20 (*dd*, *J* = 9.6, 2.9)	82.5	3.20 (*dd*, *J* = 10.1, 2.9)	82.5
H–C(5′)	3.87 (*dq*, *J* = 9.6, 6.3)	68.3	3.86 (*dq*, *J* = 9.6, 6.3)	68.2	3.86 (*dq*, *J* = 10.1, 6.3)	68.3
Me(6′)	1.24 (*d*, *J* = 6.3)	18.2	1.22 (*d*, *J* = 6.3)	18.1	1.22 (*d*, *J* = 6.3)	18.20
3′-MeO	3.45 (*s*)	58.0	3.44 (*s*)	57.8	3.43 (*s*)	57.9
Cym:						
H–C(1″)			4.75 (*dd*, *J* = 9.7, 1.9)	99.6	4.75 (*dd*, *J* = 9.7, 1.5)	99.7
H_α–C(2″)			1.65–1.69 (*m*)	35.39	1.60–1.64 (*m*)	35.46
H_β–C(2″)			2.11–2.17 (*m*)		2.11–2.16 (*m*)	
H–C(3″)			3.78–3.82 (*m*)	76.9	3.78–3.82 (*m*)	77.0
H–C(4″)			3.23 (*dd*, *J* = 9.6, 2.9)	82.6	3.23 (*dd*, *J* = 10.1, 2.9)	82.6
H–C(5″)			3.84 (*dq*, *J* = 9.6, 6.3)	68.5	3.84 (*dq*, *J* = 10.1, 6.3)	68.5
Me(6″)			1.22 (*d*, *J* = 6.3)	18.2	1.22 (*d*, *J* = 6.3)	18.26
3″-MeO			3.45 (*s*)	58.1	3.44 (*s*)	58.2
Ole:						
H–C(1″/1‴)	4.50 (*dd*, *J* = 9.9, 2.2)	101.4	4.50 (*dd*, *J* = 9.7, 1.9)	101.4	4.50 (*dd*, *J* = 9.7, 1.5)	101.4
H_α–C(2″/2‴)	1.49–1.53 (*m*)	35.3	1.48–1.52 (*m*)	35.3	1.48–1.52 (*m*)	35.3
H_β–C(2″/2‴)	2.33 (*ddd*, *J* = 12.5, 4.5, 2.2)		2.30–2.36 (*m*)		2.30–2.36 (*m*)	
H–C(3″/3‴)	3.15–3.19 (*m*)	80.5	3.14–3.20 (*m*)	80.5	3.17–3.19 (*m*)	80.6
H–C(4″/4‴)	3.13 (*t*, *J* = 8.8)	75.4	3.13 (*t*, *J* = 8.7)	75.3	3.13 (*t*, *J* = 8.7)	75.4
H–C(5″/5‴)	3.29 (*dq*, *J* = 8.8, 6.1)	71.5	3.29 (*dq*, *J* = 8.7, 6.3)	71.5	3.29 (*dq*, *J* = 8.7, 6.3)	71.5
Me(6″/6‴)	1.32 (*d*, *J* = 6.1)	18.0	1.33 (*d*, *J* = 6.3)	17.9	1.32 (*d*, *J* = 6.3)	18.0
3″- or 3‴-MeO	3.39 (*s*)	56.3	3.39 (*s*)	56.2	3.39 (*s*)	56.3

From the above data, the structure of caradalzieloside A (**1**) was unequivocally determined as (3β,5α,12β,14β,17α,20*S*)-12-acetoxy-20-(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl β-oleandropyranosyl-(1 → 4)-β-cymaropyranoside.

Caradalzieloside B (**2**) was obtained as a colorless, amorphous solid. The molecular formula was determined by HR-FAB-MS as $C_{51}H_{78}O_{17}$. The ^{1}H- and ^{13}C-NMR spectroscopic data (*Tables 1* and *2*) indicated an additional β-cymaropyranosyl unit compared to **1**. The interlinkage of the sugar chain was confirmed by the following HMBC correlations: H−C(3)/C(1′), H−C(4′)/C(1″), H−C(4″)/C(1‴). The complete assignment of the sugar resonances was compatible with the data of telosmoside A_4 reported from *Telosma procumbens* [10]. Thus, the structure of **2** was determined as (3β,5α,12β,14β,17α,20*S*)-12-acetoxy-20-(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl β-oleandropyranosyl-(1 → 4)-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside.

Caradalzieloside C (**3**), a colorless solid, was assigned the molecular formula $C_{56}H_{80}O_{17}$. The replacement of an AcO group at C(12) by a BzO group was inferred from the ^{1}H-NMR spectrum (*Table 3*), when compared with **2**. Both C=O resonances at δ(C) 166.1 and 164.1 of the BzO groups showed HMBC correlations with H−C(12) (δ(H) 4.95 (*dd*, *J* = 11.1, 4.3 Hz)) and H−C(20) (δ(H) 4.90 (*q*, *J* = 6.3 Hz)), respectively. The NMR spectroscopic data of the aglycone of **3** were basically identical to those of stalagmoside IV [8], including the deshielding effect observed between the BzO groups. Thus, the structure of **3** was elucidated as (3β,5α,12β,14β,17α,20*S*)-12,20-bis-(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl β-oleandropyranosyl-(1 → 4)-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside.

Caradalzieloside D (**4**), a colorless solid, had the molecular formula $C_{51}H_{78}O_{18}$. The aglycone of **4** was identical to those of **1** and **2** by comparison with the NMR assignments based on 2D-NMR measurements (*Table 1*). The sugars were identified as a β-cymaropyranose, a β-olendropyranose, and a 6-deoxy-3-*O*-methyl-β-allopyranose by the ^{1}H,^{1}H-COSY and NOESY spectra, as well as by means of analysis of the ^{1}H-NMR coupling constants (*Table 4*). HMBC Correlations between H−C(4′)/C(1″) and H−C(4″)/C(1‴) revealed the interlinkage of the sugar chain. Therefore, the structure of **4** was determined as (3β,5α,12β,14β,17α,20*S*)-12-acetoxy-20-(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl 6-deoxy-3-*O*-methyl-β-allopyranosyl-(1 → 4)-β-oleandropyranosyl-(1 → 4)-β-cymaropyranoside. Note that an 8-dehydroxy derivative of **4** has been isolated from the same plant collected in Mali [7].

Caradalzieloside E (**5**), a colorless solid, showed a similar specific rotation, $[\alpha]_D^{25} = +60$, as compound **3**. Its molecular formula was deduced as $C_{63}H_{92}O_{21}$ by HR-FAB-MS. According to the NMR assignment, the aglycone moiety of **5** was found to be the same as that of **3**, with two BzO groups. A detailed comparison of the ^{1}H- and ^{13}C-NMR spectroscopic data in the sugar region with those of **3** and **4** indicated that **5** corresponds to (3β,5α,12β,14β,17α,20*S*)-12,20-bis(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl 6-deoxy-3-*O*-methyl-β-allopyranosyl-(1 → 4)-β-oleandropyranosyl-(1 → 4)-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside.

All of the above five steroidal glycosides isolated from Nigerian *C. dalzielii* originate from 5,6-dihydrosarcostin instead of tomentogenin found in the species from Mali [7]. A further characteristic difference, in terms of substituents, between the Nigerian and Malian species is that the latter keep an AcO group at C(12), regardless of the diversity of ester groups at C(20). Taking these results into account, chemical races are likely present in this plant.

Table 3. *^{1}H- and ^{13}C-NMR Spectroscopic Data of the Aglycones of* **3** *and* **5**. At 400/100 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz. Assignments are based on ^{1}H,^{13}C-COSY and HMBC experiments.

Position	**3**		**5**	
	δ(H)	δ(C)	δ(H)	δ(C)
CH_2(1)	0.97–1.03 (*m*, H_α)	37.8	0.95–1.02 (*m*, H_α)	37.8
	1.63–1.68 (*m*, H_β)		1.67–1.71 (*m*, H_β)	
CH_2(2)	1.79–1.85 (*m*, H_α)	28.7	1.79–1.85 (*m*, H_α)	28.7
	1.42–1.47 (*m*, H_β)		1.42–1.48 (*m*, H_β)	
H–C(3)	3.58–3.66 (*m*, H_α)	76.8	3.58–3.66 (*m*, H_α)	76.8
CH_2(4)	1.85–1.90 (*m*, H_α)	34.0	1.85–1.91 (*m*, H_α)	34.1
	1.29–1.35 (*m*, H_β)		1.28–1.35 (*m*, H_β)	
H–C(5)	1.04–1.08 (*m*, H_α)	45.1	1.03–1.08 (*m*, H_α)	45.2
CH_2(6)	1.26–1.32 (*m*, H_α)	24.5	1.28–1.35 (*m*, H_α)	24.5
	1.53–1.58 (*m*, H_β)		1.53–1.58 (*m*, H_β)	
CH_2(7)	1.27–1.33 (*m*, H_α)	33.8	1.28–1.35 (*m*, H_α)	33.9
	1.62–1.67 (*m*, H_β)		1.63–1.69 (*m*, H_β)	
C(8)		75.8		75.8
H–C(9)	1.18–1.26 (*m*)	46.1	1.18–1.26 (*m*)	46.2
C(10)		36.2		36.2
CH_2(11)	1.68–1.74 (*m*, H_α)	24.0	1.68–1.74 (*m*, H_α)	24.0
	1.90–1.96 (*m*, H_β)		1.90–1.96 (*m*, H_β)	
H–C(12)	4.95 (*dd*, J=11.1, 4.3)	74.3	4.93 (*dd*, J=11.6, 4.3)	74.3
C(13)		56.9		56.9
C(14)		88.0		88.0
CH_2(15)	1.97–2.03 (*m*)	32.9	1.95–2.05 (*m*)	32.9
CH_2(16)	1.97–2.03 (*m*)	32.2	1.95–2.05 (*m*)	32.2
C(17)		88.2		88.2
Me(18)	1.65 (*s*)	11.2	1.65 (*s*)	11.2
Me(19)	0.92 (*s*)	12.4	0.92 (*s*)	12.4
H–C(20)	4.90 (*q*, J=6.3)	74.7	4.90 (*q*, J=6.3)	74.7
Me(21)	1.28 (*d*, J=6.3)	15.1	1.26 (*d*, J=6.3)	15.1
8-OH	2.47 (*s*)		2.46 (*s*)	
14-OH	4.65 (*s*)		4.64 (*s*)	
17-OH	3.18 (*s*)		3.14 (*s*)	
12-BzO:				
C=O		166.1		166.1
C(1)		130.7		130.8
H–C(2,6)	7.69 (*d*, J=7.7)	129.5	7.69 (*d*, J=7.7)	129.5
H–C(3,5)	7.10 (*t*, J=7.7)	128.0	7.10 (*t*, J=7.7)	128.0
H–C(4)	7.41 (*t*, J=7.7)	132.5	7.41 (*t*, J=7.7)	132.4
20-BzO:				
C=O		164.1		164.1
C(1)		129.9		129.5
H–C(2,6)	7.53 (*d*, J=7.7)	129.5	7.53 (*d*, J=7.7)	129.5
H–C(3,5)	7.32 (*t*, J=7.7)	128.1	7.32 (*t*, J=7.7)	128.1
H–C(4)	7.52 (*t*, J=7.7)	132.9	7.52 (*t*, J=7.7)	132.8

Table 4. *^{1}H- and ^{13}C-NMR Spectroscopic Data of the Sugar Moieties of* **4** *and* **5**. At 400/100 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz. Assignments are based on ^{1}H,^{13}C-COSY and HMBC experiments. Cym, Ole, and Allo refer to cymaropyranosyl, oleandropyranosyl, and 6-deoxy-3-*O*-methylallopyranosyl, resp.

Position	**4**		**5**	
	δ(H)	δ(C)	δ(H)	δ(C)
Cym:				
H–C(1′)	4.86 (*dd*, *J* = 9.7, 1.9)	95.5	4.85 (*dd*, *J* = 9.7, 1.9)	95.5
H_α–C(2′)	1.58–1.62 (*m*)	35.6	1.56–1.60 (*m*)	35.5
H_β–C(2′)	2.05–2.09 (*m*)		2.04–2.08 (*m*)	
H–C(3′)	3.78–3.80 (*m*)	76.9	3.78–3.80 (*m*)	77.2
H–C(4′)	3.20 (*dd*, *J* = 9.7, 2.9)	82.7	3.20 (*dd*, *J* = 9.7, 2.9)	82.5
H–C(5′)	3.86 (*dq*, *J* = 9.7, 6.3)	68.3	3.86 (*dq*, *J* = 9.7, 6.3)	68.3
Me(6′)	1.23 (*d*, *J* = 6.3)	18.2	1.21 (*d*, *J* = 6.3)	18.2
3′-MeO	3.44 (*s*)	58.0	3.43 (*s*)	57.9
Cym:				
H–C(1″)			4.75 (*dd*, *J* = 9.7, 1.9)	99.6
H_α–C(2″)			1.60–1.64 (*m*)	35.5
H_β–C(2″)			2.10–2.16 (*m*)	
H–C(3″)			3.78–3.80 (*m*)	77.2
H–C(4″)			3.22 (*dd*, *J* = 9.7, 2.9)	82.6
H–C(5″)			3.83 (*dq*, *J* = 9.7, 6.3)	68.5
Me(6″)			1.21 (*d*, *J* = 6.3)	18.3
3″-MeO			3.44 (*s*)	58.2
Ole:				
H–C(1″/1‴)	4.48 (*dd*, *J* = 9.7, 1.9)	101.1	4.48 (*dd*, *J* = 9.7, 1.9)	101.2
H_α–C(2″/2‴)	1.50–1.56 (*m*)	35.7	1.52 (*dd*, *J* = 12.6, 9.7)	35.8
H_β–C(2″/2‴)	2.37 (*ddd*, *J* = 12.6, 4.8, 1.9)		2.37 (*ddd*, *J* = 12.6, 4.8, 1.9)	
H–C(3″/3‴)	3.39–3.41 (*m*)	78.6	3.39–3.41 (*m*)	78.6
H–C(4″/4‴)	3.34 (*t*, *J* = 7.5)	79.0	3.34 (*t*, *J* = 7.5)	79.0
H–C(5″/5‴)	3.31–3.35 (*m*)	71.3	3.31–3.35 (*m*)	71.4
Me(6″/6‴)	1.35 (*d*, *J* = 5.8)	18.6	1.35 (*d*, *J* = 5.8)	18.6
3″- or 3‴-MeO	3.39 (*s*)	55.7	3.38 (*s*)	55.8
Allo:				
H–C(1‴/1⁗)	4.79 (*d*, *J* = 8.2)	99.1	4.79 (*d*, *J* = 8.7)	99.2
H–C(2‴/2⁗)	3.49 (*dd*, *J* = 8.2, 3.4)	71.7	3.46–3.50 (*m*)	71.8
H–C(3‴/3⁗)	3.80 (*dd*, *J* = 3.4, 2.9)	81.0	3.80 (br. *t*, *J* = 2.9)	81.0
H–C(4‴/4⁗)	3.19 (*dd*, *J* = 9.7, 2.9)	72.8	3.18 (*dd*, *J* = 9.7, 2.9)	72.8
H–C(5‴/5⁗)	3.56 (*dq*, *J* = 9.7, 6.3)	71.3	3.55 (*dq*, *J* = 9.7, 6.3)	71.4
Me(6‴/6⁗)	1.26 (*d*, *J* = 6.3)	17.8	1.26 (*d*, *J* = 6.3)	17.8
3‴- or 3⁗-MeO	3.66 (*s*)	61.9	3.66 (*s*)	61.9

Experimental Part

General. Column chromatography (CC) was performed on silica gel *60* (70–230 mesh; *Merck*) or *Sep-Pak Vac C_{18}* (10 g/35 ml; *Waters*). TLC: silica gel *60 F_{254}* and silica gel *RP-18 F_{254S}* (both *Merck*). Centrifugal liquid–liquid-partition chromatography (CPC) was performed on a *Senshu Scientific* model *CPC-240* system, the upper layer being used as the mobile phase in ascending mode at a flow rate of 5 ml/min and a centrifugation speed of 10,000 rpm. UV Spectra: *Shimadzu UV-2200* spectrometer; λ_{max} in nm.

Optical rotation: *JASCO DIP-370* polarimeter. NMR Spectra: *JEOL JNM-AL-400*, equipped with field-gradient pulse units (*NM-31010* and *NM-31020*); δ in ppm rel. to Me_4Si, *J* in Hz. Mass spectra: *JEOL JMS-700T* spectrometer; in *m/z*.

Plant Material. The aerial parts of *Caralluma dalzielii* N. E. BROWN were collected at Damaturu, Nigeria, in August 2004. The plant was identified by *M. Musa*, Department of Biological Sciences, Ahmadu Bello University, Zaria, Nigeria. A voucher specimen was deposited at the Gifu Pharmaceutical University, Gifu, Japan.

Extraction and Isolation. The dried aerial parts (85 g) of *C. dalzielii* were extracted with $CHCl_3$/MeOH 1:1 (1.5 l) at r.t. overnight (6×). The filtered soln. was concentrated *in vacuo* to yield an extract (10.8 g), part of which (10.3 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 50:1 → 1:1) to afford eight main fractions (Fr.): *Fr. A* (eluted with $CHCl_3$/MeOH 50:1), *Fr. B* (30:1), *Fr. C* (20:1), *Fr. D* (15:1), *Fr. E* (10:1), *Fr. F* (5:1), *Fr. G* (1:1), and *Fr. H* (0:1). *Fr. C* was purified by CPC (heptane/$CHCl_3$/MeOH/PrOH/H_2O 100:70:80:8:10; see *General*). The fractions containing steroidal glycosides (*Sep-Pak Vac* C_{18}; MeCN/H_2O 40:60) yielded **1** (23 mg), **2** (34 mg), and **3** (19 mg) in pure forms. *Fr. D* was applied to CPC (hexane/$CHCl_3$/MeOH/EtOH/H_2O 100:70:50:10:10) to yield, after further purification by CC (*Sep-Pak Vac* C_{18}; MeCN/H_2O 40:60) compound **5** (8 mg). *Fr. E* was separated by CPC (heptane/$CHCl_3$/MeOH/PrOH/EtOH/H_2O 120:90:80:14:10:14) and CC (*Sep-Pak Vac* C_{18}; MeCN/H_2O 40:60) to afford **4** (38 mg).

Caradalzieloside A (=*(3β,5α,12β,14β,17α,20*S*)-12-Acetoxy-20-(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl β-Oleandropyranosyl-(1 → 4)-β-cymaropyranoside*; **1**). Colorless, amorphous solid. UV (MeOH): 229. $[\alpha]_D^{25} = +19$ ($c = 0.19$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-FAB-MS (neg.): 817.4368 ($[M-H]^-$, $C_{44}H_{65}O_{14}^-$; calc. 817.4375).

Caradalzieloside B (=*(3β,5α,12β,14β,17α,20*S*)-12-Acetoxy-20-(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl β-Oleandropyranosyl-(1 → 4)-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside*; **2**). Colorless, amorphous solid. UV (MeOH): 230. $[\alpha]_D^{25} = +25$ ($c = 0.18$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-FAB-MS (neg.): 961.5165 ($[M-H]^-$, $C_{51}H_{77}O_{17}^-$; calc. 961.5161).

Caradalzieloside C (=*(3β,5α,12β,14β,17α,20*S*)-12,20-bis(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl β-Oleandropyranosyl-(1 → 4)-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside*; **3**). Colorless amorphous solid. UV (MeOH): 230. $[\alpha]_D^{25} = +51$ ($c = 0.19$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 2* and *3*. HR-FAB-MS (neg.): 1023.5320 ($[M-H]^-$, $C_{56}H_{79}O_{17}^-$, calc. 1023.5317).

Caradalzieloside D (=*(3β,5α,12β,14β,17α,20*S*)-12-Acetoxy-20-(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl 6-Deoxy-3-*O*-methyl-β-allopyranosyl-(1 → 4)-β-oleandropyranosyl-(1 → 4)-β-cymaropyranoside*; **4**). Colorless, amorphous solid. UV (MeOH): 229. $[\alpha]_D^{20} = +16$ ($c = 0.38$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *4*. HR-FAB-MS (neg.): 977.5114 ($[M-H]^-$, $C_{51}H_{77}O_{18}^-$; calc. 977.5110).

Caradalzieloside E (=*(3β,5α,12β,14β,17α,20*S*)-12,20-Bis(benzoyloxy)-8,14,17-trihydroxypregnan-3-yl 6-Deoxy-3-*O*-methyl-β-allopyranosyl-(1 → 4)-β-oleandropyranosyl-(1 → 4)-β-cymaropyranosyl-(1 → 4)-β-cymaropyranoside*; **5**). Colorless, amorphous solid. UV (MeOH): 230. $[\alpha]_D^{25} = +60$ ($c = 0.16$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 3* and *4*. HR-FAB-MS (neg.): 1183.6045 ($[M-H]^-$, $C_{63}H_{91}O_{21}^-$, calc. 1183.6053).

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