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NEW TRITERPENOID SAPONINS FROM *CORCHORUS ACUTANGULUS*

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Key Word Index—*Corchorus acutangulus*, Tiliaceae, corchorusin C_1; corchorusin D_1, corchorusin D_2; corchorusin D_3, triterpenoid saponins, structural determination.

Abstract—Four new triterpenoid glycosides, corchorusins C_1, D_1, D_2 and D_3 isolated from the aerial parts of *Corchorus acutangulus* were respectively identified as saikogenin C, 3-*O*-β-D-galactopyranoside, saikogenin B, 3-*O*-β-D-glucopyranosyl (1→2)-β-D-galactopyranoside, longispinogenin, 3-*O*-β-D-glucopyranosyl (1→2)-β-D-galactopyranoside and saikogenin C, 3-*O*-β-D-glucopyranosyl (1→2)-β-D-galactopyranoside (**6**) based on their spectroscopic properties and some chemical transformations.

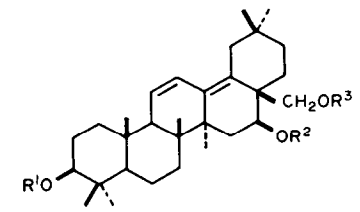
INTRODUCTION

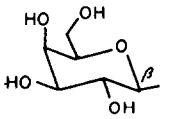
In a previous communication [1], we reported the isolation and structural elucidation of four new triterpenoid glycosides, corchorusins A–D obtained from the leaves of *Corchorus acutangulus*. The close similarity in structure of these corchorusins with the saikosaponins isolated so far only from the medicinally important *Bupleurm* sp [2–4] (Umbelliferae) of Japan, China and Korea prompted us to investigate further for the other saponin constituents of the leaves. We have been successful in isolating a further four new saikosaponin-like triterpenoid glycosides. This paper reports the isolation and structure elucidation of these biologically important saponins.

RESULTS AND DISCUSSION

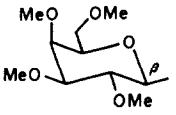
The *n*-BuOH soluble fraction of the methanolic extract of the leaves of *C. acutangulus* on chromatographic purification followed by systematic HPLC separation led to the isolation of four more new triterpenoid glycosides which we have called corchorusins C_1, D_1–D_3.

Corchorusin C_1 (**1**) on acid hydrolysis yielded a genin (**2**), and a sugar constituent, identified by PC and GC as D-galactose by comparison with an authentic sample. The genin (**2**) exhibited three UV maxima characteristic of a heteroannular diene. It was identified as saikogenin C by comparison with an authentic sample [5]. That saikogenin C (**2**) is the genuine aglycone of the saponin (**1**) was ascertained by ^{13}C NMR spectral data of the latter (Table 1) which shows the characteristic signals assignable to the carbons of the compound (**2**). The permethylate (**3**) obtained by treatment of compound (**1**) with sodium hydride–methyl iodide in hexamethylphosphoramide (HMPA) exhibited in its ^1H NMR spectrum a signal at δ4.24 (1H, *d*, $J = 7$ Hz) assignable to the H-1 of galactose indicating the β-configuration ($^4C_1$ conformation) at the anomeric centre of the sugar. The anomeric configuration was further supported by the application of Klyne's rule [6] of molecular rotation. The permethylate (**3**) on hydrolysis led to the formation of 2,3,4,6-tetra-*O*-methyl-D-galactose and 16,28-di-*O*-methyl-saikogenin C (**4**) whose acetate (**5**) showed in its ^1H NMR spectrum a



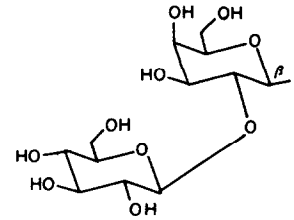
1 R^1 =  , $R^2 = R^3 = H$

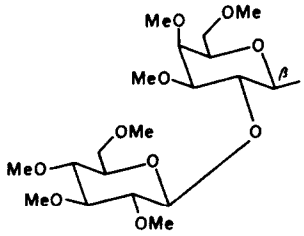
2 $R^1 = R^2 = R^3 = H$

3 R^1 =  , $R^2 = R^3 = Me$

4 $R^1 = H$, $R^2 = R^3 = Me$

5 $R^1 = Ac$, $R^2 = R^3 = Me$

6 R^1 =  , $R^2 = R^3 = H$

7 R^1 =  , $R^2 = R^3 = Me$

signal at δ4 82 (1H, *dd*, $J = 10.5$ and 6 Hz) assignable to the C-3 proton geminal to the AcO group Thus, the attachment of galactose in corchorusin C_1 was demonstrated The ^{13}C NMR data of compound (**1**) (Table 1) also supported its structure as saikogenin C3-*O*-β-D-galactopyranoside (**1**).

Corchorusin D_1 (**8**) displayed an UV absorption maximum at 280 nm characteristic of a homoannular diene system. On hydrolysis it yielded D-glucose and D-galactose (identified by GC of their alditol acetates and comparison with authentic samples) and a genin which was eventually characterised as saikogenin B (**9**) by comparison of its mp, $[\alpha]_D$ and ^{1}H NMR data with those of an authentic sample [7]. The sequence of the two hexoses in compound (**8**) was deduced by the generation of the prosapogenin (**10**) by partial hydrolysis, which on acid hydrolysis liberated the aglycone (**9**) and the only sugar constituent, identified as D-galactose. Consequently, it was demonstrated that galactose is directly linked to saikogenin B (**9**), and that glucose is present as the terminal sugar. Moreover, the permethylate (**11**) on acid hydrolysis yielded 2,3,4,6-tetra-*O*-methyl-D-glucose and 3,4,6-tri-*O*-methyl-D-galactose as sugar constituents, and 16,28-di-*O*-methyl saikogenin B (**12**). The acetate (**13**) of compound (**12**) showed in its ^{1}H NMR spectrum a characteristic signal indicating the presence of an acetoxy

Table 1 ^{13}C NMR chemical shifts δ_C ($\pm$0 1) of saikogenin C (**2**), saikogenin B (**9**), longispinogenin (**15**), corchorusin C_1 (**1**), corchorusin D_1 (**8**), corchorusin D_2 (**14**) and corchorusin D_3 (**6**) measured in pyridine

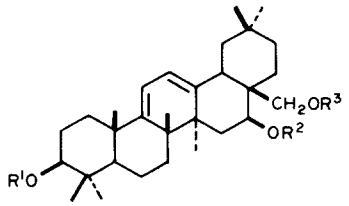
Carbon	(2)	(1)	(9)	(8)	(15)	(14)	(6)
1	37 8	38 4	37 8	37 7	38 8	39 5	38 4
2	28 0	26 5	28 7	27 1	26 8	26 3	26 4
3	78 5	89 0	77 8	88 9	78 8	89 0	89 0
4	39 7	39 6	39 6	39 7	38 9	38 9	39 6
5	55 6	55 4	51 8	52 0	55 2	55 9	55 5
6	18 9	18 5	18.6	18 4	18 3	18 4	18 5
7	33 0	32 7	32 6	33.2	32 6	33.3	32 6
8	40 2	40 3	43 1[a]	43 2[a]	39 8[a]	40 1[a]	40 4
9	54 5	54 4	154 9	154 9	46 9	47 2	54 3
10	37 0	36 7	39 0	38 4	37 0	36 7	36 6
11	127 1	127 0	116 1	116 0	23 5	24 1	127 0
12	125.8	125 7	121 2	121 2	122 3	122 6	125.8
13	136 6	136 5	145 3	145 3	143 2	143 8	136 4
14	44 4	44 3[a]	43 2[a]	42 9[a]	43 7	43 9	44 3
15	35 1	35 2	36 1	36 0	36 0	36 6	35 2
16	76 3	76 2	66 9	67 1	67 5	66 9	76 1
17	44 4	44 4[a]	40 6	40 5	40 2[a]	39 5[a]	44 3
18	133 4	133 3	42 6	42 3	44 7	44 6	133 3
19	38 7	39 5	47 0	47 1	46 9	47 2	39 6
20	32 6	32 3	31 0	31 0	30 7	30 9	32 2
21	35 3	34 9	34 1	34 2	33 8	33 5	34 8
22	30 2	29 9	26 2	26 1	26 2	26.3	29 8
23	27 8	27 4	28 8	28 4	28 0	28 1	27 3
24	15 9	16 0	16 6	16 8	16 0	16 5	16 2
25	18 3	18 2	21 0[b]	21 0[b]	15 6	15 6	18 2
26	17 2	17 1	21 3[b]	21 4[b]	16 7	16 9	17 0
27	22 1	22 0	25 5	25 4	26 8	27 0	22 0
28	64 0	63 9	69 4	69 6	70 8	69 8	63 9
29	25 0	24 8	33 2	33 2	33 0	33 0	24 9
30	32 3	32 2	24 0	24 2	23 9	23.8	32 2
Gal-1		105 7		105 5[c]		105 4[b]	105 6[a]
Gal-2		72 7		81 4		81 1	81.4
Gal-3		74 9		71 8		71 7	71 7
Gal-4		69 7		69 8		69 8	69 9
Gal-5		76 0		76 5		76 4	76 4
Gal-6		61 9		62 1[d]		62 0[c]	62 1[b]
Glc-1				105 1[c]		105 0[b]	105 1[a]
Glc-2				75 2		75 1	75 1
Glc-3				77 9		77 8	77 8
Glc-4				71 8		71 7	71 7
Glc-5				77 6		77 5	77 6
Glc-6				62 8[d]		62 7[c]	62 8[b]

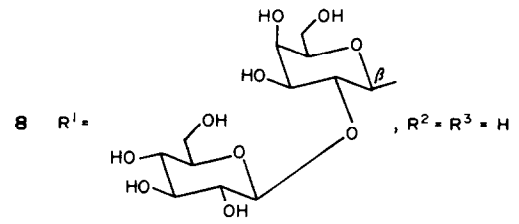
[a–d] Signals may be interchanged within each vertical column
Gal = Galactose, Glc = Glucose

function at C-3. Consequently, the linkages of the two sugar units could be demonstrated. The β-linkages ($^4C_1$ conformation) of the two anomeric protons were evident from the ^{1}H NMR spectrum of compound (**11**). The ^{13}C NMR spectrum of corchorusin D_1 (**8**) (Table 1) is in agreement with the structure shown. The signal assignments of compound (**8**) were made by comparison of the ^{13}C NMR data of the aglycone [2] (**9**) and the methyl sugars [8] using known chemical shift rules [9] and glycosylation shifts [10, 11]. Thus, corchorusin D_1 was shown to be saikogenin B 3-*O*-β-D-glucopyranosyl (1→2)-β-D-galactopyranoside (**8**).

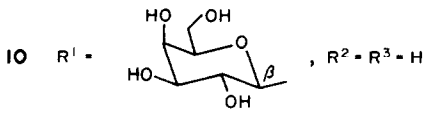
Corchorusin D_2 (**14**) was transparent in its UV spectrum above 205 nm and on acid hydrolysis it liberated D-glucose and D-galactose as sugar constituents, and longispinogenin (**15**) as the aglycone, identified by direct comparison with an authentic sample [7, 12]. Its ^{13}C NMR spectrum (Table 1) strongly suggested that the structure of its carbohydrate moiety is similar to that of corchorusin D_1 (**8**) and the complete structure of this saponin as shown was ascertained by generation of the prosapogenin (**16**), characterised as corchorusin A [1] by direct comparison and preparation of the permethylate (**17**) followed by hydrolysis and identification of the partially methylated sugars and the genin (**18**).

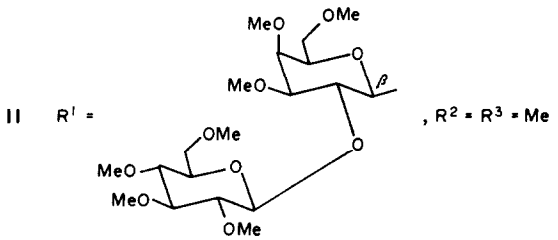
The UV spectrum of corchorusin D_3 (**6**) displayed the triple absorption maxima characteristic of heteroannular





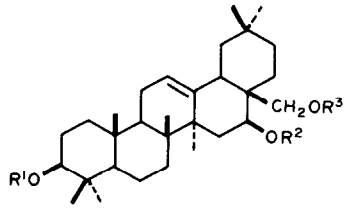
9 $R^1 = R^2 = R^3 = H$

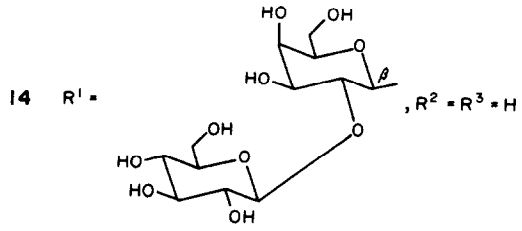




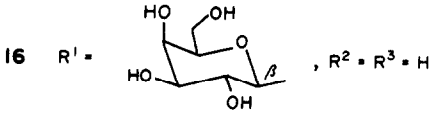
12 $R^1 = H$, $R^2 = R^3 = Me$

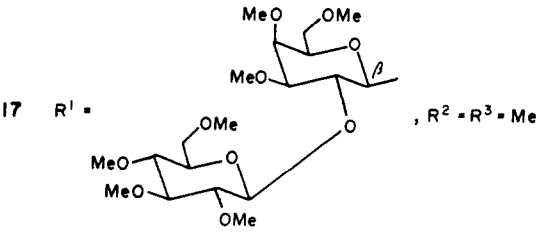
13 $R^1 = Ac$, $R^2 = R^3 = Me$





15 $R^1 = R^2 = R^3 = H$





18 $R^1 = H$, $R^2 = R^3 = Me$

diene and on acid hydrolysis it afforded D-glucose, D-galactose as sugars and saikogenin C (**2**) as the aglycone. Its structure as saikogenin C3-*O*-β-D-glucopyranosyl (1→2)-β-D-galactopyranoside (**6**) was established by the study of its ^{13}C NMR data (Table 1) and also by the preparation of its permethylate (**7**) followed by hydrolysis and identification of the partially methylated sugars.

It is noteworthy that saikosaponins containing saikogenins as aglycones and different combinations of fucose, glucose and rhamnose have been reported so far only from various medicinally used *Bupleurum* species (Umbelliferae) occurring in Japan, China and Korea [13]. Some of the saikosaponins have been reported to have antiviral [14], antiinflammatory [15], haemolytic [16] and plasma-cholesterol lowering [17] activity. *C. acutangulus* growing wild in India appears to be the only alternative plant of different genus and family so far which contains saikosaponins-like compounds. The activity profile of the corchorusins seems to be very interesting in view of their structural similarity with the saikosaponins.

EXPERIMENTAL

Mps uncorr. TLC was carried out on silica gel 60 HF_{254} (Merck) with the following solvent systems (A) benzene–$CHCl_3$–EtOAc (1:2:2), (B) H_2O–$CHCl_3$ (1:30) and then MeOH was added until the soln became clear. PC for sugars was performed on Whatman No. 1 with solvent system (C): *n*-BuOH–pyridine–H_2O (6:4:3), other solvent systems are

detailed in the text A satd soln of aniline oxalate in H_2O was used as visualization agent. GC was carried out on the following columns (i) 3% ECNSS-M at 190° for alditol acetates and (ii) OV-225 at 195° for partially methylated alditol acetates IR spectra were recorded in Nujol mulls ^{1}H NMR spectra were recorded at 100 MHz in $CDCl_3$ or C_5D_5N solns ^{13}C NMR spectra were recorded on the same instrument operating at 25 MHz using $CDCl_3$ or C_5D_5N solns with TMS as int standard HPLC analysis was done with a Spherisorb S-10-ODS reversed phase column (25 cm length, id 10 mm) with a RI detector Petrol refers to the fraction boiling in the range 60–80°

Isolation of saponins Air-dried powdered aerial parts of *C acutangulus* Lam (1.3 kg) was successively extracted with petrol $CHCl_3$ and MeOH The MeOH extract was partitioned between *n*-BuOH and H_2O The organic layer was concd to dryness under red pres to give a residue (36 g) which was chromatographed on silica gel (800 g) Gradient elution was effected with $CHCl_3$ followed by $CHCl_3$-MeOH mixts Fractions (250 ml each) were monitored by TLC Early fractions eluted with $CHCl_3$–MeOH (9 1) and (17 3) yielded previously reported [1] corchorusins A, B and C and the fractions eluted with $CHCl_3$–MeOH (87 13) and (4 1) were collected and subjected to HPLC sepn on a reversed-phase Spherisorb S-10-ODS column with MeOH–H_2O (3 1) and (7 3) Thus, corchorusin C_1 (0 16 g) D (0 25 g), D_1 (0 21 g), D_2 (0 17 g) and D_3 (0 23 g) were isolated of which the structure elucidation of corchorusin D has already been reported [1]

Corchorusin C_1 (**1**) Crystallized from $CHCl_3$–MeOH as micro-needles, mp 253–255°, $[\alpha]_D$ −45° (MeOH, *c* 0 25) (Found C, 69 9, H, 9 50 $C_{36}H_{58}O_8$ requires C, 69 97, H, 9 45%)

Hydrolysis of corchorusin C_1 (**1**) **1** (80 mg) on hydrolysis with 2 M HCl in aq MeOH (15 ml) at 100° for 5 hr followed by usual work-up yielded saikogenin C (**2**) (30 mg), mp 291–293°, $[\alpha]_D$ −46° (*c* 0 35 in pyridine) (lit [5] mp 291–294°, $[\alpha]_D$ −45 8°) ^{1}H NMR data comparable with authentic sample. The filtrate from the hydrolysate was neutralized with Ag_2CO_3, filtered and a portion of the filtrate concd under red pres and tested for sugars by PC using *n*-BuOH–pyridine–H_2O (6 4 3) Only one spot corresponding to D-galactose was obtained The other portion of the filtrate was reduced with $NaBH_4$ and worked-up in the usual way The residue was acetylated with Ac_2O–pyridine (1 1) at 100° for 1 hr, dried *in vacuo*, purified by chromatography over silica gel and subjected to GC analysis on column (i) A single peak, corresponding to D-galactitol acetate, was obtained

Permethylation of corchortsin C_1 (**1**) *and hydrolysis* A soln of **1** (80 mg) in HMPA (10 ml) was treated with NaH (400 mg) and MeI (10 ml) at room temp for 3 hr After work-up as usual the residue was purified by chromatography to yield the permethylate (**3**) (68 mg) as a colourless powder, IR (no hydroxy absorption), ^{1}H NMR ($CDCl_3$) δ0 77 (3H, s), 0 81 (3H, *s*) 0 88 (3H, *s*), 0 94 (3H, s), 1 01 (3H, *s*) 1 05 (3H, *s*), 1 20 (3H, *s*) (together 7 × Me), 3 25, 3 32, 3 45, 3 48, 3 55, 3 62 (together 6 × OMe), 3 84 (1H, *d*, *J* = 7 Hz, 28-H), 4 0 (1H, *d*, *J* = 7 Hz, 28-H') 4 28 (1H, *d*, *J* = 7 5 Hz, 1-H of galactose), 5 58 (1H, *d*, *J* = 11 Hz) and 6 40 (1H, *dd*, *J* = 11 and 2 Hz, 11-H, 12-H) The permethylate (**3**) (25 mg) was hydrolysed with 2 M HCl in aq MeOH (10 ml) for 3 hr The reaction mixt was cooled, evapd to dryness *in vacuo*, dil with H_2O and filtered The filtrate was neutralized with Ag_2CO_3 and filtered The filtrate was concd, reduced with $NaBH_4$ and worked-up in the usual manner The residue was acetylated with Ac_2O–pyridine (1 1) at 100° for 1 hr, dried *in vacuo* and subjected to GC analysis using column (ii) Only one peak was detected and this was identified as 2,3,4,6-tetra-*O*-methyl-D-galactitol diacetate by comparison with an authentic sample The residue on chromatographic purification yielded 16,28-di-*O*-methylsaikogenin C (**4**) (10 mg), mp 137–139°, $[\alpha]_D$ −45° ($CHCl_3$, *c* 0 5), (lit [18] mp 138–140°, $[\alpha]_D$ −44°)

Corchorusin D_1 (**8**) Crystallized from MeOH as needles, mp 234–236° (dec), $[\alpha]_D$ +176° (MeOH, *c* 0 19), UV λ_{max}^{MeOH} 280 nm (ε 8100) (Found C, 64 5, H, 8 8 $C_{42}H_{68}O_{13}$ requires C, 64 59, H, 8 78%)

Hydrolysis of corchorusin D_1 (**8**) **8** (80 mg) was hydrolysed with 2 M HCl in aq MeOH (10 ml) and worked-up as usual to yield D-galactose and D-glucose (identified by GC comparison of alditol acetates with authentic samples) as sugar components and saikogenin B (**9**) (22 mg), mp 268–269°, $[\alpha]_D$ +278° (MeOH, *c* 0 92), (lit [7], 267–269°, $[\alpha]_D$ +285 5°)

Permethylation of corchorusin D_1 (**8**) *and hydrolysis* Permethylation of **8** (90 mg) was done as described for corchorusin C_1 to give the permethylate (**11**) as a colourless powder (82 mg), mp 102–105°, ^{1}H NMR ($CDCl_3$) δ0 84 (3H, *s*), 0 88 (3H, *s*) 0 96 (3H, *s*), 1 08 (6H, *s*), 1 16 (3H, s), 1 28 (3H, *s*) (together 7 × Me), 3 28 (3H, s), 3 36 (3H, *s*), 3 40 (3H, *s*), 3 42 (3H, *s*), 3 52 (6H, *s*), 3 56 (6H, *s*), 3 64 (3H, *s*) (together 9 × OMe), 3 88 (1H, *d*, *J* = 8 Hz 28-H), 4 02 (1H, *d*, *J* = 8 Hz, 28-H'), 4 28 (1H, *d*, *J* = 7 Hz, 1-H of galactose unit), 4 72 (1H, *d*, *J* = 7 Hz, 1-H of glucose unit) and 5 60 (2H, *s*, 11-H, 12-H) The permethylate (**11**) (50 mg) was hydrolysed in refluxing 2 M HCl in aq MeOH (15 ml) for 3 hr The carbohydrate and aglycone fractions were worked-up as described for compound (**3**) above The peaks corresponding to 3,4,6-tri-*O*-methyl-D-galactitol triacetate and 2,3,4,6-tetra-*O*-methyl-D-glucitol diacetate were identified by comparison with authentic samples The partially methylated aglycone was purified as usual to give 16,28-di-*O*-methylsaikogenin B (**12**) (15 mg), mp 135–137°, $[\alpha]_D$ +272° ($CHCl_3$, *c* 0 81) (Found C, 79 2, H, 10 8 $C_{32}H_{52}O_3$ requires C, 79 28, H, 10 81%) The monoacetate (**13**) prepared in the usual manner shows mp 128–129°, $[\alpha]_D$ +263° ($CHCl_3$, *c* 0 52), ^{1}H NMR ($CDCl_3$) δ4 85 (1H, *dd*, *J* = 10 5 and 6 Hz, 3-H) (Found C, 77 6, H, 10 3 $C_{34}H_{54}O_4$ requires C, 77 52, H, 10 33%)

Prosapogenin (**10**) *and saikogenin B* (**9**) Corchorusin D_1 (**8**) (55 mg) was hydrolysed with 0 75 M H_2SO_4 in EtOH (6 ml) at 100° for 20 min After usual work-up the ppt was subjected to prep TLC ($CHCl_3$–MeOH, 4 1) Thus, the partially hydrolysed prosapogenin (**10**) (5 mg) and saikogenin B (**9**) were isolated in a pure state Compound (**10**) on crystallization from MeOH yielded microneedles, mp 246–248°, $[\alpha]_D$ +256° (MeOH, *c* 0 65) (Found C, 69 8, H, 9 5 $C_{36}H_{58}O_8$ requires C, 69 87, H, 9 45%) On acid hydrolysis this prosapogenin liberated saikogenin B (**9**) and D-galactose

Corchorusin D_2 (**14**), *longispinogenin* (**15**) *and prosapogenin* (**16**) Compound (**14**) crystallized from MeOH as needles, mp 222–224°, $[\alpha]_D$ +24 8° (MeOH, *c* 0 25) (Found C, 64 5, H, 9 0 $C_{42}H_{70}O_{13}$ requires C, 64 42, H, 9 01%) On usual acid hydrolysis it afforded longispinogenin (**15**) mp 220–221°, $[\alpha]_D$ +67°, (lit [7], mp 222–223°, $[\alpha]_D$ +68°), D-galactose and D-glucose Compound (**14**) on partial hydrolysis as described for (**8**) yielded prosapogenin (**16**) identical in all respects with corchorusin A [1]

Permethylate (**17**) *and partially methylated aglycone* (**18**) Compound (**14**) (75 mg) was permethylated as described for corchorusin C_1 (**1**) The permethylate (**17**) was obtained as a colourless powder (60 mg), mp 124–126°, ^{1}H NMR ($CDCl_3$) δ0 82 (3H, *s*), 0 90 (3H, *s*), 0 92 (6H, s), 0 98 (3H, s), 1 04 (3H, *s*), 1 20 (3H, *s*) (together 7 × Me), 3 28 (3H, s), 3 32 (3H, s), 3 33 (3H, *s*), 3 37 (3H, *s*), 3 48 (3H, *s*), 3 52 (3H, *s*), 3 56 (3H, *s*), 3 58 (3H, *s*), 3 60 (3H, *s*) (together 9 × OMe), 4 24 (1H, *d*, *J* = 7 Hz, 1-H of galactose), 4 70 (1H, *d*, *J* = 7 Hz, 1-H of glucose) and 5 28 (1H, *m*, 12-H) On usual acid hydrolysis it afforded 3,4,6-tri-*O*-methyl-D-galactose, 2,3,4,6-tetra-*O*-methyl-D-glucose identified as described above and 16,28-di-*O*-methyl longispinogenin [1] (**18**)

Corchorusin D_3 (**6**) *and permethylate* (**7**). Compound (**6**) crystallized from MeOH as micro-needles, mp 240–242°, $[\alpha]_D$ −19° (MeOH, *c* 0.32), λ_{max}^{MeOH} 242 (ε 22300), 251 (ε 24600) and 261 nm (ε 16400) (Found: C, 64.5; H, 8.8 $C_{42}H_{68}O_{13}$ requires C, 64.59; H, 8.78%). Compound (**6**) (70 mg) on permethylation as described above afforded the permethylate (**7**) as colourless powder (55 mg), mp 120–122°; ^{1}H NMR ($CDCl_3$): δ0.76 (3H, *s*), 0.80 (3H, *s*), 0.88 (3H, *s*), 0.96 (3H, *s*), 1.0 (3H, *s*), 1.04 (3H, *s*), 1.28 (3H, *s*) (together 7 × Me), 3.24 (3H, *s*), 3.32 (3H, *s*), 3.40 (6H, *s*), 3.46 (3H, *s*), 3.48 (3H, *s*), 3.54 (3H, *s*), 3.56 (3H, *s*), 3.62 (3H, *s*) (together 9 × OMe), 3.84 (1H, *d*, *J* = 8 Hz, 28-H), 4.0 (1H, *d*, *J* = 8 Hz, 28-H′), 4.28 (1H, *d*, *J* = 7 Hz, 1-H of galactose), 4.72 (1H, *d*, *J* = 7 Hz, 1-H of glucose), 5.57 (1H, *d*, *J* = 12 Hz) and 6.42 (1H, *dd*, *J* = 2, 12 Hz, 11-H, 12-H).

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