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SPHENOLOBANE DITERPENOIDS FROM THE LIVERWORT *ANASTROPHYLLUM DONNIANUM*

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Key Word Index—*Anastrophyllum donnianum*; Lophoziaceae; Jungermanniales; Hepaticae; liverwort; sphenolobane diterpenoids; NMR parameters.

Abstract—Four new sphenolobane diterpenoids [(3*R**,6*R**,9*R**,10*S**)-sphenoloba-13*E*,16*E*,18-trien-4-one, (3*R**,6*R**,9*R**,10*S**)-18-hydroxysphenoloba-13*E*,16*E*-dien-4-one, (3*R**,6*R**,9*R**,10*S**)-sphenoloba-13*E*,17-dien-4-one, and (6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13(14),16*E*-dien-15,18-diol] have been isolated from the liverwort *Anastrophyllum donnianum* together with two previously known sphenolobanes [(6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13*E*,16*E*-dien-18-ol and (6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13*E*,17-diene] and four known sesquiterpenoids. Structures were established using spectroscopic methods. ^{1}H and ^{13}C NMR data of the new compounds and ^{13}C data of 3α-acetoxybicyclogermacra-1(10),4-diene are reported. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

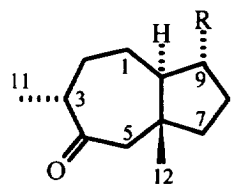
The liverwort *Anastrophyllum donnianum* (Hook.) Steph. Lophoziaceae belongs to the order Jungermanniales. *A. minutum* [1] from Germany and *A. auritum* [2] from Ecuador are the only liverworts of the genus *Anastrophyllum* to have been studied chemically so far. These investigations revealed diterpenoids with a carbon skeleton which was given the name sphenolobane (*Sphenolobus minutus* is a synonym of *A. minutum*). Although these are the only previous reports of this skeleton in liverworts, the skeleton was reported earlier (but not named) when pseudolaric acids A, B and C were isolated from *Pseudolarix kaempferi* (Pinaceae) [3], and has also been found in a deepwater sponge [4] and the Cistaceae (*Halimium viscosum*) [5, 6], the derivatives in the last case being epimeric at C-9; the name tormesane was introduced for this modified skeleton [6]. We have investigated the chemical constituents of *A. donnianum* from Scotland and in this paper report the isolation and structural characterization of four new sphenolobanes (**1**–**4**).

RESULTS AND DISCUSSION

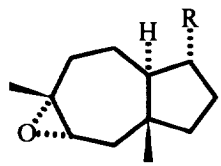
From the ether extract of *A. donnianum* collected on Beinn Damh, Wester Ross, four new sphenolobane diterpenoids (**1**–**4**) were isolated, in addition to the known sphenolobanes, (6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13*E*,16*E*-dien-18-ol (**5**) [2] and (6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13*E*,17-diene (**6**) [2], and four known sesquiterpenoids, *viz.* anastreptene [7, 8], diplophyllin [9, 10], myliol [11, 12] and 3α-acetoxybicyclogermacra-1(10),4-diene [13]. The known compounds were identified by comparison of their spectroscopic data. The ^{13}C NMR data of 3α-acetoxybicyclogermacra-1(10),4-diene are reported in the Experimental.

Compound **1**, $C_{20}H_{30}O$ ([M]$^+$ at *m/z* 286), showed a carbonyl group (ν_{max} cm^{-1}: 1690) in its IR spectrum. The UV spectrum indicated the presence of a conjugated triene (λ_{max} Et_2O nm: 275) and furthermore the characteristic fragment *m/z* 107 in the MS is consistent with partial structure **7**. The ^{1}H NMR spectrum (Table 1) showed a coupled system of three olefinic protons: δ_H 5.89 (*br d*, *J* = 10.5 Hz); 6.40 (*dd*, *J* = 15.3, 10.5 Hz) and 6.22 (*d*, *J* = 15.3 Hz). In addition, the ^{1}H NMR spectrum contained signals for a tertiary methyl, a secondary methyl, two olefinic methyls, an isolated methylene and an exomethylene. Double resonance experiments established allylic couplings between the olefinic methyl at δ_H 1.72 (*d*, *J* = 1.1 Hz) and the olefinic proton at δ_H 5.89 and also between the olefinic methyl at δ_H 1.87 (*br s*) and the exomethylene protons [δ_H 4.93 (*br s*, 2H)]. The ^{13}C NMR spectrum (Table 1) revealed the presence of a ketonic carbonyl, a trisubstituted double bond, a disubstituted double bond and an exomethylene. The spectrum showed a further 13 carbons including four methyls, five methylenes, three methines and one quaternary carbon. These data reveal that compound **1** is a bicyclic diterpenoid with three conjugated double bonds in a side chain which is represented by partial structure **7**.

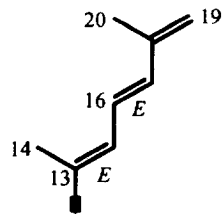
A 2D direct δ_C/δ_H correlation experiment enabled the location of all the hydrogens, with the exception of H_2-1 and H_2-8 since their carbons are isochronous, and



1 R = **7**
2 R = **10**
3 R = **11**



4 R = **12**
5 R = **10**
6 R = **11**



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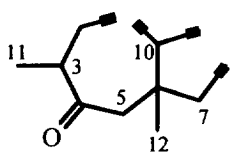

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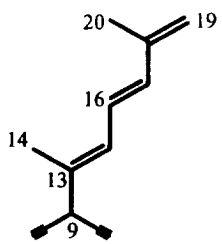

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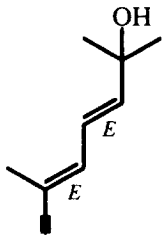

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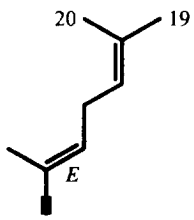

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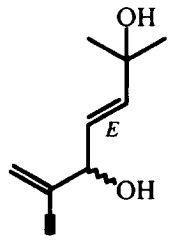

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Table 1. ^{1}H and ^{13}C NMR data of compound **1**

Site	δ_C	δ_H	
1	26.6 *t*	1.10–1.95	(*m*, 2H)
2α	33.9 *t*	1.37	(*m*)
β		1.78	(*m*)
3	47.5 *d*	2.40	(*m*)
4	215.3 *s*		
5	55.8 *t*	2.53	(*s*, 2H)
6	40.9 *s*		
7	41.6 *t*	1.30–1.65	(*m*, 2H)
8	26.6 *t*	1.10–1.95	(*m*, 2H)
9	53.2 *d*	2.33	(*dd*, *J* = 10.9, 6.4 Hz)
10	55.0 *d*	1.49	(*m*)
11	18.8 *q*	1.06	(*d*, *J* = 7.0Hz)
12	19.6 *q*	0.90	(*s*)
13	140.5 *s*		
14	13.2 *q*	1.72	(*d*, *J* = 1.1 Hz)
15	126.1 *d*	5.89	(*brd*, *J* = 10.5 Hz)
16	125.3 *d*	6.40	(*dd*, *J* = 15.3,10.5 Hz)
17	133.7 *d*	6.22	(*d*, *J* = 15.3 Hz)
18	142.3 *s*		
19	115.8 *t*	4.93	(*br s*, 2H)
20	18.6 *q*	1.87	(*br s*)

Assignments confirmed by 2D direct and long-range δ_C/δ_H correlation.

the assignment of all the protonated carbons. It was not possible to get any connectivity information for the bicyclic ring system from the ^{1}H NMR spectrum in view of its congested upfield region. Connectivity could however be deduced [14–16] from a 2D long-range δ_C/δ_H correlation experiment; the correlations observed are shown in Table 2. The protons of the C-12 methyl group (tertiary) showed correlations to C-5, C-7 and C-10 (non-quaternaries) which must arise from $^{3}J_{CH}$; the remaining correlation, to C-6 (quaternary), must therefore arise from $^{2}J_{CH}$. There is also a

Table 2. 2D long-range δ_C/δ_H correlations of compound **1**

H	Correlated C
H_2-5	4, 6, 10, 12
H_3-11	2, 3, 4
H_3-12	5, 6, 7, 10
H_3-14	9, 13
H-15	14
H-17	15
H_2-19	17, 20
H_3-20	17, 18, 19

$^3J_{CH}$ correlation of C-12 with H_2-5. The C-5 methylene is isolated, an indication together with its ^1H and ^{13}C NMR chemical shifts [δ_C 55.8 (*t*); δ_H 2.53 (*s*, 2H)] that it is bonded to a ketonic carbonyl, C-4. Therefore the correlation of H_2-5 to C-4 is $^2J_{CH}$. C-4 also has a correlation with the secondary methyl protons H_3-11 and this must be $^3J_{CH}$. These methyl protons (H_3-11) also have correlations with C-3 ($^2J_{CH}$) and C-2 ($^3J_{CH}$). This information leads to partial structure **8**. A correlation between the olefinic methyl protons (H_3-14) at δ_H 1.72 and the methine carbon at δ_C 53.2 (C-9) indicates that the side chain **7** is attached to one of the rings at this methine carbon. Thus part structure **7** can be expanded to **9**. Combination of **8** and **9** together with the two methylene carbons C-1 and C-8 (δ_C 26.6) leads to the sphenolobane structure **1** for this natural product.

The stereochemistry of the side chain was deduced as follows: the 16*E* geometry is indicated by the large vicinal coupling (J = 15.3 Hz) between H-16 and H-17. The shielded nature of the C-14 methyl carbon (δ_C 13.2) is consistent with a 13*E* configuration. Furthermore, the shielded character of H-9 [δ_H 2.33 (*dd*, J = 10.9, 6.4 Hz)] supports this conclusion since sphenolobanes with the same side chain stereochemistry exhibit this feature [1, 2]. Thus compound **1** is (3*R**,6*R**,9*R**,10*S**)-sphenoloba-13*E*,16*E*,18-trien-4-one. The sample of **1** decomposed before any NOE difference experiments could be carried out and the stereochemistry of the bicyclic ring system indicated in structure **1** is assumed by analogy with compound **2** which is discussed below.

The IR spectrum of the next compound (**2**), $C_{20}H_{32}O_2$ ([M]$^+$ at *m/z* 304.2401), revealed the presence of hydroxyl ($\nu_{max}^{CHCl_3}$ cm^{-1}: 3600) and ketonic carbonyl ($\nu_{max}^{CHCl_3}$ cm^{-1}: 1690) groups. The NMR data of **1** and **2** are similar and it is apparent that the only differences lie in the side chain, which in **2** contains a conjugated diene system [$\lambda_{max}^{Et_2O}$ cm^{-1}: 240; δ_H 5.81 (*br d*, J = 10.8 Hz); 6.44 (*dd*, J = 15.3, 10.8 Hz); 5.72 (*d*, J = 15.3 Hz)] and geminal dimethyl tertiary alcohol [δ_H 1.34 (*s*, 6H); δ_C 70.9 (*s*)] as in part structure **10**. The 13*E* side chain stereochemistry is supported by NOEs observed between H-9 and H-15 and between H_3-14 and H-16. NOE difference experiments were further used to establish the relative stereochemistry of the bicyclic nucleus. NOEs between H-9 and H_3-12 and between H_3-12 and H-3 indicate that these are on the same side of the molecule. When either H-9 or H_3-12 was irradiated there was no NOE at H-10 suggesting that the five- and seven-membered rings are *trans*-fused. On the basis of the above findings **2** is (3*R**,6*R**,9*R**,10*S**)-18-hydroxysphenoloba-13*E*,16*E*-dien-4-one.

It is clear from the NMR data of **3**, $C_{20}H_{32}O$ ([M]$^+$ at *m/z* 288), that it has the same bicyclic system as **1** and **2**, but with a modified side chain **11** containing the following groups: two trisubstituted double bonds [δ_H 5.09 (*m*, 2H); δ_C 135.8, 131.5 (both *s*); 124.8, 123.3 (both *d*)], an allylic methylene [δ_H 2.68 (*m*, 2H)] and three olefinic methyls [δ_H 1.54 (*d*, J = 1.0 Hz); 1.61 (*br s*); 1.68 (*d*, J = 1.1 Hz)]. Thus compound **3** is (3*R**,6*R**,9*R**,10*S**)-sphenoloba-13*E*,17-dien-4-one.

Sphenolobanes **1**–**6** are unstable when subjected to preparative TLC upon silica gel and undergo oxidation of the side chain. Compound **4** is probably not a natural product and it was isolated from a polar, weakly UV active band during purification of **5** on a preparative plate. It is very labile and thus only ^1H and ^{13}C NMR data were collected. Comparison of the NMR data of **4** with those of **5** and **6** [2] indicates that the compounds have the same tricyclic system; thus **4** contains a trisubstituted epoxide [δ_C 60.3, 61.0; δ_H 2.75 (*br t*, J = 7.0 Hz, 1H), 1.31 (*s*, 3H)]. Compound **4** has a different side chain from sphenolobanes **1**–**3**. The modified side chain (**12**) contains the following groups: an exomethylene [δ_C 149.8, 112.1; δ_H 5.15, 5.03 (both *br s*)], an allylic alcohol [δ_C 87.8; δ_H 4.73 (*br d*, J = 7.4 Hz)] whose proton couples vicinally with one proton of a *trans*-disubstituted double bond [δ_C 143.3, 123.7; δ_H 5.93 (*dd*, J = 157, 0.8 Hz); 5.63 (*dd*, J = 15.7, 7.4 Hz)], a tertiary hydroxyl (δ_C 70.7) and two tertiary methyls [δ_H 1.32; (*s*, 6H)]. These data lead to (6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13(14),16*E*-dien-15,18-diol for compound **4**.

Sphenolobane diterpenoids were also present in two other collections of Scottish *A. donnianum*. These two samples were small, and the crude extracts were compared with the Beinn Damh extract and the isolated sphenolobanes (except **4**) using GC. In the extract of a plant from Knoydart, 80 peaks with R_t less than 42 min were measured. Anastreptene could be identified as a minor component (R_t = 9.96 min) and sphenolobane **1** (R_t = 28.10 min) was the major component between R_t = 25 and 30 min but was still a minor component of the extract; the two major peaks, with R_t = 38.77 and 41.59 min (and accounting for approximately one quarter of the peak intensity up to 42 min), were unidentified. In the extract of a plant from the Fannaichs range, 65 peaks with R_t less than 42 min were measured. Anastreptene accounted for one sixth of this measured intensity. Sphenolobane **2** was the second most intense peak, and **1**, **5**, **6** and **3** were also observed in order of decreasing intensity among these compounds. Identities were confirmed using GC-MS, which also suggested that at least four other peaks arose from sphenolobanes in view of heaviest ions at *m/z* 286 and prominent peaks at *m/z* 107 consistent with fragment **7** or its geometric isomers [17]. In comparison, 75 peaks with R_t less than 41 min were measured in the GC of the Beinn Damh extract; seven peaks accounted for half of the measured intensity. Compound **1** (R_t = 28.12 min) was the strongest (17%) followed by anastreptene (11%, R_t = 9.96 min); the next three peaks (combined intensity 15%) were approximately equal and arose from **2** (R_t = 29.05 min), **5** (R_t = 28.45 min) and a compound (R_t = 27.50 min) thought to be a sphenolobane on the basis of the GC-MS of the Fannaichs extract; **3** (R_t = 25.83 min) and **6** (R_t = 25.17 min) were observed as minor components.

The finding of sphenolobane diterpenoids in *A.*

donnianum as well as in the two *Anastrophyllum* species investigated previously [1, 2] indicates a close chemical similarity between the three species and demonstrates consistency between the three species and the morphological classification.

EXPERIMENTAL

General. TLC: Over Merck precoated silica gel 60 F_{254} and visualized under UV light (254 nm) and by spraying with 25% H_2SO_4 and heating. Flash CC and prep. TLC: silica gel GF_{254}. GC: described elsewhere [18]. GC-MS (measured at 70 eV): HP1 fused silica capillary column (12.5 m × 0.2 mm i.d. × 0.33 μm). A linear temp. programme was used in which the column temp. was programmed from 80° (2 min) to 240° (5 min) at 5° min^{-1}. The injection port and detector temp. were 255° and 260°, respectively. NMR spectra (^1H, 200 MHz; ^{13}C, 50 MHz) were recorded for $CDCl_3$ solutions relative to $CHCl_3$ at δ_H 7.25 and $CDCl_3$ at δ_C 77.0. Assignment of ^1H NMR signals was aided by homonuclear decoupling and NOE difference experiments. Multiplicities were determined using DEPT experiments. IR spectra were measured for $CHCl_3$ solutions and UV for Et_2O solutions. EI-MS were measured at 70 eV.

Plant material. Anastrophyllum donnianum was collected (and identified) by D.S.R. at *ca* 750 m on Beinn Damh (Torridon, vice-county 105, West Ross) on 10 September 1991, at *ca* 800 m on Luinne Bheinn (Knoydart, v.-c. 97, Westerness) on 26 May 1992, and at *ca* 700 m on An Coileachan (Fannaichs range, v.-c. 106, East Ross) on 24 May 1993; voucher specimens are deposited in the herbarium of the Division of Environmental and Evolutionary Biology, Institute of Biomedical and Life Sciences, University of Glasgow.

Extraction and isolation. The sample was dried, ground (206 g) and extracted with Et_2O to give 2.85 g of crude extract, which was sepd into 20 frs by flash CC on silica gel using a petrol–Et_2O gradient. Further sepn by either prep. TLC on silica gel (petrol–Et_2O, CH_2Cl_2–Et_2O, *n*-hexane–CH_2Cl_2) or CC using Sephadex LH-20 (MeOH–CH_2Cl_2 1:1) gave in order of increasing polarity the following constituents: anastreptene (90 mg), a cycloartenol–fatty acid ester mixture (235 mg) [19], 3α-acetoxybicyclogermacra-1(10),4-diene (6 mg) [^{13}C NMR: δ_C 170.2 (*s*, C = O), 143.5 (*s*, C-10), 126.3 (*d*, C-1/5), 126.1 (*s*, C-4), 119.8 (*d*, C-1/5), 79.0 (*d*, C-3), 37.1 (*t*, C-9), 30.6 (*t*, C-2), 30.3 (*d*, C-7), 29.1 (*q*, C-12), 27.0 (*t*, C-8), 26.8 (*d*, C-6), 21.4, 21.1 (both *q*, C-14, OAc), 20.3 (*s*, C-11), 15.7, 15.4 (both *q*, C-13, C-15)], (3*R**,6*R**,9*R**,10*S**)-sphenoloba-13*E*,17-dien-4-one (**3**) (5 mg), (6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13*E*,17-diene (**6**) (3 mg), (3*R**,6*R**,9*R**,10*S**)-sphenoloba-13*E*,16*E*,18-trien-4-one (**1**) (75 mg, triglycerides (200 mg), diplophyllin (4 mg), myliol (14 mg), (3*R**,6*R**,9*R**,10*S**)-18-hydroxysphenoloba-13*E*,16*E*-dien-4-one (**2**) (11 mg), (6*R**,9*R**,10*S**)-3α,α-epoxysphenoloba-13*E*,16*E*-dien-18-ol (**5**) (5 mg) and (6*R**,9*R**,10*S**)-3α,4α-epoxysphenoloba-13(14),16*E*-dien-15,18-diol (**4**) (2 mg).

(3R*,6R*,9R*,10S*)-*Sphenoloba*-13E,16E,18-*trien*-4-*one* (**1**). Gum. GC-MS *m/z* (rel. int.): 286 $[M]^+$ (31), 107 (100), 93 (41), 77 (16), 55 (29), 41 (28). UV $\lambda_{max}^{Et_2O}$ nm: 275. IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1690 (C = O). ^1H and ^{13}C NMR: Table 1.

(3R*,6R*,9R*,10S*) - 18 - *Hydroxysphenoloba* - 13E,16E-*dien*-4-*one* (**2**). Gum. HR-MS: *m/z* 304.2401 $[M]^+$ calcd for $C_{20}H_{32}O_2$: 304.2402. EI-MS *m/z* (rel. int.): 304 $[M]^+$ (43), 286 (9), 233 (38), 205 (19), 177 (18), 161 (25), 149 (24), 133 (29), 125 (50), 107 (100), 93 (67), 81 (64); UV $\lambda_{max}^{Et_2O}$ nm: 240. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); 1690 (C = O); ^1H NMR: δ_H 6.44 (*dd*, *J* = 15.3, 10.8 Hz, H-16), 5.81 (*br d*, *J* = 10.8 Hz, H-15), 5.72 (*d*, *J* = 15.3 Hz, H-17), 2.53 (*s*, 2H-5), 2.42 (*dqd*, *J* = 11.0, 7.0, 3.2 Hz, H-3), 2.32 (*dd*, *J* = 10.8, 6.0 Hz, H-9), 1.70 (*d*, *J* = 1.3 Hz, 3H-14), 1.34 (*s*, 3H-19/3H-20), 1.20-2.00 (*m*, 9H), 1.07 (*d*, *J* = 7.0 Hz, 3H-11), 0.90 (*s*, 3H-12); ^{13}C NMR: Table 3.

(3R*,6R*,9R*,10S*)-*Sphenoloba*-13E,17-*dien*-4-*one* (**3**). Oil. GC-MS *m/z* (rel. int.): 288 $[M]^+$ (27), 109 (100), 95 (35), 82 (26), 67 (30), 55 (35), 41 (44); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695 (C = O); ^1H NMR: δ_H 5.09 (*m*, H-15/H-17), 2.68 (*m*, 2H-16), 2.52 (*s*, 2H-5), 2.42 (*m*, H-3), 2.25 (*m*, H-9), 1.68 (*d*, *J* = 1.1 Hz, 3H-14), 1.61 (*br s*, 3H-19/20), 1.54 (*d*, *J* = 1.0 Hz, 3H-19/20), 1.00-1.90 (*m*, 9H), 1.07 (*d*, *J* = 7.0 Hz, 3H-11), 0.88 (*s*, 3H-12); ^{13}C NMR: Table 3.

(6R*,9R*,10S*) - 3α,4α - *Epoxysphenoloba* - 13(14),16E-*dien*-15,18-*diol* (**4**). Gum. ^1H NMR: δ_H 5.93 (*dd*, *J* = 15.7, 0.8 Hz, H-17); 5.63 (*dd*, *J* = 15.7, 7.4 Hz, H-16), 5.15, 5.03 (both *br s*, 2H-14), 4.73

Table 3. ^{13}C NMR data for compounds **2–4**

C	**2**	**3**	**4***
1	26.6 *t*	26.5 *t*[a]	23.0
2	33.9 *t*	34.0 *t*	36.0
3	47.5 *d*	47.6 *d*	60.3
4	215.5 *s*	215.7 *s*	61.0
5	55.9 *t*	56.0 *t*	41.3
6	41.0 *s*	40.8 *s*	43.9
7	41.7 *t*	41.6 *t*	39.5
8	26.6 *t*	26.4 *t*[a]	29.2
9	53.1 *d*	52.8 *d*	45.9
10	54.9 *d*	54.6 *d*	58.5
11	18.8 *q*	18.9 *q*	23.4
12	19.7 *q*	19.7 *q*	17.8
13	139.9 *s*	135.8 *s*[b]	149.8
14	13.1 *q*	12.4 *q*	112.1
15	125.2 *d*	124.8 *d*[c]	87.8
16	122.9 *d*	27.1 *t*	143.3
17	139.3 *d*	123.3 *d*[c]	123.7
18	70.9 *s*	131.5 *s*[b]	70.7
19	29.9 *q*[a]	25.7 *q*	29.7
20	29.8 *q*[a]	17.7 *q*	29.7

*^{13}C NMR was composite-pulse-decoupled (CPD) only. Assignments were helped by comparison with **1** (Table 1) and with published data [1,2].

[a,b,c]Assignments may be interchangeable in each vertical column.

(*br d*, $J = 7.4$ Hz, H-15), 2.75 (*br t*, $J = 7.0$ Hz, H-4), 2.28 (*dd*, $J = 13.8$, 7.0 Hz, H-5β), 2.03 (*br dd*, $J = 13.8$, 7.0 Hz, H-5α), 1.32 (*s*, 3H-19/3H-20); 1.31 (*s*, 3H-11), 0.90 (*s*, 3H-12); ^{13}C NMR: Table 3.

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REFERENCES

1. Beyer, J., Becker, H., Toyota, M. and Asakawa, Y. (1987) *Phytochemistry* **26**, 1085.
2. Zapp, J., Burkhardt, G. and Becker, H. (1994) *Phytochemistry* **37**, 787.
3. Zhou, B. N., Ying, B. P., Song, G. Q., Chen, Z. X., Han, J. and Yan, Y. F. (1983) *Planta Med.* **47**, 35.
4. Kashman, Y., Hirsch, S., Koehn, F. and Cross, S. (1987) *Tetrahedron Letters* **28**, 5461.
5. Urones, J. G., Marcos, I. S., Garrido, N. M., Teresa, J. De P. and Martin, A. S. F. (1989) *Phytochemistry* **28**, 183.
6. Urones, J. G., Marcos, I. S. and Garrido, N. M. (1990) *Phytochemistry* **29**, 3243.
7. Andersen, N. H., Ohta, Y., Moore, A. and Tseng, C.-L. W. (1978) *Tetrahedron* **34**, 41.
8. Harrison, L. J. (1983) Ph.D. Thesis, p. 141, University of Glasgow.
9. Ohta, Y., Anderson, N. H. and Liu, C. -B. (1977) *Tetrahedron* **33**, 617.
10. Bhandari, P. and Rastogi, R. P. (1983) *Indian J. Chem.* **22B**, 286.
11. Benešová, V., Sedmera, P., Herout, V. and Sorm, F. (1973) *Coll. Czech. Chem. Commun.* **38**, 1084.
12. Matsuo, A. and Takaoka, D. (1990) in *Bryophytes: Their Chemistry and Chemical Taxonomy* (Zinsmeister H. D. and Mues, R., eds), pp. 59–69. Oxford University Press, Oxford.
13. Asakawa, Y., Toyota, M. and Takemoto, T. (1980) *Phytochemistry* **19**, 2141.
14. Rycroft, D. S. (1991) in *Studies in Natural Products Chemistry*, Vol. *9*, Part B (Atta-ur-Rahman, ed.), p. 93. Elsevier, Amsterdam.
15. Ngadjui, B. T., Ayafor, J. F., Sondengam, B. L., Connolly, J. D. and Rycroft, D. S. (1991) *Tetrahedron* **47**, 3555.
16. Tchouankeu, J. C., Tsamo, E., Sondengam, B. L., Connolly, J. D. and Rycroft, D. S. (1990) *Tetrahedron Letters* **31**, 4505.
17. Buchanan, M. S. (1994) Ph.D. Thesis, University of Glasgow.
18. Buchanan, M. S., Connolly, J. D. and Rycroft, D. S. (1996) *Phytochemistry* **43**, 1245.
19. Seo, S., Uomori, A., Yoshimura, Y., Takeda, K., Seto, H., Ebizuka, Y., Noguchi, H. and Sankawa, U. (1988) *J. Chem. Soc., Perkin Trans. 1*, 2407.