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Constituents of the Annonaceae species *Miliusa velutina* and *Desmos longiflorus*†

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Extraction of the stem bark of *Miliusa velutina* afforded miliusolide (1), an enediyne-γ-lactone derivative, and its dihydro-derivative (4), together with two other fatty acid-derived lactones. The stem bark of *Desmos longiflorus* yielded a triterpenoid, 15α-hydroxy-24-methylene-7,9(11)-lanostadien-3-one (7), three modified flavonoid derivatives, desmoflorin (8), 4-*O*-acetyldesmoflorin (9) and 4-*O*-epidesmoflorin (10), and an alkaloid, 3-hydroxy-2-methoxy-9,19-methylenedioxytetrahydro-protoberberine (11) (tetrahydrogroenlandicine).

The Annonaceae family is well known for its interesting biologically active secondary metabolites (e.g. alkaloids, acetogenins, terpenoids, aromatics) and has attracted the interest of chemists for many years. This paper reviews the largely unpublished results of our investigations of two species of the Annonaceae, *Miliusa velutine* and *Desmos longiflorus* collected in Bangladesh.

The ether extract of the bark of *M. velutina* afforded a complex oily mixture which was fractionated by flash chromatography. Eventually preparative tlc yielded one of the major components, miliusolide (**1**), in a pure state. The CI mass spectrum gave a peak at *m/z* 374 (M^++NH_4) consistent with a molecular formula $C_{23}H_{32}O_3$. Its IR spectrum showed characteristic absorptions for a γ-lactone (ν_{max} 1764 cm^{-1}), free and bonded hydroxyl (ν_{max} 3606 and 3446 cm^{-1}), a disubstituted acetylenic stretch (ν_{max} 2232 cm^{-1}) and olefinic CH stretches (ν_{max} 3026 and 3010 cm^{-1}). The UV spectrum revealed the presence of an enediyne chromophore (λ_{max} 283 (ε 3228), 267 (ε 3980), 253 (ε 3060) and 239 (ε 3048) nm. Its ^1H NMR spectrum showed a vinyl group at δ_H 5.79 (ddt, *J* 17.0, 10.3, 6.8 Hz), 4.98 (brd, *J* 8.7 Hz) and 5.02 (brd, *J* 17.2 Hz) and a *cis* disubstituted double bond at δ_H 6.01 (dt, *J* 10.8, 7.4 Hz) and 5.48 (brd, *J* 10.8 Hz) [a small amount of the corresponding *trans* isomer was also observed]. An oxygenated methine associated with the γ-lactone and primary hydroxyl protons appeared at δ_H 4.58 (m) and δ_H 3.84 and 3.64 (both brd, *J* 12.3 Hz) respectively. Acetylation afforded the monoacetate **2** which was used for the structural elucidation. Examination of COSY, HMQC and HMBC spectra led to the assignment of structure (**2**) to the acetylated derivative.

In the COSY spectrum the primary acetate protons 2H-23 [δ_H 4.29 (dd, *J* 12.1, 3.4 Hz) and 4.15 (dd, *J* 12.1, 5.4 Hz)] showed correlations to the oxygenated methine H-22 [δ_H 4.75 (ddt, *J* 8.4, 4.8, 4.9 Hz)]. The methine was also coupled to a methylene group 2H-21 [δ_H 2.25, 2.10 (both m)] which in turn was coupled to a methine H-2 [δ_H 2.68 (dq, *J* 5.3, 9.0 Hz)]. The COSY spectrum also indicated that this methine had another methylene neighbour 2H-3 [δ_H 1.88, 1.50 (both m)] which was probably part of a methylene chain. Evidence from the HMBC spectrum confirmed that the above coupled system formed a γ-lactone ring as in part structure **A**. Thus the lactone carbonyl carbon had $^3J_{CH}$ correlations from H-22, 2H-21 and 2H-3 and a $^2J_{CH}$ correlation from H-2 while the acetate carbonyl carbon correlated with 2H-23 and the acetate methyl. Protonated carbons were assigned using the HMQC spectrum (see Table 1).

Table 1. ^{13}C and ^1H NMR shifts of miliusolide acetate (**2**)

	^{13}C	^1H		^{13}C	^1H
1	178.8		14	65.1	
2	39.0	2.68 (dq, *J* 5.3, 9.0 Hz)	15	108.6	5.50 (brd, *J* 10.8 Hz)
3	31.0	1.88, *ca.* 1.5	16	146.6	6.10 (dt, *J* 10.8, 7.4 Hz)
4	29.2	*ca.* 1.3	17	29.8	2.49 (brq, *J* 7.4 Hz)
5	29.2		18	32.8	2.20 (*J* 7.4 Hz)
6	28.9	*ca.* 1.4	19	137.6	5.85 (ddt, *J* 17.0, 10.3, 6.5 Hz)
7	27.7		20	115.1	5.08 (brd, *J* 17.0 Hz), 5.01 (brd, *J* 10.3 Hz)
8	27.2		21	30.0	2.25 and 2.1 (m)
9	28.1	1.56 (q, *J* 7.7 Hz)	22	77.2	4.75 (ddt, *J* 8.4, 4.8, 4.9 Hz)
10	19.5	2.35 (t, *J* 7.0 Hz)	23	65.5	4.29 (dd, *J* 12.1, 3.4 Hz), 4.15 (dd, *J* 12.1, 5.4 Hz)
11	85.0		24	170.5	
12	71.9		25	20.7	2.12 (s, CH_3CO)
13	78.4				

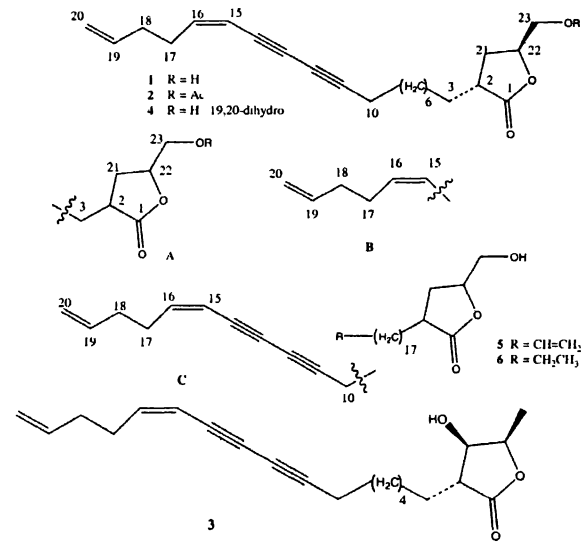
Dedicated to Professor S. M. Mukherji.

The COSY spectrum also revealed a second part structure **B** (for shifts see Table 1). Thus the terminal vinyl group protons were coupled to a methylene group 2H-18 which was also coupled to an allylic methylene group 2H-17, associated with the *cis* disubstituted double bond H-16 and H-15. H-15 showed no further vicinal coupling. Part structure **B** was supported by the HMBC spectrum. 2H-18 correlated with C-19, C-20, C-16 and C-17 while 2H-17 correlated with C-18, C-19, C-15 and C-16.

The acetylenes must be conjugated with the *cis* double bond in view of the UV absorption. The acetylenic carbons appeared at δ_C 78.4 (C-13), 65.1 (C-14), 85.0 (C-11) and 71.9 (C-12). In the HMBC spectrum H-15 showed correlations to all the acetylenic carbons while H-16 correlated with C-13 and C-14. The correlation of H-15 with C-11 represents a $^5J_{CH}$. The other end of the conjugated system was readily revealed by inspection of the COSY and HMBC spectra. H-15 showed a long-range correlation ($^7J_{HH}$) with a methylene group 2H-10 at δ_H 2.35 which is clearly coupled to a second methylene 2H-9 at δ_H 1.56. These methylenes showed some remarkable long-range correlations in the HMBC spectrum with 2H-10 correlating to all the carbons of the conjugated system. Thus part structure **B** can be extended to **C**. The two part structures **A** and **C** incorporate all the functionality of the natural product leaving five overlapping methylene group to be incorporated. Since both 2H-9 and 2H-3 couple with the methylene envelope the two part structures can be joined as shown, leading to structure (**2**) for the acetate and (**1**) for the natural product.

The relative stereochemistry as in **1** was established by NOE difference experiments. Irradiation of H-22 afforded NOEs at H-21α and the primary hydroxyl protons. In the reverse experiment irradiation of H-21α gave NOEs at H-22 and H-21β. Finally, irradiation of H-2 gave a NOE at H-21β. Compound **1**, to which we give the trivial name miliusolide, is clearly a fatty acid derivative. Such enediynes are relatively common. The compound which bears the closest relationship to miliusolide is sapanthrin (**3**) from *Sapranthus palanga* (Annonaceae)[1].

Repeated preparative tlc of UV active fractions afforded a second compound (**4**), $C_{23}H_{34}O_3$ [M$^+$ 358] whose spectroscopic properties were very similar to those of miliusolide. In particular, it had the same enediyne UV absorption spectrum. It also showed signals in its ^{1}H NMR spectrum for a *cis* disubstituted double bond [δ_H 6.02 (dt, *J* 10.8, 7.5 Hz), 5.45 (brd, *J* 10.8 Hz)] an oxygenated methine [δ_H 4.59 (m)], and a primary hydroxyl group [δ_H 3.85 (brd, *J* 12.4 Hz) and 3.64 (brd, *J* 12.2 Hz)]. The most striking difference from **1** was the absence of the terminal vinyl group. Thus **4** is 19,20-dihydromiliusolide.



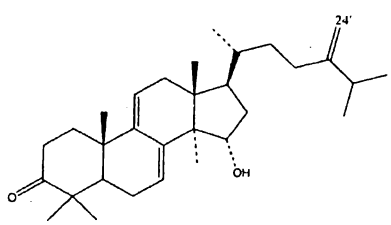
Preparative tlc of the crude extract afforded a mixture of two closely related, non UV active compounds. Both compounds contained a hydroxymethyl-substituted γ-lactone and a long polymethylene chain. One of the compounds contained a terminal vinyl group while the other was saturated. The CI mass spectrum of the mixture revealed parent ion peaks at *m/z* 380 and 382, consistent with the molecular formulae $C_{24}H_{44}O_3$ and $C_{24}H_{46}O_3$ and structures (**5**) and (**6**) for these compounds. These compounds contain an extra methylene group relative to **1** and **4**.

Column chromatography of the ethyl acetate extract of the stem bark of *D. longiflorus* afforded five known compounds which were identified as sitostenone, 4-stigmastene-3,6-dione, benzyl benzoate, crotepoxide[2] and *N*-benzoyl-*O*-(*N'*-benzoyl-L-phenylalanyl)-L-phenylalaninol[3]. 15α-Hydroxy-24-methylene-7,9(11)-lanostadien-3-one (**7**)[4] and three new modified flavonoid derivatives, desmoflorin (**8**), desmoflorin acetate (**9**) and 4-epidesmoflorin(**10**), were also isolated.

The triterpenoid (**7**), $C_{31}H_{48}O_2$ (M$^+$ 452), was obtained[4] as colourless needles, m.p. 156–158°, $[\alpha]_D$+42.6 (*c*, 2.00 in $CHCl_3$). It showed hydroxyl (ν_{max} 3400 cm^{-1}) and ketonic (ν_{max} 1715 cm^{-1}) absorption in the IR and conjugated heteroannular diene (λ_{max} 252, 243, 236 nm) absorption in the UV. Its ^{1}H NMR spectrum revealed the presence of three secondary methyls [δ_H 0.88 (d, *J* 6.4 Hz, Me-21), 1.00, 1.03 (both d, *J* 6.8 Hz, Me-26, Me-27), five tertiary methyl groups [δ_H 0.62, 0.91, 1.08, 1.11, 1.18 (Me-18, -30, -29, -28, -19)], two olefinic protons [δ_H 5.37 (d, *J* 6.0 Hz, H-11), 5.88 (d, *J* 5.0 Hz, H-7)], an exomethylene group [δ_H 4.64, 4.71 (both brs, 2H-24)], an oxygen-bearing methine [δ_H

4.27 (dd, *J* 9.8, 5.8 Hz, H-15β)] and a deshielded proton [δ_H 2.75 (ddd, *J* 14.8, 14.5, 6.0 Hz)] suggestive of H-2β in a 3-oxo triterpenoid. These data suggested a 24-methylene-7,9(11)-lanostadien-3-one derivative with an additional secondary hydroxyl group.

The ^{13}C NMR spectrum contained signals for 31 carbons including a ketone [δ_C 216.7 (C-3)], two trisubstituted double bonds [δ_C 121.6 (C-7), 141.0 (C-8), 144.7 (C-9), 117.0 (C-11)], an exomethylene [δ_C 156.5 (C-24), 106.1 (C-24')], a secondary alcohol [δ_C 74.6 (C-15)], eight methyl groups [δ_C 15.1 (C-18), 22.1 (C-19), 18.4 (C-21), 21.8 (C-26), 22.0 (C-27), 25.4 (C-28), 22.4 (C-29), 17.0 (C-30)], and seven methylenes, four methines and four quaternary carbons. Comparison with proton and carbon shifts of 15α, 26,27-trihydroxy-7,9(11),24-lanostatrien-3-one (ganoderiol B)[28] and 24-methylene-7,9(11)-lanostadien-3β-ol[29] confirmed the structure of the triterpenoid as 15α-hydroxy-24-methylene-7,9(11),24-lanostatrien-3-one (**7**). The coupling constants of H-15 (*J* 9.8, 5.6 Hz) were consistent with its β configuration. This was further confirmed by irradiation of H-15 which gave a substantial NOE at Me-18. The corresponding 3β-hydroxy derivative, suberosol, has been reported from *Polyalthia suberosa* (Annonaceae)[5].



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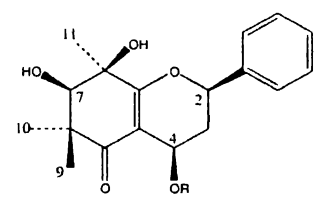
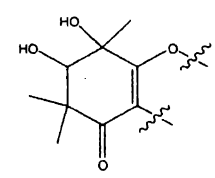
Desmoflorin (**8**), $C_{18}H_{22}O_5$ [M^+ 318.1425], $[\alpha]_D$ + 10.7 (*c*, 0.29 in $CHCl_3$) was obtained as a gum. Its IR spectrum showed hydroxyl [ν_{max} 3625, 3450 cm^{-1}], unsaturated carbonyl [ν_{max} 1649 cm^{-1}] and aromatic absorptions. The presence of an enone system was deduced from a UV band at λ_{max} 250 nm (log ε 3.45). Its ^1H NMR spectrum showed a phenyl substituent [δ_H 7.30 (m)], three tertiary methyls [δ_H 1.17, 1.33, 1.53], three oxygenated methines [δ_H 5.10 (dd, *J* 12.3, 2.2 Hz, H-2), 4.92 (dd, *J* 10.1, 6.5 Hz, H-4), 3.92 (s, H-7)], a methylene group [δ_H 2.45 (ddd, *J* 13.7, 6.5, 2.2 Hz, H-3$_{eq}$), 2.15 (ddd, *J* 13.7, 12.3, 10.1 Hz, H-3$_{ax}$)] and three hydroxyl groups [δ_H 4.65, 5.70, 2.75 (all s)]. The only obvious spin system involved the two oxygenated methines and the methylene group.

The ^{13}C NMR spectrum showed a ketonic carbonyl [δ_C 203.4], a tetrasubstituted enolic double bond [δ_C 111.0, 170.7], four oxygenated carbons [δ_C 79.5 (CH), 77.6 (CH), 73.0 (C), 62.6 (CH)], three methyl groups [δ_C 24.5, 22.0, 9.6], a methylene [δ_C 36.8], a quaternary carbon [δ_C 46.2] and the carbons of a phenyl ring. The phenyl group, ketonic carbonyl and double bond account for six of the eight double bond equivalents and hence there must be two additional rings in the molecule. In view of the lack of proton connectivity the structure was largely derived from the HMBC spectrum. The correlations of the tertiary methyls were particularly helpful. The mutual correlations of the methyls at δ_H 1.17 and 1.33 with the quaternary carbon at δ_C 46.2 showed they were a geminal pair. Both methyls showed $^3J_{CH}$ correlations to the unsaturated carbonyl group and to the oxygenated methine carbon at δ_C 79.5 (associated with the proton singlet at δ_H 3.92). The remaining methyl at δ_H 1.53 correlated with the hydroxyl-bearing carbon at δ_C 73.0 and had $^3J_{CH}$ correlations to the secondary oxygenated carbon (δ_C 79.5) and to the strongly deshielded enolic carbon (δ_C 170.0) of the unsaturated ketone system. These data led to part structure **D** which was also supported by correlations of the carbinol proton (δ_H 3.92) to all three methyl carbons and to the two quaternary carbons at δ_C 73.0 and 46.2.



8 R=H

9 R=Ac



D

Part structure **D** could be extended in the following way. The allylic carbinol proton at δ_C 4.92 correlated to both carbons of the conjugated double bond. This proton, part of the four spin system observed in the proton spectrum, also showed a correlation to its vicinal methylene carbon. The lower field methylene proton at δ_H 2.45 correlated strongly with the vinyl carbon at δ_C 111.4 and to the remaining oxygenated methine at δ_C 62.6. The attachment of the phenyl group to this oxygenated methine was revealed by correlations of its attached proton (δ_H 5.06) to the aromatic carbons at δ_C 126.4 (2) and 138.4. Formation of the pyran ring completed the structure (**8**) of desmoflorin which is clearly a methylated flavonoid derivative. The expected correlation from H-2 to C-8a across the pyran oxygen, absent in this case, was observed in a closely related compound (see below). The relative stereochemistry of **8** was deduced from NOE difference experiments. The methyls at δ_H 1.17 and

1.53 showed strong mutual NOEs and are therefore diaxial. Small NOEs from all the methyls to H-7 indicated that it was equatorial. A small NOE from the methyl group at δ_H 1.53 to H-2 showed they lie on the same face of the molecule. Coupling constants revealed that H-2 and H-4 were both axial in a half chair conformation of the pyran ring. In agreement with this proposal, irradiation of H-4 gave a NOE at H-3_{eq} and not H-3_{ax}.

The acetate (**9**), $C_{20}H_{24}O_6$ [*m/z* 246 ($M^+ - H_2O$)], $[\alpha]_D$ + 5.0 (*c*, 0.65 in $CHCl_3$) was also a gum. It was clearly closely realted to desmoflorin and had similar UV [λ_{max} 253 nm (log ε 4.10)] and IR [ν_{max} 3620, 3547, 1736, 1649, 1603 cm^{-1}], spectra apart from the presence of an ester (acetate) carbonyl band. The ^1H NMR spectrum showed peaks for a phenyl group, three tertiary methyls [δ_H 1.12, 1.29, 1.55], another methyl at δ_H 1.61 which proved to be a shielded acetate, two oxygen-bearing methines [δ_H 5.80 (t, *J* 5.7 Hz, H-4), 5.40 (t, *J* 5.4 Hz, H-2)] which both couple to a methylene group [δ_H 2.40 (2Ht, *J* 5.7 Hz, 2H-3)] whose protons are accidentally equivalent, a secondary carbinol [δ_H 3.98 (s, H-7)] and two hydroxyl protons [δ_H 2.70, 2.85]. Thus **9** appeared to be desmoflorin acetate.

The ^{13}C NMR spectrum confirmed the presence of the unsaturated ketone [δ_C 198.6 (C-5), 171.3 (C-8a), 108.2 (C-4a)] the phenyl ring, the oxygenated methines [δ_C 60.9 (C-4), 77.2 (C-7), 77.9 (C-2)], the oxygenated quaternary carbon C-8 [δ_C 73.2], the quaternary carbon C-6 [δ_C 45.8], the C-2 methylene [δ_C 33.4], an acetate [δ_C 20.6, 170.7] and three tertiary methyls [δ_C 19.6 (C-10), 20.6 (C-11), 25.1 (C-9)]. The protonated carbons were assigned using the HMQC spectrum. Structure (**19**) was deduced, as for desmoflorin, using the HMBC spectrum. The correlations of the methyl groups and H-7 revealed the same ring A structure as in **8**. The benzylic H-2 correlated with the phenyl ring as expected but, in addition, showed a correlation across oxygen to C-8a, thus establishing the pyran ring. A correlation for H-4 to the acetate carbonyl showed that the acetate was attached to C-4.

Two points about desmoflorin acetate require comment. These concern the shielded nature of the acetate methyl and the accidental equivalence of the C-3 methylene protons. The phenyl ring will shield the acetate methyl if both are axial. However irradiation of H-2 afforded a NOE at H-4 and *vice versa*, suggesting that these protons are axial. Both of these situations can be accommodated if the pyran ring is undergoing rapid conformational inversion. This would also explain the apparent equivalence of the C-3 diastereotopic methylene protons.

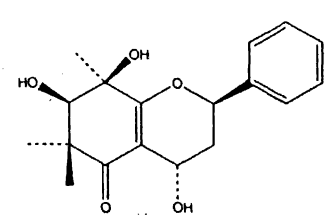
4-Epidesmoflorin (**10**), $C_{18}H_{22}O_5$ [M^+ 318] was isomeric with desmoflorin (**8**) and the two had virtually identical IR and UV spectra and very similar ^1H and ^{13}C NMR spectra (see Tables 2 and 3). The main difference in the ^1H NMR spectrum concerned the protons of the pyran ring [δ_H 4.65 (dd, *J* 4.0, 2.0 Hz, H-4), 5.13 (dd, *J* 12.2, 2.5 Hz, H-2), 2.17 (dt, *J* 14.7, 2.3 Hz, H-3_{eq}), 1.93 (ddd, *J* 14.7, 12.2, 4.0 Hz, H-3_{ax})]. The couplings of H-4 (*J* 4.0, 2.0 Hz) sug-

Table 2

	8	9	10
Ph	7.40 (m)	7.32 (m)	7.40 (m)
H-2	5.10 (dd, *J* 12.3, 2.2 Hz)	5.40 (t, *J* 5.7 Hz)	5.13 (dd, *J* 12.2, 2.5 Hz)
H-3_{ax}	2.15 (ddd, *J* 13.7, 12.3, 10.1 Hz)	2.40 (t, *J* 5.7 Hz)	1.93 (ddd, *J* 14.7, 12.2, 4.0 Hz)
H-3_{eq}	2.45 (ddd, *J* 13.7, 6.5 Hz)	2.40 (t, *J* 5.7 Hz)	2.17 (dt, *J* 14.7, 2.3 Hz)
H-4	4.92 (dd, *J* 10.1, 6.5 Hz)	5.80 (t, *J* 5.7 Hz)	4.65 (dd, *J* 4.0, 2.0 Hz)
H-7	3.92 (s)	3.98 (s)	3.82 (s)
Me-9	1.33	1.29	1.31
Me-10	1.17	1.12	1.15
Me-11	1.53	1.55	1.53
OH/Ac	5.70, 4.65/2.75	2.70, 2.85/ 1.61 Ac	2.45, 2.56, 3.10

Table 3

Carbons	8	9	10
2	79.5	77.9	76.5
3	36.8	33.4	36.4
4	62.6	60.9	58.6
4a	111.4	108.2	111.3
5	203.4	198.6	202.1
6	46.2	45.8	45.9
7	77.6	77.2	78.0
8	73.0	73.2	73.2
8a	170.7	171.3	170.3
9	24.5	25.1	24.5
10	19.6	19.6	19.5
11	22.0	20.6	22.2
1′	138.4	138.9	139.0
2′/6	126.4	125.2	126.4
3′/5′	128.9	128.6	128.8
4′	129.0	128.0	128.7
*Me*CO	–	20.6	–
Me*CO*	–	170.7	–



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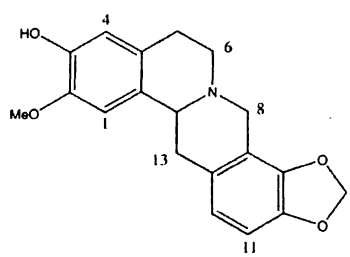
gested that it was equatorial and this was confirmed by NOEs to both H-3_{eq} and H-3_{ax}. Irradiation of H-2 (axial) gave a NOE to H-3_{eq} as expected. Thus **10** is 4-epidesmoflorin.

Flash chromatography of the methanol extract of the stem bark followed by preparative tlc afforded several known alkaloids. These included oxocrebanine[6], buxifoline[7], oxobuxifoline[8], norstephalagine[9], and atherospermidine[10]. The ^{1}H NMR spectrum of tetrahydroprotoberberine alkaloid (**11**), $C_{19}H_{19}NO_4$ [M^+ 325], $[\alpha]_D$ + 34 (*c*, 0.032 in $CHCl_3$) revealed four overlapping aromatic protons, a methylenedioxy group [δ_H 5.91, 5.96, ABq, *J* 1.4 Hz], a methoxyl [δ_H 3.88], four methylene groups [δ_H 4.10, 3.52 (ABq, *J* 15.3 Hz, 2H-8), 3.26 (dd, *J* 16.0, 4.0 Hz, H-13), 2.81 (dd, *J* 16.0, 11.0, Hz, H-13), 2.61 and 3.08 (both m, 2H-5 and 2H-6)] and a methine [δ_H 3.58 (dd, *J* 11.0, 4.0 Hz, H-14. Thus the compound was a tetrahydroprotoberberine with methylenedioxy, methoxy and hydroxy substituents. The problem of the overlapping aromatic protons was resolved by running the ^{1}H NMR spectrum in deuteriobenzene when two aromatic singlets [δ_H 6.44 (H-1), 6.79 (H-4)] and an *ortho*-coupled system [δ_H 6.66, 6.53



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(both d, *J* 8.0 Hz, H-11 and H-12)] were observed. NOE difference experiments then permitted the placement of the substituents. Irradiation of the methoxyl protons afforded a NOE at H-1 while irradiation of the latter gave NOEs at the methoxyl, H-14 and 2H-13. Irradiation of H-4 resulted in a NOE at H-5. These results confirmed the attachment of the methoxyl group to C-2 and the phenolic hydroxyl to C-3. Irradiation of H-12 gave NOEs at 2H-13 and H-11 and hence the methylenedioxy group was attached to C-9 and C-10. Thus the structure of the alkaloid was established as 3-hydroxy-2-methoxy-9,19-methylenedioxytetrahydroprotoberbe rine (**11**) which is tetrahydrogroenlandicine[11]. Comparison of ^{13}C NMR data with the known alkaloids descretanine[12] and stylophine[13] provided further confirmation.

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