Unusual indole alkaloids from *Ophiorrhiza blumeana* Korth

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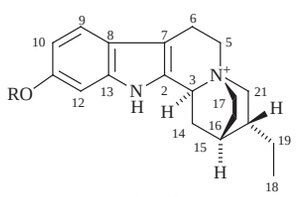
The alkaloid content of two different collections of *Ophiorrhiza blumeana* Korth. (Rubiaceae) was investigated. The first collection yielded the known alkaloid bracteatine 5 and two new alkaloids ophiorrhizine-12-carboxylate 6 and blumeanine 7. The second collection yielded the known alkaloid ophiorrhizine 1 as well as the two new alkaloids. The structures of 6 and blumeanine diacetate 8 followed from their CD and NMR spectral data. The former proved to be an unusual betaine with a carboxylate substituent on the benzenoid part of the indole and the structure was confirmed by single crystal X-ray structural determination. Bracteatine proved to be a dimeric *Corynanthé* alkaloid linked at the 9,12′ positions and is chiral about the biaryl linkage.

The plant genus *Ophiorrhiza* (Rubiaceae) is a rich source of indole alkaloids[1–7] and we have previously examined a number of Sumatran species. We recently described the isolation and structural determination of ophiorrhizine **1**, a pentacyclic quaternary indole alkaloid from *O. major* Ridl.[6] The relative stereochemistry followed from its spectroscopic properties and X-ray molecular structure, and arguments were advanced for the absolute stereochemistry which was finally verified by synthesis.[8] This alkaloid since it is structurally similar to cinchonamine **3** provides a biogenetic link between the *Cinchona* alkaloids and the *Corynanthé* alkaloids. A further link is the alkaloid **4**, which is oxygenated at the 9-position and contains an ethylidene group at the 20-position rather than an ethyl group. This alkaloid was isolated from a calabash curare preparation of unknown plant source.[9] *O. bracteata* Bl. yielded ophiorrhizine **1** and a similar alkaloid, bracteatine **5**, in which the hydroxy group is at the 12-position and is glucosylated.

We have now examined two different collections of another species namely *O. blumeana* Korth. The extract of the first collection besides bracteatine **5** contained a new zwitterionic alkaloid (betaine), ophiorrhizine-12-carboxylate **6** and a dimeric alkaloid **7**, for which we propose the trivial name blumeanine, isolated as its diacetate **8**. The extract of the second collection afforded ophiorrhizine **1**, the betaine **6** and the dimer **7**. We now describe the structural determination of these unusual alkaloids.

The crystalline betaine in its FABMS exhibited an $M + H^+$ ion at *m*/*z* 341 which was accompanied by smaller $M + Na^+$ and $M + K^+$ ions at *m*/*z* 363 and 379. There was also an ion at *m*/*z* 279 which was attributed to the loss of CO_2 from the $M + H^+$ ion. The ^{13}C NMR spectrum contained signals for 20 carbon atoms, 11 of which corresponded closely in chemical shift to the non-indolic part of ophiorrhizine **1**. The DEPT technique indicated that there were 1 methyl, 7 methylene, 5 methine and 7 quaternary carbons. Of the quaternary carbons one (δ_C 160.11) must be attached to a phenolic hydroxy group and another (δ_C 176.15) was assigned to the carbonyl group of an aromatic carboxylate. This latter assignment was supported by a band at 1625 cm^{-1} in the infrared spectrum. These data allowed the molecular formula $C_{20}H_{24}N_2O_3$ to be advanced which was confirmed by elemental analysis.

Further examination of the ^1H and ^{13}C NMR spectra of the alkaloid, which were interpreted by the assistance of the HMQC and DQF-COSY techniques enabled the substitution pattern of the homocycle of the indole to be determined. The



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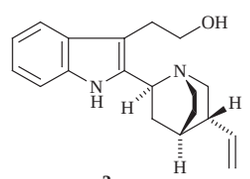
2 R = Ac



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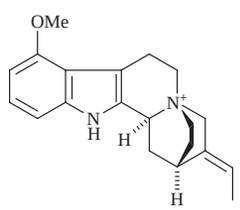

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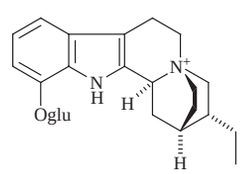

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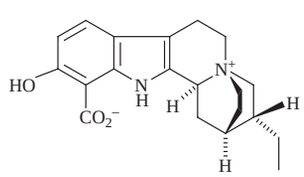

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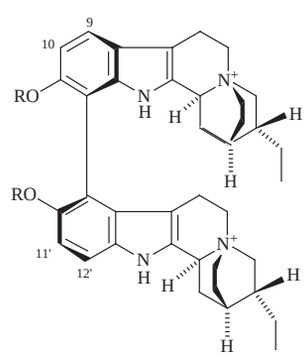


7 R = H
8 R = Ac

^1H NMR spectrum revealed the presence of two aromatic protons (δ_H 6.58 and 7.28) which were in an *ortho* relationship. From the magnitude of the coupling constant (8.5 Hz) they must be at the 9,10 or 11,12 positions rather than the 10,11 positions of the indole.[10] Of the four possible arrangements of the carboxylate and hydroxy substituents, given this restraint, that shown in structure **6** is favoured on the grounds of the congruence of the observed carbon chemical shifts for C-9, C-10, C-11 and C-12 (δ_C 123.37, 111.10, 160.11 and 103.98) with those calculated (δ_C 124.3, 113.3, 159.6 and 107.0) by applying the carboxylate substituent shifts[11] to the chemical shifts for ophiorrhizine **1**.[6] The absolute stereochemistry is

Table 1 Non-aromatic ring torsion angle (degrees). Atoms are denoted by number, the number of the nitrogen atom is italicized

Atoms	Angle	Atoms	Angle
Ring C		Ring D	
7–2–3–*4*	15(1)	14–3–*4*–17	−46.2(9)
2–3–*4*–5	−45.9(8)	3–*4*–17–16	63(1)
3–*4*–5–6	65(1)	*4*–17–16–15	−10(1)
4–5–6–7	−46(1)	17–16–15–14	−53(1)
5–6–7–2	14(1)	16–15–14–3	69(1)
6–7–2–3	1(1)	15–14–3–*4*	−16.7(9)
Ring E		Other	
21–*4*–17–16	−54(1)	2–3–*4*–17	79.6(8)
4–17–16–15	−10(1)	14–3–*4*–5	−171.6(7)
17–16–15–20	67(1)	2–3–*4*–21	−163.9(7)
16–15–20–21	−54(1)	14–3–*4*–21	70.3(8)
15–20–21–*4*	−11(1)	14–15–20–21	65(1)
20–21–*4*–17	65.8(9)	3–*4*–21–20	−54.0(9)
		5–*4*–17–16	−171.8(8)
		5–*4*–21–20	−174.0(8)
18–19–20–15	−63(1)	7–2–3–14	136.6(8)
17–*4*–5–6	−60(1)	18–19–20–21	172(1)
21–*4*–5–6	−176.4(8)	3–14–15–20	−49(1)
16–15–20–19	178.9(9)	14–15–20–19	−63(1)
2–3–14–15	−138.0(7)	19–20–21–*4*	118.3(9)

confirmed by the CD spectrum of the betaine which is similar to that of ophiorrhizine **1**.

As far as we are aware this is the first example of a monoterpenoid indole alkaloid with a carboxylate substituent present on the indole homocycle. The origin of the extra carbon atom is a matter for speculation. A possibility is the introduction of a methyl group from *S*-adenosylmethionine at some stage in the biosynthesis followed by its oxidation to a carboxylic acid. In view of this unusual structure we have confirmed it and the relative stereochemistry by X-ray molecular structure determination. The results of the room-temperature single crystal X-ray structure determination are consistent in terms of stoichiometry, connectivity and stereochemistry with the formulation of **6** [Fig. 1(a)] albeit as a dihydrate; incorporation of the water molecules into the lattice is associated with the development of a columnar array of hydrogen-bonding contacts parallel to *c* [Fig. 1(b), (c)], presumably arising from the polar constituents of the parent molecule, in particular the closely disposed phenolic and carboxylate moieties. Despite the limited precision of the study consequent primarily on small specimen size, all hydrogen atoms have been plausibly located and refined in $(x, y, z\ U_{iso})_H$. Within the molecule an intramolecular hydrogen bond is found between phenolic H(11) and the carboxylate [H(11)···O(11,121) 1.01(8), 1.51(8) Å, O(11)···O(121) 2.52(1) Å]; the C–O carboxylate distances are ostensibly equal [1.28(1), 1.26(1) Å], while phenolic C(11)–O(11) is as expected also, 1.37(1) Å. O(11)–C(11)–C(10,12) are essentially equal [118.1(8), 119.5(8)°] as are C(121)–C(12)–C(11,13) [123.1(7), 122.4(7)°], while within the ring C(11)–C(12)–C(13) is only 114.4(7)°, in keeping with the short C(12)–C(121) distance [1.44(1) Å]. A hydrogen bond is found between the water molecules: H(01a)···O(01,02) 1.05(7), 1.77(7) Å [O(01)···O(02), 2.73(1) Å], H(01b) bonding to one of the carboxylate oxygen atoms {H(01b)[O(01)]···O(121) $(1\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$ 2.2(1), [2.88(1)] Å}. From O(02), one hydrogen approaches O(121) at a short distance [H(02a)···O(02,121) being 1.31(9), 1.49(9) Å], the other hydrogen H(02b), having no other affiliations. The overall result is a 2_1 spiral of carboxylate and water moieties parallel to *a*. The interplanar carboxylate C_2O_2–phenyl C_6 dihedral angle is 6.0(3)°. In ring C, N(4)–C(5) lies oblique to C(2)–C(7), while the three rings subtended by N(4) and C(15) are all classical 'boats' (Table 1).

In order to obtain the dimeric alkaloid blumeanine in a pure state it was necessary to convert it into the diacetate. An examination of the ^{13}C NMR spectrum revealed the presence of

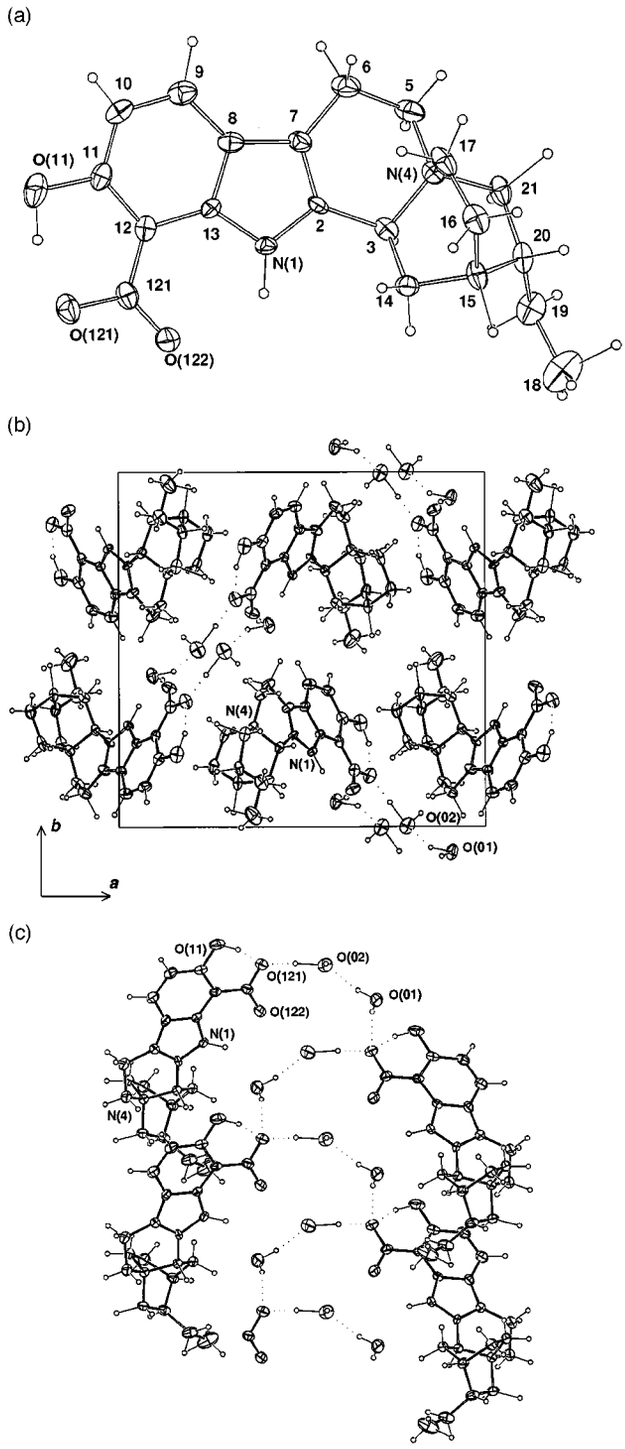
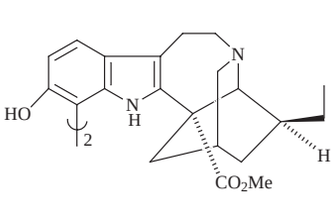


Fig. 1 (a) The molecule of **6** projected normal to the fused aromatic system plane. 20% Thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. (b) Unit cell contents projected down *c*, showing the hydrogen bonding, both intramolecular and intermolecular to the water molecules in the lattice. (c) The hydrogen-bonded column of molecules of **6** and associated water.

42 carbon atoms of which 22 corresponded closely in chemical shift to those of the non-indolic part of ophiorrhizine acetate **2**. The ^1H NMR spectrum and the DQF-COSY technique demonstrated the presence of two sets of *ortho*-coupled protons (δ_H 6.95 and 7.58, *J* 8.5 Hz; δ_H 7.08 and 7.51, *J* 8.7 Hz) which from the magnitude of the coupling constants must be in 9,10 or 11,12 positions rather than 10,11 positions on separate indole entities.[10] The FABMS showed an apparent molecular ion at *m*/*z* 675 and a prominent ion at *m*/*z* 633 ascribed to the loss of ketene. High resolution indicated the molecular formula

$C_{42}H_{51}N_4O_2$ for the peak at *m/z* 675 which probably arises by double loss of HCl by thermal Hofmann elimination[12] from the dication (M_r 676) to give an $M + H^+$ ion. The true molecular formula of the dication is therefore $C_{42}H_{52}N_4O_2$ which formally corresponds to a dimer of ophiorrhizine acetate. The dimer cannot be symmetrical on account of both the ^1H and ^{13}C NMR spectra.

Calculations for the ^{13}C NMR chemical shifts for the benzenoid carbons of a number of possible dimers were made. These were based on the values for ophiorrhizine acetate **2** and known oxygenated indole alkaloids[13] particularly compounds **9**[14] and **10**.[9] These calculations also took into account the results of DEPT and HMQC experiments on blumeanine diacetate. The values thus calculated are given followed by the observed values in parentheses: δ_C 112.6 (113.4, C-12′), 115.8 (116.1, C-10), 118.4 (118.9, C-11′), 118.9 (114.2, C-12), 119.5 (119.6, C-9), 124.3 (124.9, C-8), 124.8 (118.1, C-9′), 129.1 (126.2, C-8′), 136.4 (137.0, C-13′), 137.6 (138.5, C-13), 144.7 (144.0, C-10′) and 147.5 (146.7, C-11). The closest agreement with the observed values was given by structure **8** which is therefore proposed. It is assumed that the stereochemistry in the non-indolic part of the molecule is the same as that in ophiorrhizine.



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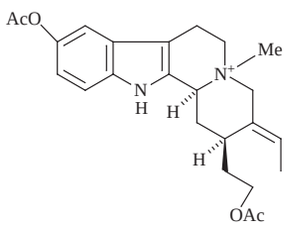

10

The CD spectrum of blumeanine diacetate suggests that it is one atropenantiomer. The electronic spectrum of blumeanine diacetate exhibits a strong band near 220 nm which may be attributed to a ^1L_a transition the direction of the moment of which is parallel to the long axis of the indole chromophore.[15] In the CD spectrum of blumeanine diacetate there is strong ($\Sigma\Delta\varepsilon \sim 53$) exciton splitting[16] centred at 231 nm with a negative first Cotton effect which indicates that the absolute configuration of the chiral axis is (*R*).

Experimental

General directions have been given before.[17] NMR spectra were determined in deuteriomethanol solution on a Bruker ARX-500 spectrometer. $\Delta\nu_{\frac{1}{2}}$ (full width at half height) and *J* values are given in Hz. CD spectra were determined on a JASCO J-710 instrument. $[\alpha]_D$ Values are given in units of 10^{-1} deg cm^2 g^{-1}.

Extraction of *O. blumeana* Korth

(a) Sample 1. The botanical material was collected at Mount Tandikat, near Padang Panjang, West Sumatra in 1994. A herbarium specimen (YA-7) was deposited in the Herbarium Bogoriense (BO) and the Herbarium Universitas Andalas (AND). Finely chopped aerial parts of the plant (12 kg) were allowed to stand with methanol (15 dm^3) for 5 days, the methanol decanted off and then the process was repeated. The combined extract was evaporated under reduced pressure and the concentrated solution (1 dm^3) was diluted with acetic acid (20 cm^3) and filtered. The filtrate was washed with ethyl acetate (3 × 300 cm^3), basified with ammonia, again washed with ethyl acetate (3 × 300 cm^3) and finally extracted with butanol (5 × 400 cm^3). The combined butanolic extracts were evaporated to dryness under reduced pressure which gave a brown gum (34.0 g). A portion of the gum (30.0 g) was preadsorbed on silica gel and chromatographed over a column of silica gel with 25–75% methanol–ethyl acetate as eluant. Fractions which gave a positive Dragendorff test were combined and chromatographed twice more over silica gel with 1% acetic acid in methanol–ethyl acetate (1 : 2) as eluant. Early fractions which gave a positive Dragendorff test and showed one spot on TLC were combined and the residue was crystallized from methanol–ethyl acetate to afford *ophiorrhizine*-12-*carboxylate* **6** as prisms (20 mg), mp 278–281 °C decomp; $[\alpha]_D^{27}$ −52 (*c* 0.0015, MeOH) (Found: C, 63.8; H, 7.9; N, 7.5. $C_{20}H_{24}N_2O_3{\cdot}2H_2O$ requires C, 63.8; H, 7.5; N, 7.45%); λ_{max}(MeOH)/nm 229.5, 291 and 320.5 (ε 10 800, 2900 and 2900); CD λ_{max}(MeCN)/nm 211, 245 infl., 264 and 300 ($\Delta\varepsilon$ −7.9, −0.54, 0.21 and −0.33); ν_{max}(KBr)/cm^{-1} 1625, 1598, 1574, 1508, 1457, 1446, 1405, 1384, 1312, 1289, 1264, 1225, 1133 and 825; δ_H 1.03 (3H, t, $J_{18,19}$ 7.4, 18-H), 1.69 (2H, AB of ABMX$_3$, 19-H), 1.84–1.92 (3H, m, 14-H and 16-H), 2.09 (1H, m, 20-H), 2.19 (1H, br, $\Delta\nu_{\frac{1}{2}}$ 11.0, 15-H), 2.75 (1H, ddd, $J_{14,14}$ 13.7, $J_{14,3}$ 9.3, $J_{14,15}$ 4.4, 14-H), 2.80 (1H, dd, $J_{6,6}$ 16.9, $J_{6,5}$ 5.0, 6-H), 2.98 (1H, dddd, $J_{6,6}$ 16.9, $J_{6,5}$ 12.5, $J_{6,5}$ 5.0, $J_{6,3}$ 2.5, 6-H), 3.12–3.19 (2H, m, 17-H and 21-H), 3.36 (1H, ddd, $J_{5,5} = J_{5,6} = 12.5$, $J_{5,6}$ 5.0, 5-H), 3.45 (1H, dd, $J_{5,5}$ 12.5, $J_{5,6}$ 5.0, 5-H), 3.54 (1H, m, 17-H), 3.84 (1H, dd, $J_{21,21}$ 13.2, $J_{21,20}$ 10.5, 21-H), 4.71 (1H, br t, $J_{3,14}$ 9.3, $J_{3,14}$ 8.8, 3-H) and 6.58 and 7.28 (2H, AB, $J_{9,10}$ 8.5, 10-H and 9-H); δ_C 12.07 (C-18), 18.02 (C-6), 25.07 (C-15), 26.24 (C-16), 26.56 (C-14), 27.97 (C-19), 38.16 (C-20), 49.12 (C-17), 60.99 (C-5), 62.19 (C-3), 65.29 (C-21), 103.98 (C-12), 105.14 (C-7), 110.10 (C-10), 119.74 (C-8), 123.37 (C-9), 126.99 (C-2), 138.80 (C-13), 160.11 (C-11) and 176.15 (CO); *m/z* (FAB) 379 (M^+ + 39, 3%), 363 (M^+ + 23,36), 341 (M^+ + 1, 100), 323(20), 297(33) and 245(11).

Later fractions from the column were combined and yielded a gum (3.3 g). A portion of this gum (1.6 g) was preadsorbed on silica gel and chromatographed twice over silica gel with increasing amounts of acetic acid in methanol–ethyl acetate (1 : 1) as eluant. The less polar fractions were combined and the residue was crystallized from methanol–ethyl acetate which afforded bracteatine **5** (23 mg), identical with an authentic sample. The more polar fractions were rechromatographed and the fractions showing a Dragendorff test were acetylated during 3 h on a steam bath with acetic anhydride (1 cm^3) and pyridine (1 cm^3). The crude product was twice subjected to radial chromatography with increasing amounts of acetic acid in acetonitrile–ethyl acetate (1 : 1) as eluant. Those fractions which showed one spot on TLC were then passed through a column of Sephadex LH-20 with methanol–ethyl acetate (1 : 1) as eluant. The yellowish gum so obtained crystallized from methanol–ethyl acetate as plates (21 mg) of *blumeanine diacetate* **8**, decomp. without melting at 250 °C; $[\alpha]_D^{32}$ −155 (*c* 0.003, MeOH); HRMS (FAB) *m/z* 675.3869 (M^+ + 1). $^{12}C_{42}{}^1H_{51}{}^{14}N_4{}^{16}O_2$ requires 675.3910; λ_{max}(MeOH)/nm 220.5 and 291 (ε 25 400 and 7600); CD λ_{max}(MeOH)/nm 201, 222, 240, 271, 284 infl. and 307 ($\Delta\varepsilon$ −23.0, 26.5, −26.3, 21.4, 13.9 and −5.4); ν_{max}(KBr)/cm^{-1} 1752 and 1213; δ_H *inter al.*, 0.98 and 1.00 (each 3H, t, $J_{18,19} = J_{18',19'} = 7.4$, 18-H and 18′-H), 1.66 (4H, m, 19-H and 19′-H), 1.81 and 1.92 (each 1H, m, 14-H and 14′-H), 4.97 and 5.22 (each 1H, br t, $J_{3,14} = J_{3',14'} = 9.5$, 3-H and 3′-H), 6.95 and 7.58 (2H, AB, *J* 8.5, 10-H and 9-H) and 7.08 and 7.51 (2H, AB, *J* 8.7, 11′-H and 12′-H); δ_C 11.96 and 12.04 (C-18 and C-18′), 18.15 and 18.55 (C-6 and C-6′), 20.48 and 20.55 (each *C*H$_3$CO), 25.15 and 25.21 (C-15 and C-15′), 26.04, 26.37, 26.71, 27.75, 27.88 and 27.96 (C-14, C-14′, C-16, C-16′, C-19 and C-19′), 37.94 and 38.03 (C-20 and C-20′), 49.28 and 49.29 (C-17 and C-17′), 60.77 and 61.10 (C-5 and C-5′), 61.83 and 61.99 (C-3 and C-3′), 65.18 and 65.24 (C-21 and C-21′), 106.26 and 106.60 (C-7 and C-7′), 113.43 (C-12′), 114.19 (C-12), 116.13 (C-10), 118.10 (C-9′), 118.88 (C-11′), 119.62 (C-9), 124.87 and 126.21 (C-8 and C-8′), 131.43 and 131.59 (C-2 and C-2′), 136.96 and 138.47 (C-13 and C-13′), 144.02 (C-10′), 146.70 (C-11) and 171.44 and 171.81 (each CH$_3$*C*O); *m/z* (FAB) 675 (M^+ + 1, 100%), 633 (12), 338 (30), 308 (19) and 245 (36).

(b) Sample 2. The botanical material was collected in

November 1996 in the same location. Herbarium specimens (DR-153) were deposited as above. Extraction of the aerial parts of the plant as already described gave after extensive chromatography, in order of increasing polarity, first ophiorrhizine **1** (0.004%) identical with an authentic sample. Ophiorrhizine **1** on treatment with acetic anhydride and pyridine afforded the acetate **2** which crystallized from methanol–ethyl acetate as needles, mp 253 °C decomp.; $[a]_D^{32}$ −52 (*c* 0.0015, MeOH); λ_{max}(MeOH)/nm 231 and 279 (ε 5400 and 7100); ν_{max}(KBr)/cm^{-1} 1753, 1628, 1574, 1467, 1444, 1372, 1217, 1134 and 1014; δ_H 1.04 (3H, t, $J_{18,19}$ 7.4, 18-H), 1.70 (2H, AB of ABMX$_3$, 19-H), 1.90–1.99 (3H, m, 14-H and 2 × 16-H), 2.16 (1H, m, 20-H), 2.26 (1H, br, 15-H), 2.28 (3H, s, CH_3CO), 2.76 (1H, ddd, $J_{14,14}$ 13.0, $J_{14,3}$ 9.4, $J_{14,15}$ 5.0, 14-H), 3.02 (1H, br d, $J_{6,6}$ 17.0, 6-H), 3.12 (1H, dddd, $J_{6,6}$ 17.0, $J_{6,5}$ 12.5, $J_{6,5}$ 2.3, 6-H), 3.26–3.32 (2H, m, 17-H and 21-H), 3.57–3.65 (3H, m, 2 × 5-H, 17-H), 3.85 (1H, dd, $J_{21,21}$ 12.6, $J_{21,20}$ 10.5, 21-H), 5.02 (1H, br t , $J_{3,14}$ 9.4, 3-H), 6.83 (1H, dd, $J_{10,9}$ 8.5, $J_{10,12}$ 2.0, 10-H), 7.13 (1H, d, $J_{12,10}$ 2.0, 12-H) and 7.47 (1H, d, $J_{9,10}$ 8.5, 9-H); δ_C 12.01 (C-18), 18.10 (C-6), 21.00 (CH_3CO), 25.14 (C-15), 26.22 (C-16), 26.79 (C-14), 27.93 (C-19), 38.09 (C-20), 49.30 (C-17), 61.97 (C-3), 65.28 (C-21), 105.65 (C-7), 105.76 (C-12), 115.38 (C-10), 119.67 (C-9), 124.85 (C-8), 130.50 (C-2), 138.62 (C-13), 148.50 (C-11) and 171.89 (CH_3CO); *m*/*z* (FAB) 339 ($M^+ + 1$, 100%) and 297 (51). Ophiorrhizine-12-carboxylate **6** (0.0002%) was next eluted followed by blumeanine which was converted into its diacetate **8** (0.000 04%).

Structure determination for compound 6

Available specimens were small in size, that used for data collection being 0.30 × 0.13 × 0.13 mm; a hemisphere of data was measured using a single counter/'four-circle' instrument at room temperature ($2\theta_{max} = 50°$, 2θ–θ scan mode; graphite monochromated Mo-Kα radiation, $\lambda = 0.7107_3$ Å; *T ca.* 295 K). A total of 6314 reflections were obtained and merged to a unique set (1915 independent reflections) disregarding effects of $\Delta f''$ and of absorption which were deemed negligible ($R_{int} = 0.083$). 1146 reflections with $I > \sigma(I)$ were considered 'observed' and used in the full matrix least squares refinement after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; significant difference map residues were modelled as the oxygen atoms of two molecules of water of crystallization accompanying each parent molecule, site occupancies set at unity after trial refinement. All hydrogen atoms were clearly evident in difference maps, their credibility being enhanced by meaningful refinement in (x, y, z $U_{iso})_H$ despite the limited data. Conventional residuals R, R_w on $|F|$ at convergence were 0.055, 0.051 [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Computation used the Xtal 3.4 program system.[18] The chirality adopted follows that expected from the chemistry.

Crystal data. $C_{20}H_{24}N_2O_3 \cdot 2H_2O$, $M = 376.5$. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 16.093(8)$, $b = 15.623(6)$, $c = 7.496(2)$ Å, $V = 1885$ Å^3. D_c ($Z = 4$) = 1.32(7) g cm^{-3}; $F(000) = 808$. $\mu_{Mo} = 1.0$ cm^{-1}.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/237.

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