Revised Structure of Haemoventosin

David S. Rycroft[a], Joseph D. Connolly[a], Siegfried Huneck*[,b], Uwe Himmelreich[b]

[a] Department of Chemistry, University of Glasgow, Glasgow G 12 8QQ, Scotland, UK
[b] Institute of Plant Biochemistry, PSF 250, D-06018 Halle/Saale, Germany

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The structure of the lichen pigment haemoventosin has been revised to 3,4,6,9-tetrahydro-5,10-dihydroxy-7-methoxy-3S-methyl-1,6,9-trioxo-1H-naphtho-[2,3-c]pyran (**3**), mainly on the basis of long-range δ_C/δ_H correlations observed in 2D HMBC NMR experiments and long-range δ_H/δ_D isotope effects observed in partial deuteriation experiments with 10-*O*-acetylhaemoventosin; *ortho*- and *para*-quinonoid structures were distinguished by means of the transacetylation inferred in the sodium dithionite reduction of 10-*O*-acetylhaemoventosin.

Introduction

The crustose lichen *Ophioparma ventosa* (L.) Norman [syn. *Haematomma ventosum* (L.) Massal. (Lecanoraceae)] is characterized by blood red apothecia, the colour of which turns to blue on treatment with potassium hydroxide. Bruun and Lamvik [1] isolated the pigment (haemoventosin) of the apothecia and proposed structure **1** for this lichen metabolite. Twenty years later Maksimov *et al.* [2] put forward the alternative *o*-quinonoid structure **2** for haemoventosin which they isolated from *Ophioparma lapponica* (Rasänen) Hafellner & R. W. Rogers (syn. *Haematomma lapponicum* Rasänen); this proposal relied on the formation with *o*-phenylene diamine of a derivative assumed to be a quinoxaline.

We have revised the structure of haemoventosin to the *p*-quinone-δ-lactone **3**, mainly on the basis of the results of extensive NMR experiments with the monoacetate of haemoventosin. Initially NMR experiments were performed at 4.7 T; more recently an 11.7 T spectrometer was also used, and the sensitivity advantage of inverse experiments was applied to good effect.

The original structure of haemoventosin and its ^{1}H NMR spectrum were used as models when considering dihydrofuran isomeric possibiities of some isofuranonaphthoquinones [3]; such comparisons are invalid as haemoventosin does not contain a dihydrofuran.

* Reprint requests to S. Huneck, Fliederweg 34a, D-06179 Langenbogen, BRD.

Results and Discussion

We have isolated haemoventosin from *O. ventosa* from Bulgaria and Mongolia and have investigated this compound and its monoacetate using IR, ^{1}H and ^{13}C NMR, and CD spectroscopy.

Haemoventosin is not very soluble in the normal spectroscopic solvents, but forms a monoacetate **4** which is more amenable to spectroscopic investigation in solution. Reaction of haemoventosin with acetic anhydride/sulphuric acid gave a product whose physical properties corresponded to those reported for the monoacetate prepared using acetic anhydride/pyridine [1]. Monoacetylhaemoventosin reveals in the carbonyl region of the IR spectrum bands at 1716 (quinone CO) and 1750 cm^{-1}. The latter band is incompatible with **1** and **2**, but points to a δ-lactone ring, connected to the naphthoquinone.

The ^{1}H NMR spectrum (200 MHz) of monoacetylhaemoventosin at ambient temperature showed one aromatic and one hydroxyl proton, an acetate, a secondary methyl and a methoxyl group. The signals anticipated for the CH_2CH moiety were unexpectedly broad; the secondary methyl signals were also broad and appeared to show an asymmetric doubling. In an attempt to remove the presumed exchange-broadening, the ^{1}H spectrum was measured at 333 K; the signals sharpened, although the methine signal at δ 4.61 ($W_{1/2}$ 24 Hz) was still

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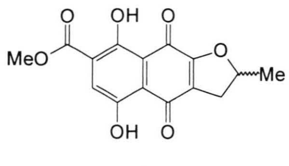

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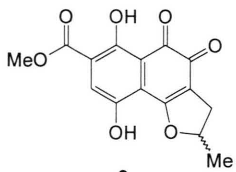

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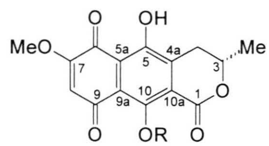


3 R = H
4 R = Ac

broad and featureless. Surprisingly the methoxyl signal in the 333 K spectrum appeared as a symmetrical doublet, splitting 0.4 Hz, and the aromatic proton was a quartet with the same splitting; this immediately suggested that haemoventosin contained an aromatic methyl ether rather than a methyl ester. The ^{13}C NMR spectrum (50 MHz) of monoacetylhaemoventosin at ambient temperature showed broadening and asymmetric doubling of some signals, and some quaternary aromatic signals were missing (compared to the molecular formula). At 333 K some of the signals collapsed to sharp singlets, but the higher temperature exacerbated the relaxation time problems associated with observing weak quaternary aromatic carbon signals and several were still missing. On the other hand at 243 K the spectrum improved and signals for 17 carbon atoms were observed, of which all except 3 were doubled in a *ca.* 2:1 ratio; it was also possible to measure the direct and long-range ^{13}C, ^{1}H coupling constants for the major isomer from a spectrum obtained with the proton decoupler switched off. Evidently at ambient temperature there is an exchange process occurring at an intermediate rate on the NMR timescale. At 243 K the ^{1}H NMR spectrum showed doubling of all the signals, also in a *ca.* 2:1 ratio; both protons of the CH_2 group appeared as doublets of doublets for both conformers, but with slightly different coupling constants; homodecoupling of the methoxyl signals confirmed the presence of spin-spin coupling to the aromatic proton. The NMR data are given in Table I.

The carbons in the neighbourhood of the hydroxyl group were identified by measurement at ambient temperature of deuterium isotope effects

Table I. ^{1}H and ^{13}C NMR parameters[a] of monoacetylhaemoventosin[b] (**4**).

Position	Major conformer δ_H	Minor conformer δ_H	Proton mult.	Major conformer J (Hz)	Minor conformer J (Hz)	Major conformer δ_C	Minor conformer δ_C	Carbon mult.	J (Hz)	$\Delta\delta_C$ (OH–OD) (ppb)[c]
1						159.79	159.97	s		
3β	4.578	4.7	m			74.54	74.29	dm	149	
4α	2.674	2.763	dd	17.7 12.2	17.7 10.7	28.75	28.39	tm	132	
4β	3.321	3.303	dd	17.7 2.7	17.7 3.3					
4a						137.89	137.54	qd	8, 3	120
5-OH	12.502	12.491	s			156.13	156.21	dd	5, 2	277
5a						115.54	115.65	d	5	
6						184.94		d	8	71
7						158.20	158.16	quin	4	
8	6.094	6.098	q	0.3	0.3	112.68		d	166	24
9						181.54	181.47	d	2	
9a						121.28	121.02	d	5	
10						142.74	142.43	d	1	
10a						126.38	126.53	d	5	
3-Me	1.544	1.510	d	6.4	6.4	20.66	20.47	qm	128	
7-OMe	3.890	3.892	d	0.3	0.3	56.80		q	147	
OCO<u>Me</u>	2.420	2.423	s			20.89	21.08	q	130	
O<u>CO</u>Me						169.54	170.01	q	7	

[a] Shifts relative to $CHCl_3$ at δ_H 7.25 and $CDCl_3$ at δ_C 77.0; [b] $CDCl_3$ solution, 243 K, 4.7 T; [c] isotope shifts, at 297 K (see text).

in the ^{13}C spectrum (50 MHz) of monoacetylhaemoventosin where the hydroxyl group had been partially deuteriated by shaking a $CDCl_3$ solution with 3 drops of H_2O and 2 drops of D_2O [4,5]. The isotope shifts observed are included in the Table I. The largest isotope shift $\Delta\delta_C$(OH–OD) is 277 ppb (for the signal at δ_C 156.1) and is associated with the carbon bearing the hydroxyl group.

The assignments of the protons at C-4, C-3 and Me-3 were confirmed by H/H COSY at 500 MHz (11.7 T). The correlations of the carbon atoms at 4, 3, Me-3, the methoxyl, and the acetate methyl group with their attached protons observed in a proton-detected heteronuclear direct δ_C/δ_H correlation experiment at 11.7 T (HMQC [6]) confirmed the conclusions derived from the coupled ^{13}C spectrum. Correlations in the ROESY spectrum (11.7 T) confirmed the proximity of the 7-OMe protons and H-8.

To prove the connectivity and to assign the quaternary carbon astoms we performed 2D long-range δ_C/δ_H correlation experiments. The COLOC experiment had recently been published [7] when we started this work; however a COLOC spectrum obtained at 328 K and 4.7 T displayed correlations

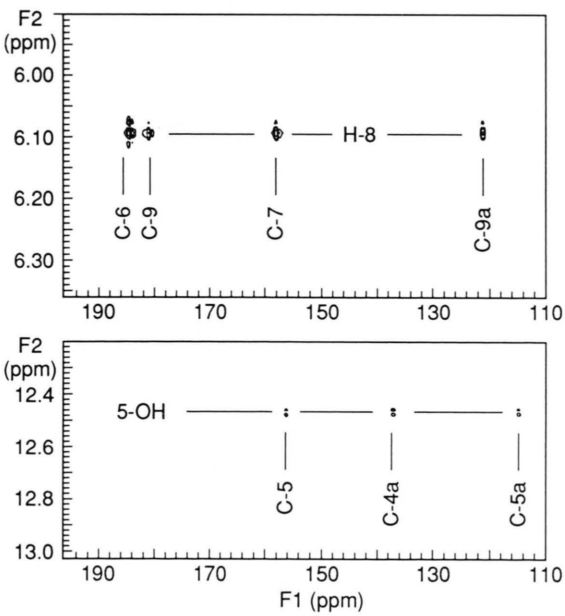


Fig. 1. Deshielded region of the inverse-detected long-range $^1H/^{13}C$ HMBC NMR spectrum of monoacetylhaemoventosin (**4**) in $CDCl_3$. The delay τ_1 was set appropriate to the value of $^1J_{CH}$, and τ_2 was set to 140 ms.

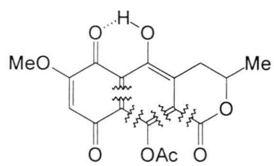
Table II. Logical sequence for the deduction of the bond connectivity of monoacetylhaemoventosin using correlations from HMBC spectra and other information.

Signals which show correlation [*or* other observed fact]	**Bond deduced**
H-3 with H-4 (COSY)	C-3 to C-4
H-3 with 3-C<u>H</u>$_3$ (COSY)	C-3 to 3-<u>C</u>H$_3$
[$\Delta\delta_C$(OH–OD) C-5 = 277 ppb]	HO-5 to C-5
HO-5 with C-5	(2-bond coupling)
HO-5 with C-4a	C-5 to C-4a
HO-5 with C-5a	C-5 to C-5a
C-5 with H-4	C-4a/5a to C-4
C-4a with H-4	C-4a to C-4
[δ(H-3) = 4.578]	C-3 to O-2
C-10a with H-4	C-10a to C-4a
C-1 with H-3	C-1 to O-2
[$\Delta\delta_C$(OH–OD) C-6 = 71 ppb]	C-5a to C-6
C-7 with 7-OC<u>H</u>$_3$	C-7 to O-7
7-OC<u>H</u>$_3$ with H-8 (ROESY)	C-7 to C-8
H-8 with C-7	(2-bond coupling)
H-8 with C-9 (τ_2 = 140 ms) (2-bond coupling)	C-8 to C-9
H-8 with C-6 (τ_2 = 70 ms) (3-bond coupling)	C-7/9 to C-6
H-8 with C-9a	C-9/7 to C-9a
[δ(C-10) = 142.74]	C-10 to OAc

corresponding to only some of the couplings observed in the proton-coupled carbon spectrum. In contrast inverse HMBC experiments [8] performed at ambient temperature and 11.7 T displayed more correlations; with the delay τ_2 set to 70 ms the largest correlations should arise from long-range C,H coupling constants of *ca.* 7 Hz (a typical value for 3-bond couplings in aromatic compounds, 2-bond couplings having smaller values) whereas with τ_2 set to 140 ms the largest correlations should arise from couplings of *ca.* 3 Hz; all these correlations are assumed to arise from 2- and 3-bond interactions. The deshielded proton region of the HMBC spectrum of monoacetylhaemoventosin with τ_2 = 140 ms is shown in Fig. 1.

A sequence for the logical extension of the bond connectivity is be presented in Table II and this reasoning results in the fragments shown as structures **5** or **6**. The onyl geometrically reasonable structures produced by connecting the free bonds are **4**, **7**, **8**, and **9**. We have been unable to find examples of structures closely related to **8** and **9**. One would expect the hydrogen bond in the indene ring system to be weaker than that in the naphthalene system; the closest analogues we could find were related to dengibsin **10** [9], a derivative of 1-hydroxy-9-fluorenone, where the chemical shift of the hydrogen-bonded phenolic proton is always close to δ_H 9. The hydroxyl proton chemical shift in monoacetylhaemoventosin (δ_H 12.5) suggests the presence of a much stronger hydrogen bond than in **10** and indeed δ_H of a *peri*-hydrogen-bonded hydroxyl proton is typically around 13 ppm in naphthoquinones [10,11]. Hence structures **8** and **9** are rejected. The question of deciding between the *para-* and *ortho*-quinonoid nature of structures **4** and **7** was resolved by noting that dithionite reduction [10] of 10-*O*-acetyl-*semi*-xanthomegnin **11** did not produce the expected hydroquinone **12** but rather **13**, in which transesterification had occurred to produce a hydroxyl group strongly hydrogen-bonded (δ_H 13.04) to the lactone carbonyl group. In the case of structure **4** similar behaviour might be expected to produce **14** (with a strongly dishielded hydroxyl proton) whereas in the reduction of structure **7** it would not be possible for intramolecular transesterification to occur and the product **15** would not show any strongly deshielded hydroxyl protons. Reduction of monoacetylhaemoventosin was carried out in an NMR tube; a dilute $CDCl_3$ solution was shaken with drops of aqueous sodium dithionite solution, which was added until the colour change from yellow-orange to pale yellow indicated that reduction was complete. Intermediate stages were monitored by observing the ^1H NMR spectrum (200 MHz); the spectrum of monoacetylhaemoventosin was steadily and cleanly replaced by that of a new species with three phenol groups [δ_H 12.53 (sharp), 8.78 (broad), and 6.56 (broad)], assigned structure **14** on account of the signal at δ_H 12.53. When the aqueous layer was pipetted off and the $CDCl_3$ solution washed with water the colour changed to pale pink-orange and the broad phenolic proton signals sharpened slightly but the spectrum was otherwise essentially unchanged. Hence monoacetylhaemoventosin is assigned the *para*-quinonoid structure **4**. H-8 is deshielded in **14** compared to **4** and the chemical shift (δ_H 6.85) is the same as in **13** [10]. In contrast to **4** the signals for the CH_2CHCH_3 moiety in **14** are sharp at ambient temperature [δ_H 1.54 (3H-11, d, J 6.3 Hz), 2.68 (H-4α, dd, J 16.7, 11.1 Hz), 3.30 (H-4β, dd, J 16.7, 3.3 Hz), 4.64 (H-3, m)]; the remaining signals are δ_H 2.37 (OAc, s) and 4.00 (OMe, s).

Haemoventosin has a centre of chirality at C-3 and should be optically active. Bruun and Lamvik [1] did not report the optical rotation of haemoventosin or its acetate. We found that monoacetylhaemoventosin indeed is optically active; it has the large specific rotation of $[\alpha]_{578}^{24} + 354.5$ and the CD spectrum is shown in Fig. 2, along with that of 10-*O*-acetyl-*semi*-xanthomegnin (**11**). The two CD spectra are nearly mirror images of each other. **11** has been shown to have the 3*R* configuration by comparison with *R*-mellein [10], and therefore **4** has the 3*S* configuration; the additional hydroxyl group at C-5 should have little influence on the CD of **4** in comparison to **11**. Hence haemoventosin is 3,4,6,9-tetrahydro-5,10-dihydroxy-7-methoxy-3*S*-methyl-1,6,9-trioxo-1 H-naphtho[2,3-c]-pyran **3** and monoacetylhaemoventosin is the corresponding 10-*O*-acetate **4**. A related naphthoqui-



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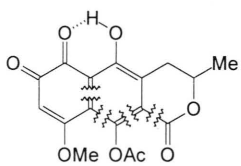

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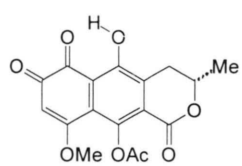

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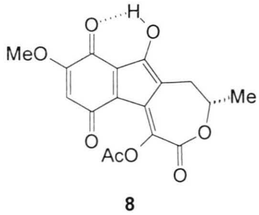

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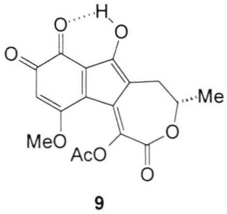

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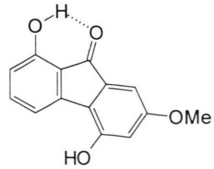

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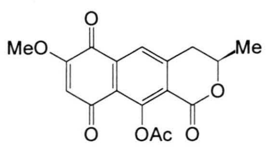

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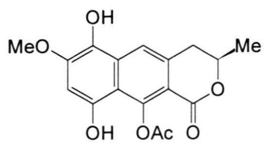

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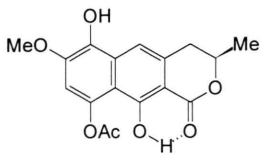

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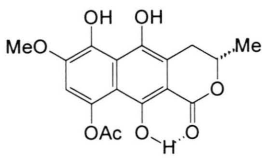

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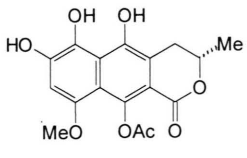

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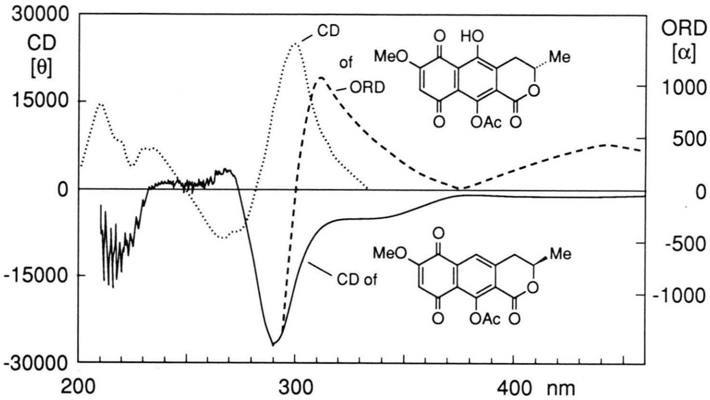
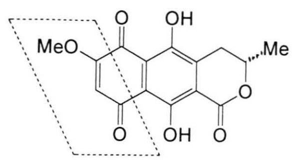


Fig. 2. CD spectra of 10-*O*-acetylhaemoventosin (**4**, in MeCN) and 10-*O*-acetyl-*semi*-xanthomegnin (**11**, in MeOH), and ORD curve of **4** (in MeOH).

none, anhydrofusarubin lactone **16**, has been isolated from the fungus *Nectria haematococca* [11]; the structure has been shown variously, without discussion, as both **16a** [11] and **16b** [12].

The finding of Bruun and Lamvik [1] that haemoventosin can be hydrolyzed with 10% NaOH to a compound, m.p. *ca.* 200 °C, with the formula $C_{14}H_{10}O_7$ (found M^+ 290.0429), which led to the proposal of a methyl ester in **1**, deserves comment. This simple saponification is still readily accounted for in the revised structure **3**, as it contains a vinylogous ester moiety, marked by a dotted line in formula **17**. The product of hydrolysis is therefore **18**.



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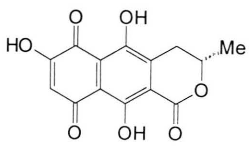

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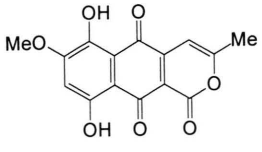
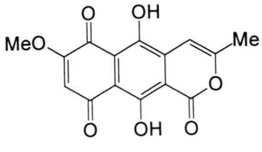


16a



16b

Conformation isomerism

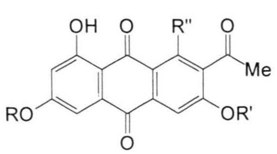
The exchange process referred to earlier that results in broadening of the NMR spectra of **4** can now be understood in terms of conformational isomerism about the C-10 to acetate bond. Steric hindrance exerted by the *peri*-oxygen atoms of the C-1 and C-9 carbonyl groups will force the 10-*O*-

acetyl group to lie either above or below the plane of the aromatic ring, the faces of which are rendered inequivalent by the chiral centre C-3. The steric hindrance which causes the conformational isomerism is evidently sufficient to slow the rate of conformational interchange to one that is intermediate on the NMR timescale at ambient temperatures. This view is consistent with the observation that the ^{1}H NMR spectrum of the reduction product **14** is sharp at ambient temperature: in **14** the 9-*O*-acetyl group has a *peri*-interaction with only one oxygen atom and conformational interchange is not restrained.

It is noteworthy that Bruun and Lamvik [1] gave few details of the ^{1}H NMR spectrum of monoacetylhaemoventosin; similarly Zeeck *et al.* [10] did not report any ^{1}H NMR data for 10-*O*-acetyl-*semi*-xanthomegnin **11**, which might be expected to display similar conformational behaviour to **4**, and similar complications in the NMR spectra.

Chemotaxonomy

According to Rogers and Hafellner [13] the genus *Haematomma* comprises two groups, the *ochroleucum* group and the *puniceum* group, from which the superficially similar genus *Ophioparma* has been separated. *Ophioparma* differs from *Haematomma* in its ecology, anatomy of the apothecia and chemistry (*Haematomma* with atranorin, *Ophioparma* without atranorin but with thamnolic acid). There is another important difference between the two genera, *viz.* the nature of the pigments from the apothecia. We have found the anthraquinones haematommone (**19**) and nemetzone (**20**) in the apothecia of *Haematomma puniceum* (Ach.) Massal. [14] and *Haematomma nemetzii* Steiner [15] respectively, while the apothecia of *Ophioparma ventosa* and *Ophioparma lapponica* contain the naphthoquinone haemoventosin [1,2, this paper]. The chemotaxonomy is interesting in that the biosynthesis of the pigments starts from related, but different, precursors: haemoventosin is derived from a heptaketide whereas haematommone and nemetzone are derived from an octaketide.



	R	R'	R''
19	H	H	OH
20	Me	Ac	H

The apothecia play a very important role in the reproduction of lichens, but little is known, unfortunately, about the significance of the pigments. *Ophioparma ventosa* contains, according to TLC analysis, numerous other red pigments in its apothecia. These minor components, which could not be isolated in a pure state because of the small quantities, will be investigated further after collection of fresh lichen material.

Ophioparma ventosa seems to exist in at least two chemical races: one (from Bulgaria) contains haemoventosin, (+)-usnic acid, and divaricatic acid, whereas the other (from Mongolia) contains haemoventosin, (+)-usnic acid, and diffractaic acid. The lipid fraction (mainly a mixture of glycerides) of the extract from the Mongolian collection was saponified, the acid part methylated with diazomethane, and the mixture of methyl esters analysed by GLC and MS. The following fatty acids were found: tridecadienic, hexadecatrienic, palmitic, linolic, oleic, stearic, nonadecenic, arachidic, and behenic acids.

Experimental

NMR experiments were performed with Bruker WP200SY and AM200SY instruments (4.7 T) operating at 200.13 (^{1}H) and 50.325 (^{13}C) MHz, and with a Varian UNITY 500 spectrometer (11.7 T) operating at 499.85 (^{1}H) and 125.7 (^{13}C) MHz. Solutions of monoacetylhaemoventosin (0.03 g at 4.7 T, 0.01 g at 11.7 T) in $CDCl_3$ (0.5 ml) were used. Chemical shifts are referred to internal $CHCl_3$ (δ_H 7.25) and $CDCl_3$ (δ_C 77.00) for ^{1}H and ^{13}C spectra respectively. 2D H/H COSY-90 spectra were recorded according to standard pulse programs. Direct δ_H/δ_C correlation was achieved with the 2D ^{1}H-detected heteronuclear multiple quantum coherence experiment (HMQC); fixed delays were set for $^{1}J_{CH}$ = 160 Hz. Long-range δ_H/δ_C correlation came from 2D ^{1}H-detected heteronuclear multiple bond connectivity experiments (HMBC) using the pulse sequence RD-90°(^{1}H)-τ_1-90°(^{13}C)-τ_2-90°(^{13}C)-t_1/2-180°(^{1}H)-t_1/2-90°(^{13}C)-t_2(acquire ^{1}H) the delay τ_1 was set for $^{1}J_{CH}$ =160 Hz, and τ_2 was set to 70 ms or 140 ms to give maximum correlation intensity for long-range J_{CH} of *ca.* 7 Hz or *ca.* 3 Hz respectively.

Ophioparma ventosa. Voucher specimens of *O. ventosa* are deposited at the botanical Museum in Berlin-Dahlem (B). Origin: (**a**) Bulgaria, Witoscha

Mountains, Malak Rezen, on granitic rocks, alt. *ca.* 2000 m; leg. et det. S. Huneck, 28. 9. 1978. (**b**) Mongolia, Archangai Aimak, Tarbagatai, on basaltic rocks 4 km west of the Solon-Got pass, alt. *ca.* 2500 m; leg. et det. S. Huneck, 1. 7. 1978.

Extraction. (**a**) The air-dried and ground lichen (405 g) was extracted (4 days) with Et_2O and the extract treated as described by Bruun and Lamvik [1]. The fraction insoluble in cold benzene yielded (+)-usnic acid (18.27 g, 4.5%) and divaricatic acid, while the more soluble fraction gave after crystallization from benzene haemoventosin (**3**) as red-brown crystals with m.p. 202–204° (0.3 g, 0.07%). $C_{15}H_{12}H_7$ (found *m/z* 304.25). (**b**) The lichen (694 g) was treated as above and yielded (+)-usnic acid (25.4 g, 3.65%), diffractaic acid (1.76 g, 0.25%) and haemoventosin (1.05 g, 0.15%).

Monoacetylhaemoventosin (**4**). Haemoventosin (0.3 g) was treated with a mixture (3 ml) of acetic anhydride (6 ml) and conc. sulphuric acid (1 drop) at 20° and left for 24 hours. The usual work-up, chromatography over silica gel and crystallization from methanol gave yellow needles, m.p. 203–204° (dec.), lit. [1] m.p. 193–194° (dec.). $C_{17}H_{14}O_8$ (found *m/z* 346.28). $[\alpha]_{578}^{24}$ +354.5 ($CHCl_3$, c 1.145). IR, ν_{max}^{KBr} (cm^{-1}): 724, 752, 780, 792, 826, 882, 958, 1012, 1066, 1114, 1190, 1220, 1307, 1368, 1426, 1606, 1634, 1716, 1750, 2950, 3480. MS, *m/z* 348 (35%, M^++2H), 346 (30, M^+), 306 (97), 304 (100), 302 (78), 289 (67), 288 (92), 273 (40), 260 (43), 245 (30).

ORD (MeOH): $[\alpha]$	+158	+406	+17	+1076	0	−1412	
λ	500	438	376	314	300	294	nm.

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