Wrightiin, a New Chlorinated Depside from *Erioderma wrightii* Tuck (Ascolichenes)

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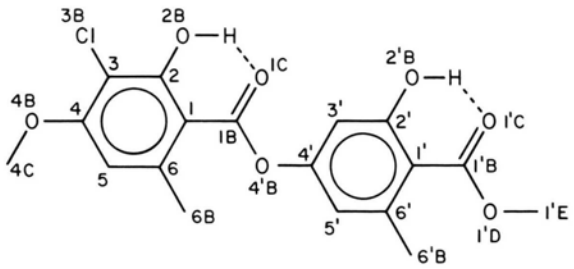
Z. Naturforsch. **41b,** 1589–1592 (1986);
received January 8, 1986

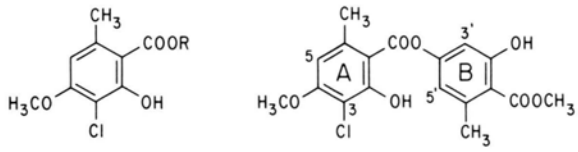
Erioderma wrightii, Lichen Depside,
Methyl 3-Chloroevernate, Crystal Structure,
Mass Spectra

The structure of wrightiin, a depside metabolite of *Erioderma wrightii* is shown by X-ray crystalography to be **2.** The mass spectrum is anomalous.

Among the numerous chlorinated constituents of the lichen genus *Erioderma* [1–3] a new depside has been identified as the main lipophilic constituent of the tropical species *E. wrightii.* The compound was obtained in yields of 2–9% from materials that had been collected in Jamaica during various seasons between 1977 and 1979. It was most readily extracted with chloroform and recrystallized from acetone to give large colorless needles, m.p. 216.5 °C (dec.). The empirical formula $C_{18}H_{17}ClO_7$ was established by elemental analysis, spectroscopic data, the formation of two methylated derivatives, a monomethylwrightiin (m.p. 138–139 °C) and a dimethylwrightiin (m.p. 109–110 °C), and chemical degradation. Acid hydrolysis and base catalyzed methanolysis gave methyl orsellinate and the acid 1 (m.p. 247 °C with foaming) or its methylester 2 (m.p. 168.5–169 °C) respectively.



Structure **3** (methyl 3-chloroevernate) was established by X-ray crystallography [4]. Crystallographic measurements were obtained with a Picker 4-circle



1: R = H
2: R = CH_3

3

Table I. Atomic coordinates (e.s.d.'s). E.s.d. of zero indicates a coordinate not refined. H positions from ΔF map (hydroxyl and methyl) or assumed (C–H = 1.08 Å).

Atom	*x*	*y*	*z*
C(1)	0.5882(7)	0.3414(3)	0.6445(9)
C(1B)	0.4614(7)	0.4173(3)	0.6661(9)
O(1C)	0.3017(6)	0.4186(3)	0.6104(8)
C(2)	0.5144(7)	0.2642(3)	0.5722(9)
O(2B)	0.3374(5)	0.2603(2)	0.5251(7)
C(3)	0.6221(7)	0.1886(3)	0.5510(9)
Cl(3B)	0.5287(2)	0.09546(9)	0.4699(3)
C(4)	0.8074(7)	0.1864(3)	0.5864(9)
O(4B)	0.9019(5)	0.1092(2)	0.5551(6)
C(4C)	1.0912(8)	0.1041(4)	0.5819(12)
C(5)	0.8813(7)	0.2617(3)	0.6545(9)
C(6)	0.7766(7)	0.3386(3)	0.6841(9)
C(6B)	0.8760(8)	0.4148(3)	0.7593(10)
C(1′)	0.3027(7)	0.7369(3)	0.8817(9)
C(1′B)	0.2126(8)	0.8246(3)	0.9194(9)
O(1′C)	0.0528(5)	0.8434(2)	0.9045(7)
O(1′D)	0.3227(5)	0.8831(2)	0.9779(7)
C(1′E)	0.2420(9)	0.9702(4)	1.0165(12)
C(2′)	0.1919(7)	0.6721(3)	0.8099(9)
O(2′B)	0.0116(5)	0.6875(2)	0.7826(7)
C(3′)	0.2592(7)	0.5888(3)	0.7709(9)
C(4′)	0.4409(7)	0.5688(3)	0.7938(9)
O(4′B)	0.5325(5)	0.4879(2)	0.7589(6)
C(5′)	0.5537(7)	0.6306(3)	0.8639(9)
C(6′)	0.4876(7)	0.7142(3)	0.9082(9)
C(6′B)	0.6226(8)	0.7760(4)	0.9829(10)
H2B	0.2796(0)	0.3229(0)	0.5750(0)
H4C1	1.1329(0)	0.0379(0)	0.5250(0)
H4C2	1.1390(0)	0.1176(0)	0.5250(0)
H4C3	1.1293(0)	0.1316(0)	0.7002(0)
H5	1.0245(0)	0.2598(0)	0.6811(0)
H6B1	0.9750(0)	0.4182(0)	0.7055(0)
H6B2	0.8595(0)	0.4451(0)	0.8921(0)
H6B3	0.8356(0)	0.4562(0)	0.6952(0)
H1′E1	0.1676(0)	0.9722(0)	0.8672(0)
H1′E2	0.3381(0)	1.0034(0)	1.0250(0)
H1′E3	0.1703(0)	0.9666(0)	1.0830(0)
H2′B	−0.0300(0)	0.7540(0)	0.7942(0)
H3′	0.1714(0)	0.5403(0)	0.7250(0)
H5′	0.6956(0)	0.6131(0)	0.8839(0)
H6′B1	0.6372(0)	0.8074(0)	0.8828(0)
H6′B2	0.6053(0)	0.8106(0)	1.1327(0)
H6′B3	0.7278(0)	0.7444(0)	1.0239(0)

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Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0340–5087/86/1200–1589/$ 01.00/0

diffractometer, using Ni-filtered CuK_α radiation at T = 24 °C. Crystal data: $C_{18}H_{17}ClO_7$ (380.8), colourless needle 0.02×0.04×0.8 mm, triclinic, $P\bar{1}$, a = 7.702(4), b = 16.504(4), c = 6.877(4) Å, α = 103.54(4), β = 100.26(4), γ = 80.85(4)°, V = 830.0 Å^3, Z = 2, Dx = 1.523 g cm^{-3}, μ = 24 cm^{-1}. Intensity data from $\theta-2\theta$ scans ($2\theta \leqslant 130°$); 1417 reflections observed ($I \geqslant 3\sigma$) of 2784 scanned. No absorption corrections. Block-diagonal least squares refinement converged at R = 0.06 (observed reflections only).

NMR data of **3:** ^{1}H NMR ($CDCl_3$), δ (ppm) = 2.58 (d, d, J = 0.6 Hz, 3H), 2.68 (d, J = 0.7 Hz, 3H), 3.98 (d, 2×3H), 6.44 (s, 1H, 22% nOe by irrad. at frequency of methoxyls), 6.60 (d, $^4J_{meta}$ = 2.5 Hz, m, ^4J = 0.7 Hz, 1H), 6.70 (d, $^4J_{meta}$ = 2.5 Hz, m, ^6J = 0.6 Hz, 1H), 11.47 (s, 1H, e), 11.53 (s, 1H, e); ^{13}C NMR (CD_3SOCD_3), δ = 19.39 (C^6–Me), 21.18 ($C^{6'}$–Me), 51.84 (ester MeO), 56.35 (C^4–MeO), 106.4 (C^5–H), 106.7 (C^3–Cl), 107.0 ($C^{3'}$–H), 111.87 ($C^{1'}$), 113.9 ($C^{5'}$–H), 118.8 (C^1), 137.8 (C^6 or $C^{6'}$), 138.0 ($C^{6'}$ or C^6), 151.3 ($C^{4'}$–OR), 154.3

Table II. Thermal parameters U_{ij} (U for H), ×100, and their e.s.d.'s. (E.s.d. of zero indicates a parameter not refined.) The temperature factor for anisotropic atoms is $\exp[-2\pi^2(U_{11}a^{*2}h^2+\cdots+2U_{12}a^*b^*hk+\cdots)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3.48(31)	2.90(28)	4.51(39)	−0.44(23)	0.95(27)	0.78(25)
C(1B)	3.49(31)	3.13(29)	5.64(43)	−0.05(24)	1.16(28)	0.76(28)
O(1C)	3.86(25)	3.81(24)	12.76(47)	0.08(19)	0.32(27)	−0.12(27)
C(2)	2.98(30)	3.42(30)	4.98(42)	−0.32(23)	0.74(27)	0.85(27)
O(2B)	2.99(21)	3.37(21)	7.86(33)	−0.55(17)	0.71(21)	0.55(21)
C(3)	3.85(32)	2.80(27)	4.97(42)	−0.97(24)	0.52(28)	0.55(26)
Cl(3B)	4.33(8)	3.15(7)	8.68(13)	−1.14(6)	0.72(8)	0.79(7)
C(4)	3.22(30)	2.75(28)	5.48(43)	0.13(22)	0.70(27)	1.08(26)
O(4B)	3.27(21)	2.93(20)	8.22(35)	−0.17(17)	0.82(21)	0.53(21)
C(4C)	3.18(33)	3.64(32)	11.18(65)	0.03(26)	0.91(36)	0.30(37)
C(5)	3.38(31)	3.16(29)	4.78(39)	−0.52(23)	0.09(27)	0.73(27)
C(6)	3.20(29)	3.02(28)	4.75(40)	−0.29(23)	1.16(27)	1.17(26)
C(6B)	5.01(39)	3.02(31)	7.68(52)	−1.76(27)	1.56(35)	0.20(32)
C(1′)	3.35(30)	2.82(28)	5.52(41)	0.23(23)	0.78(27)	0.80(26)
C(1′B)	4.25(35)	3.68(32)	4.97(43)	0.15(26)	0.34(29)	0.73(29)
O(1′C)	4.26(25)	3.93(24)	9.67(39)	0.84(19)	1.16(24)	0.89(24)
O(1′D)	4.73(26)	3.06(22)	9.40(38)	0.01(19)	0.73(25)	0.69(23)
C(1′E)	6.67(50)	3.28(35)	10.58(65)	0.11(32)	0.95(44)	1.03(38)
C(2′)	3.07(30)	3.99(32)	4.86(42)	−0.06(25)	0.74(27)	0.66(29)
O(2′B)	3.06(22)	4.51(24)	9.15(37)	0.20(18)	0.86(22)	1.08(24)
C(3′)	3.63(31)	3.36(29)	5.26(42)	−0.46(23)	1.20(28)	0.93(27)
C(4′)	3.74(33)	2.83(28)	4.64(40)	0.37(24)	0.86(28)	0.40(27)
O(4′B)	3.38(22)	2.91(20)	7.07(31)	−0.12(16)	0.40(20)	0.73(20)
C(5′)	3.38(30)	3.19(29)	5.00(41)	−0.05(23)	0.89(27)	0.93(27)
C(6′)	3.63(32)	3.75(31)	3.88(38)	−0.39(24)	0.69(27)	0.87(27)
C(6′B)	4.06(34)	3.51(31)	7.00(49)	−0.84(26)	0.13(32)	0.33(31)
H2B	10.0(0)					
H4C1	10.0(0)					
H4C2	10.0(0)					
H4C3	10.0(0)					
H5	6.0(0)					
H6B1	10.0(0)					
H6B2	10.0(0)					
H6B3	10.0(0)					
H1′E1	10.0(0)					
H1′E2	10.0(0)					
H1′E3	10.0(0)					
H2′B	10.0(0)					
H3′	6.0(0)					
H5′	6.0(0)					
H6′B1	10.0(0)					
H6′B2	10.0(0)					
H6′B3	10.0(0)					

(C^2–OH), 156.1 ($C^{2'}$–OH), 157.3 (C^4–OMe), 166.4 (C=O), 167.8 (C=O of methylester).

Assignments of methyls, methoxyls and aryl C–H groups were obtained with the aid of heteronuclear $^{13}C-^{1}H$ correlations and those of quaternary carbons by long range $^{13}C-^{1}H$ couplings. The assignments are consistent with ^{13}C data of the hydrolysis products and with those reported by Huneck *et al.* [5] for methyl 3-chlorodivaricatate, a homologous depside in which *n*-propyl side chains are present instead of the aromatic methyl groups.

The electron impact mass spectrum of wrightiin showed strong dichlorinated ions at *m/z* 396, 398, and 400, corresponding to $C_{18}H_{14}Cl_2O_6$, presumably due to dimerisation of the clorinated ring moiety. Ions at *m/z* 380 and 382, corresponding to $C_{18}H_{17}ClO_7$, were of extremely low abundance. Ring A and B fragment ions were formed as expected. However, ions corresponding to the ring A methylester $C_{10}H_{11}ClO_4$ were observed also and appear to be the products of a transesterification reaction.

These experimental results suggest caution in interpreting the mass spectra of crude depside mixtures such as encountered during "lichen mass spectrometry".

We thank Dr. John Walter for heteronuclear $^{13}C-^{1}H$ *J* correlation spectra obtained with a Bruker MSL 300 NMR spectrometer, Dr. Don Hooper of the Atlantic Region Magnetic Resonance Centre, Halifax, N.S., for ^{1}H and ^{13}C coupled and decoupled spectra recorded on a Nicolet 360 NB spectrometer, and Mr. Don Embree for accurate mass measurements using a CEC 21-110B mass spectrometer.

Table III. Bond lengths and angles (e.s.d.'s where appropriate) in Å and °.

C(1)–C(1B)	1.456(7)	C(1'B)–O(1'C)	1.212(7)
C(1)–C(2)	1.423(7)	C(1'B)–O(1'D)	1.330(7)
C(1)–C(6)	1.424(7)	O(1'D)–C(1'E)	1.456(7)
C(1B)–O(1C)	1.220(7)	C(2')–O(2'B)	1.358(7)
C(1B)–O(4'B)	1.340(6)	C(2')–C(3')	1.370(8)
C(2)–O(2B)	1.352(6)	C(3')–C(4')	1.375(8)
C(2)–C(3)	1.377(8)	C(4')–O(4'B)	1.397(6)
C(3)–Cl(3B)	1.731(5)	C(4')–C(5')	1.388(8)
C(3)–C(4)	1.401(8)	C(5')–C(6')	1.375(7)
C(4)–O(4B)	1.353(6)	C(6')–C(6'B)	1.513(8)
C(4)–C(5)	1.395(7)	O(1C)···O(2B)	2.521(7)
O(4B)–C(4C)	1.428(7)	O(1C)···H2B	1.57
C(5)–C(6)	1.384(7)	O(2B)–H2B	1.06
C(6)–C(6B)	1.516(7)	O(1'C)–O(2'B)	2.564(7)
C(1')–C(1'B)	1.487(8)	O(1'C)···H2'B	1.66
C(1')–C(2')	1.418(8)	O(2'B)–H2'B	1.08
C(1')–C(6')	1.404(8)		
C(1B)–C(1)–C(2)	116.1(5)	C(1'B)–C(1')–C(2')	116.9(5)
C(1B)–C(1)–C(6)	125.6(5)	C(1'B)–C(1')–C(6')	125.0(5)
C(2)–C(1)–C(6)	118.3(5)	C(2')–C(1')–C(6')	118.1(5)
C(1)–C(1B)–O(1C)	124.3(5)	C(1')–C(1'B)–O(1'C)	124.4(5)
C(1)–C(1B)–O(4'B)	114.7(5)	C(1')–C(1'B)–O(1'D)	114.4(5)
O(1C)–C(1B)–O(4'B)	121.0(5)	O(1'C)–C(1'B)–O(1'D)	121.2(5)
C(1)–C(2)–O(2B)	122.8(5)	C(1'B)–O(1'D)–C(1'E)	116.8(5)
C(1)–C(2)–C(3)	120.9(5)	C(1')–C(2')–O(2'B)	122.6(5)
O(2B)–C(2)–C(3)	116.3(5)	C(1')–C(2')–C(3')	122.3(5)
C(2)–C(3)–Cl(3B)	120.0(4)	O(2'B)–C(2')–C(3')	115.1(5)
C(2)–C(3)–C(4)	120.4(5)	C(2')–C(3')–C(4')	118.1(5)
Cl(3B)–C(3)–C(4)	119.5(4)	C(3')–C(4')–O(4'B)	125.9(5)
C(3)–C(4)–O(4B)	116.1(5)	C(3')–C(4')–C(5')	121.3(5)
C(3)–C(4)–C(5)	119.0(5)	O(4'B)–C(4')–C(5')	112.8(4)
O(4B)–C(4)–C(5)	124.8(5)	C(1B)–O(4'B)–C(4')	126.0(4)
C(4)–O(4B)–C(4C)	118.0(4)	C(4')–C(5')–C(6')	121.2(5)
C(4)–C(5)–C(6)	121.8(5)	C(1')–C(6')–C(5')	119.1(5)
C(1)–C(6)–C(5)	119.4(5)	C(1')–C(6')–C(6'B)	124.3(5)
C(1)–C(6)–C(6B)	124.9(5)	C(5')–C(6')–C(6'B)	116.6(5)
C(5)–C(6)–C(6B)	115.8(5)	O(1C)···H2B–O(2B)	146
		O(1'C)···H2'B–O(2'B)	137

[1] W. S. G. Maass, Abstracts of Second International Mycol. Congress, Univ. of South Florida, Tampa **2,** 406 (1977).
[2] J. D. Connolly, A. E. Freer, K. Kalb, and S. Huneck, Phytochemistry **23,** 857 (1984).
[3] W. S. G. Maass, unpublished results.
[4] Supplementary data available: Observed and calculated structure factors available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK; any request should be accompanied by the full literature citation for this communication.
[5] S. Huneck, G. Sundholm, and G. Follmann, Phytochemistry **19,** 645 (1980).