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Structure of Pannarin: a Natural Depsidone

BY DENIS BLASER AND HELEN STOECKLI-EVANS*

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

Abstract. 2-Chloro-3-hydroxy-8-methoxy-1,6,9-trimethyl-11-oxo-11*H*-dibenzo[*b,e*][1,4]dioxepin-4-carbaldehyde, $C_{18}H_{15}ClO_6$, $M_r = 362.8$, monoclinic, $P2_1/c$, $a = 4.301$ (1), $b = 22.832$ (3), $c = 16.531$ (2) Å, $\beta = 95.09$ (1)°, $V = 1616.9$ Å^3, $Z = 4$, D_m (flotation in KI/H$_2$O) = 1.44, $D_x = 1.490$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 2.6$ cm^{-1}, $F(000) = 752$, room temperature, $R = 0.052$ for 1763 reflections. The central dioxepin-11-one ring exists in a boat conformation. It is fused on either side to highly substituted phenyl rings which are inclined to one another at 123.6 (1)°. Hence the molecule appears to be folded about an axis passing through the ether oxygen in the central seven-membered heterocycle.

Introduction. Pannarin is a natural depsidone isolated essentially from lichen genera *Pannaria* (*fulvesencs, lurida, pityrea* and *rubiginosa*). Depsidones are characterized by the presence of a seven-membered oxygen heterocycle fused on either side to highly substituted phenyl rings. More than twenty examples have been isolated from lichens (Culberson, 1969). The correct chemical structure of pannarin was given by Jackman, Sargent & Elix (1975). In the same year Huneck & Lamb published the structure of argopsin, a depsidone extracted from the lichen *Argopsis friesiana*, which could also be obtained by the chlorination of pannarin. Another

depsidone, vicanicin, has been correlated with argopsin by a Clemmensen reduction (Bodo & Molho, 1974). The crystal structure analysis of the iodoacetate derivative of vicanicin (Dyer, Baillie, Balthis & Bertrand, 1964) was already proof of the structure of argopsin and indirectly of that of pannarin. Hence it could be shown that pannarin possesses the basic structure of a depsidone and that the two phenyl rings were of the β-orcinol type.

Experimental. Transparent rod-like crystals were obtained from a THF/heptane solution. A crystal of dimensions 0.23 × 0.23 × 0.42 mm was used for data collection using a Stoe–Siemens AED-2 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 3% intensity variation for three standard reflections measured every hour. Accurate cell parameters from ± ω values of 44 reflections in the range $15 < 2\theta < 25°$. 2974 reflections were measured by the $\omega/2\theta$ scan mode with $\theta_{max} = 25°$, and index limits h −5 to 5, k 0 to 2, l 0 to 19. 2874 unique reflections, $R_{int} = 0.037$, 1763 [$I > 2\sigma(I)$] were considered observed and used for all further calculations. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986). Refinement and all further calculations were carried out using the *NRCVAX* system (Gabe, Le Page, Charland & Lee, 1989). H atoms located from difference maps and refined isotropically. Weighted full-matrix least-squares refinement for 1763 reflections gave $R =$

* Author to whom correspondence should be addressed.

Table 1. Atomic parameters and B_{iso} values, with e.s.d.'s in parentheses

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	$B_{iso}(\text{Å}^2)$
C(1)	0.1646 (3)	0.62328 (5)	0.23629 (7)	5.32 (6)
O(1)	−0.6872 (7)	0.46650 (13)	0.09701 (17)	4.63 (14)
O(2)	−0.4619 (6)	0.38215 (12)	0.11418 (16)	3.81 (12)
O(3)	−0.2373 (6)	0.38003 (11)	0.27841 (14)	3.61 (11)
O(4)	0.2806 (10)	0.45658 (15)	0.46169 (21)	7.14 (20)
O(5)	0.2979 (9)	0.55288 (14)	0.37652 (21)	5.41 (17)
O(6)	0.1567 (7)	0.22248 (13)	0.05423 (16)	4.44 (14)
C(1)	−0.2510 (8)	0.46678 (17)	0.19464 (22)	3.10 (15)
C(2)	−0.1500 (9)	0.43802 (16)	0.26581 (23)	3.14 (16)
C(3)	0.0251 (10)	0.46512 (17)	0.33032 (24)	3.63 (18)
C(4)	0.1228 (10)	0.52369 (17)	0.31899 (25)	3.85 (19)
C(5)	0.0320 (10)	0.55209 (16)	0.24621 (24)	3.60 (18)
C(6)	−0.1516 (9)	0.52556 (17)	0.18387 (23)	3.43 (16)
C(7)	−0.2266 (8)	0.34347 (16)	0.14223 (23)	3.08 (15)
C(8)	−0.1298 (9)	0.30498 (17)	0.08430 (22)	3.26 (15)
C(9)	0.0726 (9)	0.26027 (15)	0.11309 (25)	3.44 (17)
C(10)	0.1762 (11)	0.25598 (18)	0.1940 (3)	3.70 (18)
C(11)	0.0811 (9)	0.29599 (16)	0.25101 (22)	3.43 (16)
C(12)	−0.1215 (9)	0.34009 (16)	0.22316 (22)	3.22 (16)
C(13)	−0.4742 (10)	0.44028 (18)	0.13269 (23)	3.38 (16)
C(14)	0.1064 (13)	0.43615 (21)	0.4070 (3)	5.08 (24)
C(15)	−0.2276 (17)	0.55795 (25)	0.1057 (3)	4.8 (3)
C(16)	−0.2517 (14)	0.3095 (3)	−0.0034 (3)	4.43 (23)
C(17)	0.3473 (15)	0.17331 (22)	0.0790 (4)	5.0 (3)
C(18)	0.1955 (15)	0.2890 (3)	0.3391 (3)	5.0 (3)

0.052 and $wR = 0.065$; function minimized $\Sigma w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F_o) + 0.001(F_o^2)$. In the final cycle of refinement the max. shift/σ ratio was 0.077. Residual density limits in final difference map were +0.23 and −0.21 e Å^{-3}. Neutral complex atom scattering factors in *NRCVAX* from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional and equivalent isotropic thermal parameters are given in Table 1,* and interatomic distances and angles in Table 2. The numbering scheme used is illustrated in Fig. 1.

Discussion. The central dioxepin-11-one ring is best described as having a boat conformation relative to the plane defined by atoms C(1), C(2), C(7) and C(12). Atom O(3) is displaced by −0.619 (5) Å from the above plane, while atoms C(13) and O(2) are displaced by −0.692 (7) and −0.729 (6) Å, respectively. Hydroxyl O(5) lies almost in plane I, while atoms C(14) and C(15) are displaced 0.090 (8) and −0.078 (9) Å, respectively, and the Cl atom by −0.053 (6) Å. Planes I and II are inclined to one another at 123.6 (1)°, so that the molecule appears to be folded about an axis passing through atom O(3) and bisecting bond C(13)—O(2), see Fig. 2.

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54405 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances (Å), angles (°) and selected torsion angles (°), with e.s.d.'s in parentheses

Cl—C(5)	1.735 (4)	C(3)—C(4)	1.419 (6)
O(1)—C(13)	1.204 (5)	C(3)—C(14)	1.445 (6)
O(2)—C(7)	1.391 (4)	C(4)—C(5)	1.392 (6)
O(2)—C(13)	1.364 (5)	C(5)—C(6)	1.381 (6)
O(3)—C(2)	1.397 (4)	C(6)—C(15)	1.500 (6)
O(3)—C(12)	1.412 (5)	C(7)—C(8)	1.390 (5)
O(4)—C(14)	1.215 (6)	C(7)—C(12)	1.376 (5)
O(5)—C(4)	1.338 (5)	C(8)—C(9)	1.397 (5)
O(6)—C(9)	1.373 (5)	C(8)—C(16)	1.501 (6)
O(6)—C(17)	1.428 (6)	C(9)—C(10)	1.376 (6)
C(1)—C(2)	1.383 (5)	C(10)—C(11)	1.399 (6)
C(1)—C(6)	1.424 (5)	C(11)—C(12)	1.384 (5)
C(1)—C(13)	1.470 (6)	C(11)—C(18)	1.504 (6)
C(2)—C(3)	1.395 (5)	O(5)—H(O5)	0.83 (6)
		H(O5)···O(4)	1.88 (6)

C(7)—O(2)—C(13)	125.8 (3)	O(2)—C(7)—C(8)	115.2 (3)
C(2)—O(3)—C(12)	113.6 (3)	O(2)—C(7)—C(12)	121.7 (3)
C(9)—O(6)—C(17)	118.2 (3)	C(8)—C(7)—C(12)	122.8 (3)
C(2)—C(1)—C(6)	118.6 (3)	C(7)—C(8)—C(9)	116.3 (3)
C(2)—C(1)—C(13)	122.2 (3)	C(7)—C(8)—C(16)	121.4 (4)
C(6)—C(1)—C(13)	119.0 (3)	C(9)—C(8)—C(16)	122.2 (4)
O(3)—C(2)—C(1)	120.6 (3)	O(6)—C(9)—C(8)	114.4 (3)
O(3)—C(2)—C(3)	116.1 (3)	O(6)—C(9)—C(10)	124.2 (4)
C(1)—C(2)—C(3)	123.2 (3)	C(8)—C(9)—C(10)	121.4 (4)
C(2)—C(3)—C(4)	117.6 (3)	C(9)—C(10)—C(11)	121.3 (4)
C(2)—C(3)—C(14)	122.7 (4)	C(10)—C(11)—C(12)	117.7 (3)
C(4)—C(3)—C(14)	119.7 (4)	C(10)—C(11)—C(18)	119.5 (4)
O(5)—C(4)—C(3)	122.0 (4)	C(12)—C(11)—C(18)	122.8 (4)
O(5)—C(4)—C(5)	118.7 (4)	O(3)—C(12)—C(7)	119.2 (3)
C(3)—C(4)—C(5)	119.3 (4)	O(3)—C(12)—C(11)	120.2 (3)
Cl—C(5)—C(4)	116.7 (3)	C(7)—C(12)—C(11)	120.5 (4)
Cl—C(5)—C(6)	120.7 (3)	O(1)—C(13)—O(2)	114.6 (4)
C(4)—C(5)—C(6)	122.6 (4)	O(1)—C(13)—C(1)	123.9 (4)
C(1)—C(6)—C(5)	118.6 (3)	O(2)—C(13)—C(1)	121.4 (3)
C(1)—C(6)—C(15)	121.8 (4)	O(4)—C(14)—C(3)	124.2 (4)
C(5)—C(6)—C(15)	119.6 (4)	O(5)—H(O5)···O(4)	147 (6)

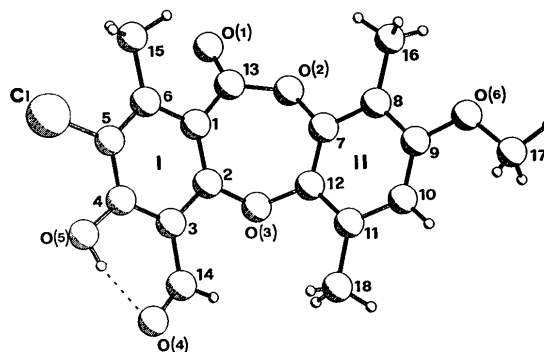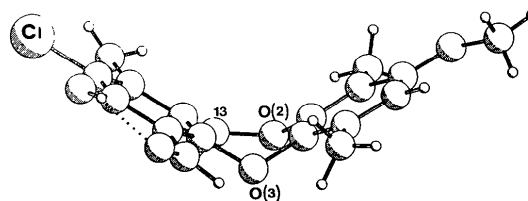|			
C(17)—O(6)—C(9)—C(10)	4.3 (3)	C(4)—C(3)—C(14)—O(4)	−7.2 (2)

Fig. 1. A *PLUTO* (Motherwell & Clegg, 1978) view of pannarin showing the numbering scheme used.

Fig. 2. A *PLUTO* (Motherwell & Clegg, 1978) side view of pannarin.

Table 3. *Dihedral angles (°) between planes* I *and* II *and the carboxylate group, plane* —COO—

	I, II	I, —COO—	II, —COO—
Pannarin	123.6	39.2	41.9
Eriodermin	115.0	44.7	45.5
Variolaric acid	120.5	49.8	41.3
2-Chlorounguinol	117.5	42.7	45.5

There is a relatively strong intramolecular hydrogen bond involving the formyl substituent at C(3) and the hydroxyl substituent at C(4); see Table 2 and Fig. 1.

The Cambridge Structural Database (1991, Version 4.20) contains information on five depsidones only; namely, the iodoacetate derivative of vicanicin, nidulin (McMillan, 1964), eriodermin (Connolly, Freer, Kalb & Huneck, 1984), the diacetate derivative of variolaric acid (Brassy, Bodo & Molho, 1977), and 2-chlorounguinol monohydrate (Kawahara, Nakajima, Satoh, Yamazaki & Kawai, 1988). Atomic coordinates were available for the last three only and showed the bond lengths and angles in rings I and II and the heterocycle to be very similar to those in pannarin. The overall conformations of eriodermin and 2-chlorounguinol are very similar, but different to those in variolaric acid and pannarin as shown in Table 3.

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Structure and Coloration of 1,1'-Spirobiindan-4,4',7,7'-tetrol

BY H. UEKUSA, S. OHBA* AND Y. SAITO

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan

AND T. TANAKA†

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

Abstract. Mo $K\alpha$, $\lambda = 0.71073$ Å. Dihydrate, (I), $C_{17}H_{16}O_4.2H_2O$, $M_r = 320.33$, monoclinic, $I2/a$, $a = 14.371$ (2), $b = 10.229$ (2), $c = 10.469$ (1) Å, $\beta = 99.44$ (1)°, $V = 1518.1$ (4) Å^3, $Z = 4$, D_m (CH_2Cl_2/CCl_4) = 1.40 (2), $D_x = 1.40$ Mg m^{-3}, $\mu = 0.099$ mm^{-1}, $F(000) = 680$, $T = 297$ (2) K, $R = 0.044$ for 926 unique reflections. Monohydrate, (II), $C_{17}H_{16}O_4.H_2O$, $M_r = 302.31$, monoclinic, $P2_1/c$, $a = 10.562$ (2), $b = 13.131$ (2), $c = 9.921$ (2) Å, $\beta = 91.13$ (1)°, $V = 1375.7$ (4) Å^3, $Z = 4$, $D_x = 1.46$ Mg m^{-3}, $\mu = 0.100$ mm^{-1}, $F(000) = 640$, $T = 120$ (2) K, $R = 0.049$ for 2268 unique reflections. Sesquidioxane solvate, (III), $C_{17}H_{16}O_4.1.5C_4H_8O_2$, $M_r = 416.45$, triclinic, $P\bar{1}$, $a = 9.351$ (1), $b = 12.394$ (1), $c =$

* To whom correspondence should be addressed.
† Present address: 2461-20, Seiran, Kasemachi-Nakabaru, Saga 840, Japan.