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9-Methylrubrofusarin: 5,6-Dihydroxy-8-methoxy-2,9-dimethyl-4*H*-naphtho[2,3-*b*]pyran-4-one

By E. RODULFO DE GIL, A. VALENTINA RIVERA AND MILES KEOGH

Departamento de Quimica, Facultad de Ciencias and Instituto de Investigaciones Quimicas, Facultad de Farmacia, Universidad de Los Andes, Merida, Venezuela

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Abstract. C₁₆O₅H₁₄, monoclinic, *P*2₁/*c*, *a* = 10.910 (5), *b* = 8.245 (5), *c* = 14.459 (8) Å, β = 99.24 (3)°, *Z* = 4, *U* = 1284 Å³, *D*_x = 1.48 g cm⁻³. The structure was determined by direct methods and refined to an *R* of 0.065 for 834 unique diffractometer data. The ring system is essentially planar and there are no intermolecular hydrogen bonds.

Introduction. Structural studies by spectroscopic means on this natural product were not conclusive (Keogh & de Gil, 1977). The present crystallographic study was undertaken to provide information on the structure of the molecule.

A crystal 0.25 × 0.25 × 0.30 mm was mounted along *a* on a Norelco Pailred diffractometer and 2299 intensities were collected with Mo *K*α radiation (graphite monochromator). Averaging equivalent reflexions after application of *L*_p corrections gave 834 unique data with *I* > 3σ(*I*). No absorption corrections were applied. The structure was solved by direct methods, all the data being used in the calculation of the overall scale and temperature factors by Wilson's method, the *F*'s normalized in parity groups and the geometry of the molecule taken into account. The phase solution with the highest 'combined figure of merit' obtained from the application of *MULTAN* to 200 reflexions with *E* > 1.69 gave an *E* map from which the positions of all the ring atoms were obtained. The terminal atoms were found by successive Fourier syntheses. The structure was refined by full-matrix least squares with isotropic temperature factors for all the atoms in the rings (anisotropic for the terminal atoms). All the H atoms were inserted in geometrically cal-

culated positions, except those of the two hydroxyl groups which were in the positions located from a difference map. Unit weights were used throughout the refinement which finally converged to an *R* of 0.065.

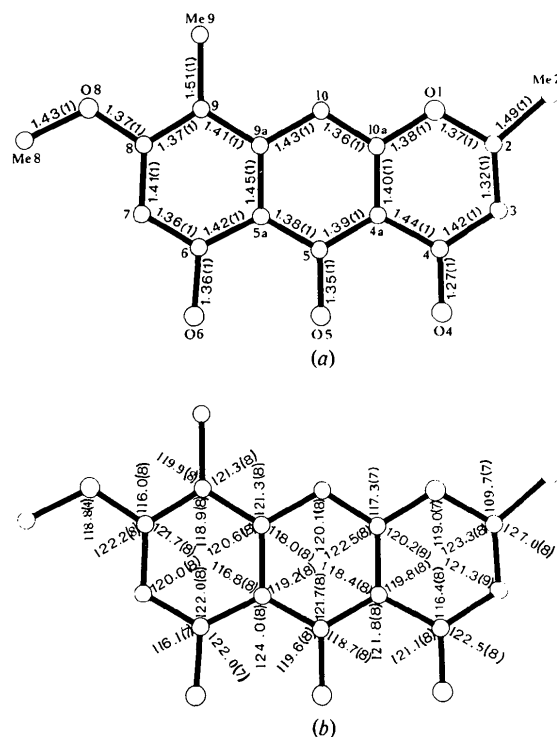


Fig. 1. (a) Bond lengths (Å) and (b) bond angles (°) for 9-methylrubrofusarin.

Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
O(1)	6341 (5)	2628 (8)	-685 (4)	38 (2)
C(2)	7530 (8)	2057 (11)	-627 (6)	37 (2)
Me(2)	8090 (8)	2676 (13)	-1434 (6)	*
C(3)	8062 (8)	1111 (12)	55 (6)	41 (3)
C(4)	7422 (8)	616 (12)	790 (6)	38 (2)
O(4)	7909 (5)	-308 (9)	1449 (4)	*
C(4a)	6180 (7)	1221 (11)	751 (7)	29 (2)
C(5)	5457 (8)	820 (12)	1430 (6)	34 (2)
O(5)	5948 (5)	-154 (8)	2144 (4)	*
C(5a)	4261 (7)	1405 (11)	1392 (6)	31 (2)
C(6)	3486 (7)	1039 (11)	2066 (6)	33 (2)
O(6)	3873 (5)	67 (8)	2816 (4)	*
C(7)	2311 (7)	1633 (11)	1997 (6)	32 (2)
C(8)	1832 (8)	2628 (12)	1236 (6)	36 (2)
O(8)	646 (5)	3218 (8)	1120 (4)	*
Me(8)	-57 (8)	3029 (13)	1863 (5)	*
C(9)	2505 (8)	2999 (11)	540 (6)	33 (2)
Me(9)	1918 (8)	3980 (13)	-294 (6)	*
C(9a)	3737 (7)	2433 (11)	618 (6)	27 (2)
C(10)	4491 (7)	2817 (11)	-71 (6)	35 (2)
C(10a)	5662 (7)	2219 (11)	8 (6)	29 (2)

* Anisotropic temperature factors have been deposited (see footnote below).

Table 2. Hydrogen atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
H(Me21)	8119	3900	-1429	70
H(Me22)	7584	2327	-2053	70
H(Me23)	8960	2259	-1414	70
H(3)	8955	727	65	57
H(O5)	6336	-990	1790	89
H(O6)	4741	-313	2869	63
H(7)	1775	1327	2480	57
H(Me81)	355	3574	2452	70
H(Me82)	-157	1832	2011	70
H(Me83)	-915	3497	1682	70
H(Me91)	1890	3301	-892	70
H(Me92)	2414	4981	-375	70
H(Me93)	1050	4291	-241	70
H(10)	4148	3520	-628	57

Positional and isotropic thermal parameters are given in Tables 1 and 2, and the resulting bond lengths and angles in Fig. 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32345 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The whole molecule does not appear to be planar since the standard deviation of the atoms from the least-squares plane is 0.046 Å, with a maximum deviation of 0.143 Å for Me(8). The ring system is essentially planar with Me(9) lying below the plane (0.139 Å) and Me(8) above (0.141 Å).

A comparison between 9-methylrubrofusarin and rubrofusarin (Stout & Jensen, 1962) reveals a close similarity in bond lengths and angles, except for C(3)—C(4) (1.42 vs 1.48 Å) and the orientation of Me(8)—O(8). In 9-methylrubrofusarin Me(8)—O(8) is rotated 120° from the corresponding orientation in rubrofusarin, which could be due to steric effects. The mean C—C distance in the two benzenoid rings is 1.398 Å; however, C(5a)—C(9a) shows a significant deviation from the mean. The C—O single bonds are as expected. The pyrone ring is closer in angles and distances to those reported for 4'-bromo-5-hydroxyflavone (Hayashi, Kawai, Ohno, Iitaka & Akimoto, 1974) and genisteine (Breton, Precigoux, Courseille & Hospital, 1975) than those for rubrofusarin (Stout & Jensen, 1962) and 3',5,5',6-tetramethoxyflavone (Ting, Watson & Dominguez, 1972).

A difference synthesis showed peaks for H(O5) and H(O6) 0.99 Å from their respective O atoms. Even though the positions of these H atoms are less certain, there appear to be intramolecular hydrogen bonds asymmetrically located and somewhat displaced from the line joining O(4)···O(5) and O(5)···O(6), with approximate angles of 100 and 115° for C(5)—O(5)—H(O5) and C(6)—O(6)—H(O6) respectively. Other angles are C(4)—O(4)···H(O5) = 95°, O(4)···H(O5)—O(5) = 113°, C(5)—O(5)···H(O6) = 104° and O(5)···H(O6)—O(6) = 135°. Distances O(4)···O(5), O(5)···O(6), H(O5)···O(4) and H(O6)···O(5) are 2.509 (8), 2.609 (8), 1.94 and 1.82 Å. No intermolecular hydrogen bonds are formed.

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