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## Coarctatin Dibromide

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**Abstract.**  $C_{11}H_{10}O_5Br_2$ , M.W. 382, monoclinic,  $P2_1/c$ ,  $Z=8$ , two molecules in the asymmetric unit;  $a=8.2146$  (17),  $b=26.6474$  (41),  $c=14.3132$  (32) Å,  $\beta=124.287$  (16)°,  $V=2588.59$  Å<sup>3</sup>,  $D_x=1.181$  g cm<sup>-3</sup>.  $R=0.089$  for 3712 measured intensities. This study confirms the structure recently proposed for coarctatin on the basis of its spectroscopic properties.

**Introduction.** Coarctatin (7,8-dihydro-8-ethylidene-4-methoxy-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione,  $C_{11}H_{10}O_5$ , Fig. 1) is a metabolite of the fungus *Chaetomium coarctatum*. Crystals of both this compound and its dibromo derivative (Fig. 2) were examined and the latter were selected as the more amenable to structure determination by X-ray crystallography.

Crystals were supplied by Dr W. B. Turner, ICI Ltd (Pharmaceuticals Division). Three-dimensional intensity data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer by the moving-crystal moving-counter technique in the range  $3^\circ \leq \theta \leq 70^\circ$  using graphite-monochromatized  $Cu K\alpha_1$  X-rays,  $\lambda=1.54051$  Å. Of 4902 independent reflexions accessible in principle, 3712 were measured and used in the analysis. The systematic absences  $0k0$  for  $k=2n+1$  and  $h0l$  for  $l=2n+1$  determined the space group as  $P2_1/c$  (No. 14). Lorentz and polarization factors were applied to the intensity data and approximate values of the temperature and scale factors were obtained from a Wilson plot. No correction was made for absorption.

Initially we attempted to locate the bromine atoms from a three-dimensional Patterson map, but there was so much overlapping of the Br-Br vectors that the individual peaks could not be isolated successfully. However, these atoms were readily located using *MULTAN* (Germain, Main & Woolfson, 1971), although

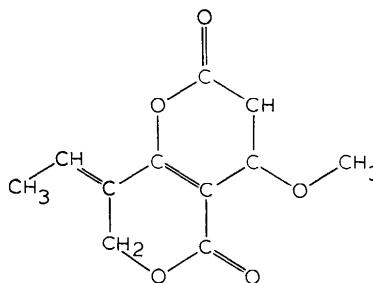


Fig. 1. Coarctatin.

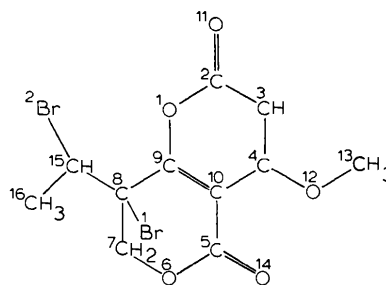


Fig. 2. Coarctatin dibromide.

Table 1. Fractional atomic coordinates ( $\times 10^5$ ) and their estimated standard deviations

	Molecule A			Molecule B		
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Br(1)	47377 (23)	7233 (7)	45328 (13)	122783 (23)	7525 (7)	114496 (12)
Br(2)	-5150 (25)	10046 (7)	48449 (15)	94031 (24)	6048 (7)	75768 (12)
O(1)	1661 (118)	11986 (31)	28764 (31)	78899 (106)	10302 (32)	90708 (64)
C(2)	-10953 (155)	14772 (50)	18490 (96)	61207 (151)	13016 (50)	86449 (90)
C(3)	-6438 (160)	19906 (48)	18775 (89)	61802 (166)	18254 (47)	85031 (95)
C(4)	9661 (161)	22055 (46)	27975 (92)	79139 (169)	20660 (48)	88852 (87)
C(5)	42133 (157)	20766 (44)	47700 (90)	116965 (164)	20084 (47)	101333 (96)
O(6)	51334 (111)	17893 (32)	57131 (64)	132502 (111)	17194 (33)	104665 (72)
C(7)	40589 (184)	14037 (46)	58302 (95)	129494 (173)	12387 (48)	99236 (109)
C(8)	28513 (166)	10838 (45)	47660 (99)	113022 (172)	9541 (52)	98499 (96)
C(9)	17399 (167)	14229 (46)	37712 (92)	95927 (149)	12765 (43)	94628 (86)
C(10)	22289 (154)	18967 (44)	37914 (89)	97185 (152)	17745 (45)	94501 (85)
O(11)	-23960 (122)	12344 (39)	11042 (71)	47121 (117)	10445 (37)	83742 (70)
O(12)	14803 (123)	26840 (33)	28869 (68)	81105 (123)	25484 (34)	87535 (72)
C(13)	2190 (208)	30095 (52)	19173 (108)	63098 (190)	28334 (56)	79613 (111)
O(14)	50867 (126)	24275 (36)	47571 (73)	119865 (122)	24352 (34)	104881 (71)
C(15)	16601 (192)	6724 (48)	48740 (113)	108165 (187)	4299 (51)	92242 (105)
C(16)	28410 (234)	3355 (53)	59649 (114)	125881 (233)	1143 (63)	95437 (138)

on the electron-density map produced using the phases determined by *MULTAN* the lighter atoms could not be distinguished. Using the phase angles specified by the bromine atoms alone a three-dimensional Fourier synthesis revealed the positions of all the remaining non-hydrogen atoms.

The positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations on the 1906A computer of Leeds University Computing Laboratory using the X-RAY 70 suite of programs (Stewart, Kundell & Baldwin, 1970) to an *R* value of 0.089. The 1190 unmeasured weak reflexions were assigned an intensity equal to one half of the minimum measured intensity and an additional cycle of *SFLS* calculations which included these reflexions gave a residual *R* = 0.116. The atomic scattering factors used were those in *International Tables for X-ray Crystallography* (1962). The positions of the hydrogen atoms were not determined.

A diagram showing the numbering of the atoms is given in Fig. 2. Atomic coordinates with their estimated standard deviations are in Table 1. Bond lengths, bond angles, and important torsional angles are given in Tables 2, 3 and 4.\*

**Discussion.** The structure of coarctatin shown in Fig. 1 has recently been proposed from an analysis of its i.r., u.v., p.m.r. and c.m.r. spectra (Burrows, Turner & Walker, 1975). However, from this work it was not possible to define the double-bond stereochemistry by chemical means, so an X-ray crystallographic analysis of the dibromo derivative was undertaken and this study confirms the proposed structure.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31014 (24 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) (*e.s.d.'s in parentheses*)

	Molecule A	Molecule B
O(1)—C(2)	1.439 (21)	1.417 (18)
O(1)—C(9)	1.343 (23)	1.348 (17)
C(2)—C(3)	1.412 (20)	1.415 (19)
C(2)—O(11)	1.189 (20)	1.206 (17)
C(3)—C(4)	1.360 (24)	1.364 (21)
C(4)—C(10)	1.454 (22)	1.451 (21)
C(4)—O(12)	1.327 (16)	1.322 (16)
C(5)—O(6)	1.353 (18)	1.328 (17)
C(5)—C(10)	1.509 (27)	1.481 (23)
C(5)—O(14)	1.185 (17)	1.213 (16)
O(6)—C(7)	1.425 (19)	1.445 (17)
C(7)—C(8)	1.526 (22)	1.502 (22)
C(8)—Br(1)	2.005 (17)	2.026 (20)
C(8)—C(9)	1.488 (21)	1.463 (20)
C(8)—C(15)	1.534 (22)	1.584 (20)
C(9)—C(10)	1.320 (18)	1.332 (17)
O(12)—C(13)	1.460 (21)	1.470 (23)
C(15)—Br(2)	1.973 (18)	2.010 (25)
C(15)—C(16)	1.574 (24)	1.511 (25)

Table 3. Bond angles (°) (*e.s.d.'s in parentheses*)

	Molecule A	Molecule B
C(9)—O(1)—C(2)	119.8 (10)	120.2 (10)
O(1)—C(2)—O(11)	113.7 (12)	114.5 (12)
O(1)—C(2)—C(3)	116.4 (9)	117.1 (11)
C(3)—C(2)—O(11)	129.9 (11)	128.2 (12)
C(2)—C(3)—C(4)	122.2 (10)	121.2 (11)
C(3)—C(4)—C(10)	118.5 (12)	118.7 (12)
C(3)—C(4)—O(12)	125.6 (10)	125.7 (11)
C(10)—C(4)—O(12)	115.9 (9)	115.6 (12)
O(6)—C(5)—C(10)	116.8 (11)	117.9 (11)
O(6)—C(5)—O(14)	117.3 (9)	118.1 (10)
C(10)—C(5)—O(14)	125.7 (11)	123.7 (12)
C(5)—O(6)—C(7)	119.4 (8)	118.8 (8)
O(6)—C(7)—C(8)	112.5 (13)	111.1 (14)
C(7)—C(8)—C(9)	108.6 (10)	111.4 (12)
C(7)—C(8)—Br(1)	107.8 (9)	106.7 (7)
C(7)—C(8)—C(15)	113.1 (13)	114.5 (14)
Br(1)—C(8)—C(9)	104.3 (11)	105.6 (11)
Br(1)—C(8)—C(15)	105.7 (9)	102.6 (9)
C(9)—C(8)—C(15)	116.6 (10)	114.9 (9)
O(1)—C(9)—C(10)	124.3 (10)	123.3 (11)
C(8)—C(9)—O(1)	112.6 (10)	114.9 (11)
C(8)—C(9)—C(10)	123.0 (9)	121.7 (12)
C(4)—C(10)—C(5)	122.1 (11)	122.6 (11)
C(4)—C(10)—C(9)	118.6 (9)	118.6 (11)
C(5)—C(10)—C(9)	118.7 (9)	118.4 (10)
C(4)—O(12)—C(13)	117.5 (8)	117.5 (10)
C(8)—C(15)—C(16)	115.8 (11)	115.3 (10)
C(8)—C(15)—Br(2)	107.4 (9)	104.7 (18)
Br(2)—C(15)—C(16)	108.8 (13)	107.8 (13)

Table 4. Torsion angles (°)

	Molecule A	Molecule B
Br(2)—C(15)—C(8)—C(7)	71.8	-74.3
Br(2)—C(15)—C(8)—C(9)	-54.7	56.5
C(16)—C(15)—C(8)—C(9)	-176.4	174.7
C(16)—C(15)—C(8)—C(7)	-49.9	43.9
Br(2)—C(15)—C(8)—Br(1)	-170.3	170.5
C(16)—C(15)—C(8)—Br(1)	68.0	-71.3
C(13)—O(12)—C(4)—C(3)	-0.1	-11.7
C(13)—O(12)—C(4)—C(10)	-178.4	165.8

There are no unusual features in the molecule. All bond lengths and angles are within the normally accepted range of values. The two molecules in the asymmetric unit are almost mirror images of each other. The only significant deviations from exact mirror symmetry lie in the torsion angles about C(15)—C(8) and C(4)—O(12) (see Table 4). We note that the bond C(4)—O(12) (1.327 Å in molecule A and 1.322 Å in molecule B) has considerable double-bond character which restricts the torsion angle C(3)—C(4)—O(12)—C(13) to values close to zero. The repulsion of the bulky bromine atoms constrains the angle Br(1)—C(8)—C(15)—Br(2) to values close to 180°.

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## 1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN)

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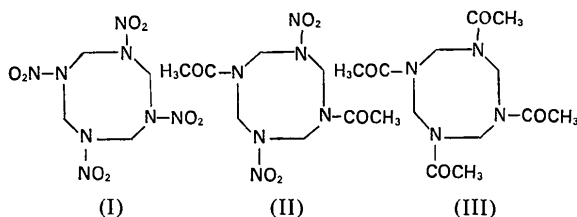
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**Abstract.**  $C_8H_{14}N_6O_6$ , monoclinic,  $P2_1/c$ ,  $a=7.422(1)$ ,  $b=13.253(2)$ ,  $c=6.156(1)$  Å,  $\beta=103.38(1)^\circ$ ,  $Z=2$ ,  $D_x=1.636$ ,  $D_m=1.63$  g cm $^{-3}$ ,  $F(000)=304$ . X-ray intensities were measured with Mo  $K\alpha$  radiation. The structure was solved by direct methods and refined by full-matrix least-squares calculations to final  $R$  and  $R_w$  values of 4.1 and 4.8%, respectively, for 1149 observed reflections.

**Introduction.** Tetraazacyclooctane derivatives are important intermediates in the synthesis of cyclotetramethylenetetranitramine (I), also known as HMX, which is a well known explosive and a by-product in the manufacture of cyclotrimethylenetrinitramine (RDX). One such derivative, 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (II), hereafter referred to as DADN, is obtained in good yields from 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane without formation of triazine products (Yoshida, Sen & Thyagarajan, 1973; Siele, Warman & Gilbert, 1974).



Chemically, DADN is closely related to HMX and to its tetraacetyl analog, 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane, also known as TAT (III). All these compounds are based on the same eight-mem-

bered C–N ring, but the side groups vary from compound to compound. The presence of two –NO<sub>2</sub> and two –COCH<sub>3</sub> groups suggests that many important structural features in DADN must be different from those found in the  $\alpha$ ,  $\beta$  and  $\delta$  modifications of HMX and in the stable phase of TAT (Eiland & Pepinsky, 1955; Cady, Larson & Cromer, 1963; Choi & Boutin, 1970; Cobble-dick & Small, 1974; Choi, Abel, Dickens & Stewart, 1973). The X-ray study of DADN, therefore, was undertaken not only to provide information necessary for the characterization of the compound, but also to permit a comparison of the packing and of the molecular configuration of DADN with those of the previously determined structures.

Colorless crystals of DADN were obtained by evaporation of a benzene solution. Crystal symmetry and approximate lattice parameters were determined from zero- and upper-level precession photographs. The  $2\theta$  angles of 12 strong reflections in the range 20–45° were measured with a diffractometer using Mo  $K\alpha$  radiation ( $\lambda=0.710688$  Å) and the cell parameters were refined by least-squares analysis.

A plate-like crystal of approximate dimensions 0.2 × 0.35 × 0.5 mm was mounted on a three-circle diffractometer equipped with a Si(Li) solid-state detector (Hubbard, 1973). Intensities were measured with the  $2\theta$  scan method for all the reflections in a hemisphere with  $2\theta$  up to 55° with Mo  $K\alpha$  radiation. In total, 3064 reflections were measured. Intensities which were less than four times the standard deviation were considered ‘unobserved’. Equivalent reflections were merged into a unique set of 1342 reflections of which 193 were unobserved (the agreement index of equivalent reflections was 0.025). The observed in-