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An Aglycone Precursor of Anthracycline Antibiotics: $C_{23}H_{22}O_9$

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Abstract. Methyl 5-(1,4-dihydroxy-9,10-dioxo-2-anthryl)-2,3-isopropylidene-α-D-lyxofuranoside, $M_r = 442$, trigonal, $P3_221$ (No. 154), $a = 10.654$ (2), $c = 31.981$ (4) Å, $U = 3144$ (2) Å^3, $Z = 6$, $D_m = 1.40$ (1) (carbon tetrachloride/n-pentane flotation), $D_x = 1.38$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ(Mo $K\alpha$) = 1.02 cm^{-1}, $F(000) = 1392$, $T = 298$ K, R $(wR) = 0.026$ (0.026) for 1379 reflections with $I > 3\sigma(I)$. In the crystal structure of this anthracyclinone precursor, in a relatively uncommon space group, there are intramolecular chelate hydrogen bonds with 2.54 (1) and 2.56 (1) Å O—O distances between ketone and hydroxyl groups on each side of the rigid planar quinizarin moiety and a 2.70 (1) Å intramolecular bond from O(15) on the bridging C atom to the ring O(17) atom of the isopropylidene-blocked lyxofuranose ring. Torsion angles at the new C(15)—O(15)H chiral C atom are 14.1 (4)° with C(2)—C(3) of the quinizarin and 64.3 (3)° with C(16)—C(17) in the bridge to the sugar.

Introduction. Structure analyses of precursors to synthetic anthracyclinone anti-cancer antibiotics can be helpful in establishing the diastereomeric products in stereospecific condensation reactions (Johnson, Jones, Mincher & Shaw, 1983). In its formation (Mincher, Shaw & Declercq, 1983), methyl 5-(1,4-dihydroxy-9,10-dioxo-2-anthryl-2,3-isopropylidene-α-D-lyxofuranoside forms a new chiral atom, C(15), linking the planar tricyclic quinizarin (or 1,4-dihydroxyanthraquinone) moiety to the furanose ring. If the persistence of the D sugar is accepted, the analysis confirms the prediction of an S isomer as predominant, in accord with an extension of Cram's rule (Cram & Elhafez, 1952) of asymmetric induction. It also provides an accurate determination of the dimensions of the quinizarin moiety.

Experimental. Dark-red well-formed rhombohedral crystals (provided by Dr D. J. Mincher). X-ray photographic study initially indicated a C-centred orthohexagonal cell with systematic absences in 00l reflections for $l \neq 3n$ consistent with 3_1, 3_2, 6_2 or 6_4 screw axes parallel to c. A second crystal mounted parallel to the 32 Å c axis gave 60° axial separations in Weissenberg photographs indicating a hexagonal axis system. The morphology of the well-developed rhombohedral crystals suggested point group 32. Crystal dimensions $0.3 \times 0.3 \times 0.4$ mm. Enraf-Nonius CAD-4F diffractometer (Rothamstead Experimental Station) with graphite-monochromatized Mo $K\alpha$ X-radiation used to confirm cell dimensions (from 25 reflections with $18 < 2\theta < 21°$) and to collect intensity data from the unique part ($\frac{1}{6}$th) of reciprocal space: bisecting mode, ω–2θ scan, maximum time 90 s, 2θ range 2.5–50.0°, index range $h,k -11l/-1$ and h,k 0/11 for l 0/34; no significant decline in intensities of $4\bar{4}4$ and $0,\bar{3},10$ standard reflections (remeasured every 3 h). 2903 measured data with 2557 observed. Observation of (formally Friedel) equivalent reflections among the data collected suggested the enantiomorphous pair of space groups $P3_121$ and $P3_221$ rather than $P3_112$ and $P3_212$.

Direct-methods solution by MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) in $P3_121$ with 2508, formally unique, data led to the opposite enantiomer from that required based on the known sugar configuration. Coordinates inverted and space group changed to $P3_221$. The diffraction (Laue) symmetry of $P3_221$ is, however, $3m$ and so the 2557 observed data were merged (neglecting the effects of anomalous scattering for such light atoms with Mo X-radiation and assuming $F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$) to give 1514 averaged data ($R_{int} =$

Table 1. *Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\mathring{A}^2 \times 10^3$)*

	x	y	z	U_{eq}*
C(1)	10946 (3)	4948 (3)	7481 (1)	51 (1)
C(2)	12243 (3)	4888 (3)	7461 (1)	51 (1)
C(3)	12325 (3)	3971 (3)	7178 (1)	59 (1)
C(4)	11179 (3)	3118 (3)	6905 (1)	58 (1)
C(5)	6243 (3)	1592 (3)	6391 (1)	59 (1)
C(6)	5024 (3)	1699 (4)	6405 (1)	70 (2)
C(7)	4900 (3)	2618 (3)	6685 (1)	65 (2)
C(8)	6032 (3)	3449 (3)	6957 (1)	58 (1)
C(9)	8478 (3)	4207 (3)	7241 (1)	54 (1)
C(10)	8726 (3)	2310 (3)	6636 (1)	54 (1)
C(11)	7395 (3)	2416 (3)	6659 (1)	50 (1)
C(12)	7281 (3)	3342 (3)	6946 (1)	49 (1)
C(13)	9801 (3)	4129 (3)	7211 (1)	47 (1)
C(14)	9920 (3)	3195 (3)	6916 (1)	49 (1)
O(1)	10888 (2)	5854 (2)	7767 (1)	74 (1)
O(4)	11370 (2)	2247 (3)	6639 (1)	87 (1)
O(9)	8331 (2)	4968 (2)	7506 (1)	81 (1)
O(10)	8817 (2)	1488 (2)	6378 (1)	77 (1)
C(15)	13526 (3)	5867 (3)	7734 (1)	56 (1)
O(15)	14754 (2)	5877 (2)	7563 (1)	76 (1)
O(16)	13229 (2)	4074 (2)	8252 (1)	54 (1)
C(16)	13294 (3)	5442 (3)	8196 (1)	51 (1)
C(17)	14477 (3)	6479 (3)	8495 (1)	51 (1)
C(18)	14581 (3)	5476 (3)	8817 (1)	50 (1)
C(19)	13463 (3)	3958 (3)	8682 (1)	49 (1)
O(17)	15876 (2)	7190 (2)	8301 (1)	56 (1)
O(18)	15986 (2)	5661 (2)	8763 (1)	60 (1)
O(19)	12210 (2)	3552 (2)	8922 (1)	61 (1)
C(20)	11124 (4)	2072 (4)	8862 (1)	82 (2)
C(21)	16864 (3)	7020 (3)	8565 (1)	58 (1)
C(22)	17505 (4)	8238 (3)	8883 (1)	87 (2)
C(23)	17942 (4)	6899 (5)	8295 (1)	85 (2)

*Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

0·0407). Blocked-cascade least-squares refinement on F_o with *SHELXTL* (Sheldrick, 1981) on a Data General 'Desktop' minicomputer with scattering factors from *International Tables for X-ray Crystallography* (1974). All non-H atoms refined anisotropically; all non-hydroxyl H atoms incorporated at geometric 'riding' positions for locations of hydroxyl H atoms from difference Fourier map. All H atoms subsequently refined as unconstrained isotropic atoms. Weights $w^{-1} = [\sigma^2(F_o) + g|F_o|]$, $g = 0·00015$; 377 parameters refined with 1379 data $[F_o > 6\sigma(F_o)]$ to give R $(wR) = 0·0263$ $(0·0263)$. No corrections for absorption or extinction; maximum shift: e.s.d. in last four cycles 0·04; final $\Delta\rho$ peaks and troughs $< 0·12$ e $\mathring{A}^{-3}$.

Discussion. Final fractional coordinates of C and O atoms are given in Table 1,* and bond lengths, C—C—C and C—C—O bond angles in Table 2. The asymmetric unit in the non-centrosymmetric crystal

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and interbond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51970 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths ($\mathring{A}$) and bond angles (°)*

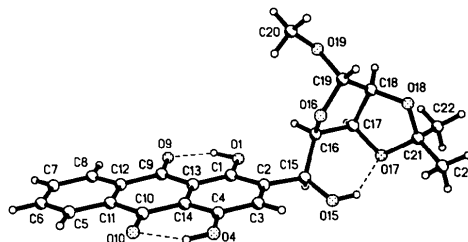|			
C(1)—C(2)	1·416 (5)	C(1)—C(13)	1·390 (3)
C(1)—O(1)	1·352 (4)	C(2)—C(3)	1·367 (4)
C(2)—C(15)	1·513 (3)	C(3)—C(4)	1·403 (3)
C(4)—C(14)	1·385 (5)	C(4)—O(4)	1·347 (4)
C(5)—C(6)	1·360 (5)	C(5)—C(11)	1·390 (3)
C(6)—C(7)	1·381 (5)	C(7)—C(8)	1·390 (3)
C(8)—C(12)	1·392 (5)	C(9)—C(12)	1·480 (3)
C(9)—C(13)	1·456 (5)	C(9)—O(9)	1·237 (4)
C(10)—C(11)	1·480 (5)	C(10)—C(14)	1·454 (3)
C(10)—O(10)	1·241 (4)	C(11)—C(12)	1·396 (4)
C(13)—C(14)	1·421 (4)	C(15)—O(15)	1·412 (4)
C(15)—C(16)	1·531 (3)	O(16)—C(16)	1·435 (4)
O(16)—C(19)	1·416 (4)	C(16)—C(17)	1·526 (3)
C(17)—C(18)	1·529 (4)	C(17)—O(17)	1·431 (3)
C(18)—C(19)	1·515 (3)	C(18)—O(18)	1·419 (4)
C(19)—O(19)	1·406 (3)	O(17)—C(21)	1·429 (4)
O(18)—C(21)	1·421 (3)	O(19)—C(20)	1·427 (3)
C(21)—C(22)	1·514 (4)	C(21)—C(23)	1·495 (5)
C(2)—C(1)—C(13)	120·9 (3)	C(2)—C(1)—O(1)	117·2 (2)
C(13)—C(1)—O(1)	121·9 (3)	C(1)—C(2)—C(3)	118·4 (2)
C(1)—C(2)—C(15)	120·6 (3)	C(3)—C(2)—C(15)	121·0 (3)
C(2)—C(3)—C(4)	121·9 (3)	C(3)—C(4)—C(14)	120·1 (3)
C(3)—C(4)—O(4)	117·2 (3)	C(14)—C(4)—O(4)	122·8 (2)
C(6)—C(5)—C(11)	120·4 (3)	C(5)—C(6)—C(7)	120·9 (3)
C(6)—C(7)—C(8)	119·9 (3)	C(7)—C(8)—C(12)	119·5 (3)
C(12)—C(9)—C(13)	118·7 (3)	C(12)—C(9)—O(9)	119·6 (3)
C(13)—C(9)—O(9)	121·7 (2)	C(11)—C(10)—C(14)	118·7 (3)
C(11)—C(10)—O(10)	120·3 (2)	C(14)—C(10)—O(10)	121·0 (3)
C(5)—C(11)—C(10)	119·8 (3)	C(5)—C(11)—C(12)	119·3 (3)
C(10)—C(11)—C(12)	120·8 (2)	C(8)—C(12)—C(9)	119·6 (3)
C(8)—C(12)—C(11)	120·0 (2)	C(9)—C(12)—C(11)	120·4 (3)
C(1)—C(13)—C(9)	119·6 (3)	C(1)—C(13)—C(14)	119·6 (3)
C(9)—C(13)—C(14)	120·7 (2)	C(4)—C(14)—C(10)	120·3 (3)
C(4)—C(14)—C(13)	119·1 (2)	C(10)—C(14)—C(13)	120·5 (3)
C(2)—C(15)—O(15)	107·3 (2)	C(2)—C(15)—C(16)	113·3 (2)
O(15)—C(15)—C(16)	112·8 (3)	C(16)—O(16)—C(19)	106·7 (2)
C(15)—C(16)—O(16)	109·8 (2)	C(15)—C(16)—C(17)	116·0 (2)
O(16)—C(16)—C(17)	105·1 (2)	C(16)—C(17)—C(18)	103·8 (2)
C(16)—C(17)—O(17)	112·2 (2)	C(18)—C(17)—O(17)	103·9 (2)
C(17)—C(18)—C(19)	105·1 (2)	C(17)—C(18)—O(18)	105·2 (2)
C(19)—C(18)—O(18)	109·0 (2)	O(16)—C(19)—C(18)	105·2 (2)
O(16)—C(19)—O(19)	112·0 (2)	C(18)—C(19)—O(19)	107·0 (2)
C(17)—O(17)—C(21)	108·4 (2)	C(18)—O(18)—C(21)	107·8 (2)
C(19)—O(19)—C(20)	112·8 (2)	O(17)—C(21)—O(18)	104·0 (2)
O(17)—C(21)—C(22)	109·4 (3)	O(18)—C(21)—C(22)	111·1 (2)
O(17)—C(21)—C(23)	108·3 (2)	O(18)—C(21)—C(23)	108·2 (3)
C(22)—C(21)—C(23)	115·2 (2)		

Fig. 1. Projection of the molecular structure showing the atom numbering and intramolecular hydrogen bonds.

structure consists of one molecule (Fig. 1), *i.e.* one diastereomer. Since the mode of synthesis implies persistence of the D sugar, the configuration at the C(15) atom [the benzylic C(1') chiral C atom in sugar nomenclature] is *S*. This is consistent with application of Cram's rule-of-thumb as to nucleophilic attack on the less sterically hindered face of the

carbonyl, *i.e.* that of the smallest substituent group. The new chiral centre, C(15), makes a torsion angle C(3)—C(2)—C(15)—O(15) of 14·1 (3)° with the rigid planar quinizarin and 64·3 (3)° with the sugar C(16)—C(17) (made more rigid by the isopropylidene blocking group). Within the quinizarin, there is intramolecular chelate hydrogen bonding [2·537 (4) and 2·559 (4) Å] between the hydroxyls [C—OH shortened to 1·350 (4) Å] and ketonic O atoms [C=O lengthened to 1·239 (4) Å]. These bond-length consequences of chelation have been noted elsewhere (Courseille, Busetta, Geoffre & Hospital, 1979); they also occur in anthracyclinone antibiotics such as steffimycin B (Arora, 1985). Ring bond lengths are close to those in 1,4-dihydroxyanthraquinone (Nigam & Deppisch, 1980), with high aromaticity in ring *A* [C(5) to C(8)] and some alternation in lengths in ring *C* [C(2)—C(3) is as short as 1·367 (4) Å].

Within the lyxose, the *gauche–gauche* orientation of O(15) with respect to O(17) facilitates a 2·701 (4) Å intramolecular hydrogen bond between these atoms. The blocking group causes O(17) and O(18) to be almost eclipsed and the furanose ring adopts an envelope conformation in which O(16) is displaced 0·51 (5) Å above the C(16)—C(17)—C(18)—C(19) plane [C(17) and C(18) correspond to carbohydrate C(3') and C(2'), respectively]. The dihedral angle of 63·7 (3)° between lyxose C(16)—C(17)—C(18)—C(19) and blocking-group plane O(17)—C(17)—C(18)—O(18) is almost identi-

cal to that in 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (Sheldrick, Mackie & Akrigg, 1985).

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Structure of Hexa-2,4-diyne-1,6-diyl Bis(4-methylbenzoate)

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Abstract. $C_{22}H_{18}O_4$, $M_r = 346\cdot4$, monoclinic, $P2_1/c$, $a = 10\cdot556$ (4), $b = 12\cdot129$ (8), $c = 14\cdot991$ (5) Å, $\beta = 108\cdot12$ (3)°, $U = 1824\cdot2$ Å^3, $Z = 4$, $D_x = 1\cdot25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0\cdot081$ mm^{-1}, $F(000) = 728$, room temperature, $R = 0\cdot062$, $wR = 0\cdot056$ for 1059 reflections with $F_o > 4\sigma(F_o)$. Only one crystal form was obtained from a variety of solvents and these crystals do not undergo heat- or radiation-induced polymerization. The main feature of the crystal structure is an alignment of all the 4-methylbenzoate rings perpendicular to the *z* direction. The shortest *trans* separations between reactive acetylenic C atoms in neighbouring molecules are alternately 4·25 and 6·43 Å.

Introduction. Hexa-2,4-diyne-1,6-diyl bis(benzenesulfonate) (I) (Ando, Bloor, Hursthouse & Motevalli, 1985) and hexa-2,4-diyne-1,6-diyl bis(4-methylbenzenesulfonate) (II) (Enkelmann, Leyrer & Wegner, 1979) both crystallize with molecules arranged in an inclined stack, and both compounds undergo solid-state *trans*-1,4 polymerization according to Scheme