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14. The Crystal and Molecular Structure of 12,13-Dibromopseurotin

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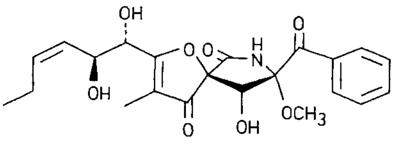
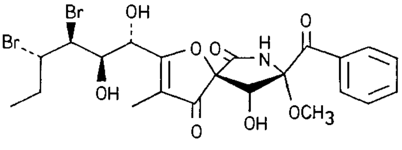
(17. XI. 75)

Summary. The crystal structure of 12,13-dibromopseurotin has been determined by single crystal X-ray analysis. The crystals belong to space group $P2_1$ with $a = 16.75$, $b = 9.63$, $c = 7.42$ Å, $\beta = 95.9°$, $Z = 2$. The structure was solved by the heavy atom technique and refined to $R = 0.062$ with 819 significant reflexions for 299 parameters.

The isolation, chemical and spectral characterisation of pseurotin (**1**), a minor metabolite from the culture filtrate of *Pseudeurotium ovalis* STOLK, is reported in the preceding paper [1]. Although many of the structural fragments of the molecule were identified by spectroscopic data, an X-ray analysis was necessary to reveal the complete structure with the unexpected spiro ring-system. Crystals of the 12,13-dibromo derivative **2** turned out to be suitable for this purpose (*cf.* [1]).



1 Pseurotin



2

Crystal Data. – The 12*S*,13*S*-dibromo derivative of pseurotin, $C_{22}H_{25}Br_2NO_8$, $M = 591.3$, was crystallised from cyclohexane/ethyl acetate 1:1. The thin prismatic crystals belong to the monoclinic space group $P2_1$, $a = 16.75(1)$, $b = 9.631(4)$, $c = 7.425(3)$ Å, $\beta = 95.80(4)°$, $V = 1192$ Å^3, $Z = 2$, $d_c = 1.65$ g cm^{-3}.

Data were determined on a CAD-4 diffractometer using graphite monochromatized Mo$K\alpha$-radiation, ω: $2\,\theta$ scan mode, $\Delta\omega = 1.2° + 0.6 \tan \theta$, 6000 counts per reflexion with a time limit of 120 s. A total of 1654 unique reflexions in the range $1.5° \leqslant \theta \leqslant 22.5°$ were measured, 819 of which had a significant intensity $[I \geqslant 3\sigma(I)$ where $\sigma(I) = (P + B)^{1/2} + 0.02\,(P - B)]$. The observed intensities were converted to absolute structure factors by means of a *Wilson* statistic [2]: $\overline{B} = 4.7$ Å^2, $<|E|> = 0.803$, $<|E^2 - 1|> = 0.871$, $<|E|^2> = 1.001$. No absorption correction was applied.

Structure Analysis and Determination of the Absolute Configuration. – The positions of the non-hydrogen atoms were determined by the heavy atom method. Least squares refinement with anisotropic vibrational parameters for the two bromine atoms and isotropic B-values for C, N and O atoms resulted in an $R = 0.076$. At this stage a structure factor calculation was performed including the anomalous scattering effect of bromine ($f'' = 2.5$ for Mo$K\alpha$-radiation [3]), resulting in $R = 0.0771$. A similar calculation for the inverted structure yielded an R value of 0.0742. According to *Hamilton*'s R factor ratio test [4] the absolute configuration of the structure with the lower R factor is the true configuration at a probability level greatly in excess of 0.995. Further anisotropic refinement of all heavier atoms, with hydrogen atoms in fixed positions[1]), one scale factor and an isotropic extinction factor G [5], reduced the R factor to 0.062 (819 significant reflexions, 299 parameters, final value of $G = 0$ (1), assuming $\overline{T} = 0.02$ cm). Table 1 gives a list of coordinates for the heavier atoms with mean e.s.d.'s. A complete list of structure factors and atomic parameters can be obtained from the authors upon request.

Table 1. *Fractional Coordinates of 12,13-dibromo-pseurotin.* The mean radial LS-computed e.s.d.s' of atomic positions are $\sigma(\text{Br}) = 0.004$, $\sigma(\text{O}) = 0.015$, $\sigma(\text{N}) = 0.018$, $\sigma(\text{C}) = 0.020$ Å

	x	y	z		x	y	z
O(1)	0.9178	0.3746	0.5234	C(18)	1.2126	0.2930	0.9938
C(2)	0.8574	0.4585	0.4467	C(19)	1.2530	0.4102	0.9559
C(3)	0.8582	0.5918	0.5102	C(20)	1.3387	0.4083	0.9969
C(4)	0.9251	0.6004	0.6439	C(21)	1.3803	0.2953	1.0744
C(5)	0.9583	0.4510	0.6752	C(22)	1.3348	0.1827	1.1079
C(6)	0.9256	0.3902	0.8501	C(23)	1.2560	0.1740	1.0663
N(7)	0.9900	0.3561	0.9628	C(24)	1.1019	0.5259	1.1821
C(8)	1.0672	0.3928	0.9109	C(4)—O	0.9534	0.7017	0.7251
C(9)	1.0488	0.4266	0.6945	C(6)—O	0.8541	0.3695	0.8668
C(10)	0.7979	0.3892	0.3197	C(8)—O	1.0936	0.5216	0.9840
C(11)	0.7424	0.3089	0.4337	C(9)—O	0.9534	0.7017	0.7251
C(12)	0.6706	0.2381	0.3124	C(10)—O	0.8323	0.2846	0.2151
C(13)	0.6041	0.1620	0.4102	C(11)—O	0.7123	0.3941	0.5638
C(14)	0.5600	0.2433	0.5434	C(17)—O	1.0984	0.1590	0.9085
C(15)	0.4860	0.1588	0.6023	C(12)—Br	0.6137	0.3714	0.1500
C(16)	0.7985	0.7021	0.4683	C(13)—Br	0.6630	0.0019	0.5298
C(17)	1.1275	0.2745	0.9391				

Results. – The six-membered side chain C(2) to C(15) has four C–C–C–C conformations, three *transplanar* and one (+)-*synclinal*. The *synclinal* fragment contains the two bromine substituted carbon atoms C(12) and C(13) in the middle with a *transplanar* arrangement of Br–C–C–Br (see Fig. 1).

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[1]) Approximate positions for the hydrogen atoms of the C(3)-methyl and the C(8)-methoxy group could be taken from a *ΔF-Fourier* map. However, no definite indications for the location of the three hydroxyl hydrogen atoms could be observed, and therefore these atoms were ignored in the refinement.

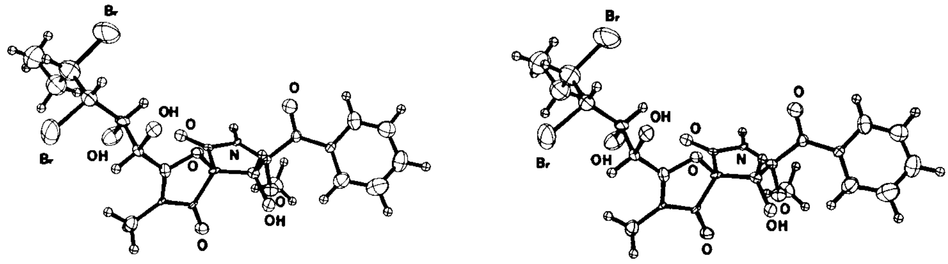

Fig. 1. *Stereoscopic projections of 12,13-dibromopseurotin*

The spiro ring system consists of two five-membered rings: an unsaturated furanone ring, which has a flat envelope conformation with the spiro atom C(5) as flap, and a lactam ring in a rather flat twist conformation with an approximate twofold axis passing through the C(6) carbonyl group and the middle of the C(8)–C(9) bond (see torsion angles in Fig. 2). In the benzoyl group the plane of the carbonyl group is inclined at about 20° to that of the phenyl ring.

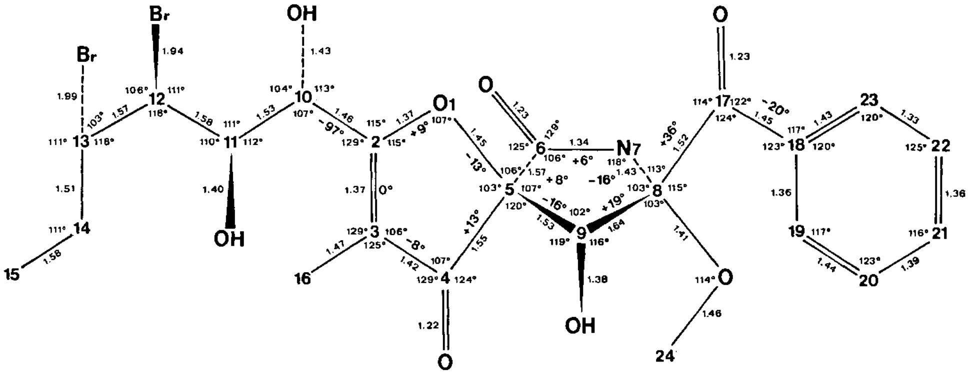

Fig. 2. *Molecular parameters of 12,13-dibromopseurotin.* E.s.d.'s for bond lengths are about 0.03 Å, and for bond angles and torsion angles around 3°

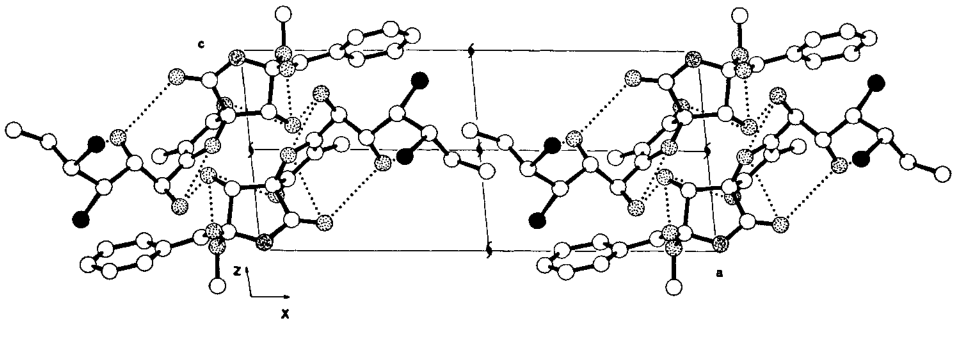

Fig. 3. *Packing of 12,13-dibromopseurotin in the crystal.* Short non-bonded interatomic distances are indicated by dotted lines.

○ = C, ● = Br, rings with points = O, rings with stars = N

The packing of the molecules in the crystal is shown in Fig. 3. A number of short *intra-* and *inter*-molecular distances are summarized in Table 2 and Fig. 3. The final *ΔF-Fourier* map did not give conclusive evidence as to the position of the hydroxyl hydrogen atoms, so that unequivocal assignment of a set of hydrogen bonds was not possible.

Table 2. *Short non-bonded interatomic distances in 12,13-dibromopseurotin*

Atom 1	Atom 2	*d* (Å)	
C(11)–OH	C(6)–O	3.12	*intra*-molecular
C(11)–OH	C(12)–Br	3.34	
C(10)–OH	O(1)	2.71	
C(4)–O	C(9)–OH	3.11	
O(1)	C(6)–O	2.86	
C(9)–OH	C(8)–O	2.66	
C(10)–OH	C(9)–OH	2.96	*inter*-molecular
C(10)–OH	C(6)–O	2.78	

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15. Azidiniumsalze

16. Mitteilung [1]

Struktur-Reaktivitätsbeziehungen in Serien quartärer N-Heteroaromaten: Kinetik der Reaktion heterocyclischer Azidiniumsalze mit Sulfit-Ionen

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Structure-Reactivity-Relationships in Series of Quaternary Heterocyclic Compounds: Reaction Kinetics of Heterocyclic Azidinium Salts with Sulfite Ions. – *Zusammenfassung.* Die Reaktion der Azidiniumsalze **1a–f** mit Sulfit-Ionen, die Isomerisierungs- und Zerfallsreaktion der entstandenen Sulfotriazene **4a–f** und **5a–f** wurden mittels kinetischer Methoden untersucht. Die Säuredissoziationskonstanten der Sulfotriazene **4a–f** und **5a–f** wurden bestimmt und die Geschwindigkeits- und Aciditätskonstanten mit σ_{Het}-Werten korreliert.

In einer früheren Mitteilung [2] wurde der Mechanismus der Reaktion von 2-Azido-3-äthyl-benzthiazolium-tetrafluoroborat (**1e**) mit Sulfit-Ionen untersucht. Die Geschwindigkeits- und Säuredissoziationskonstanten sowie die UV.-Spektren der Edukte und Produkte wurden gemessen. Die Reaktion wurde wie im *Schema 1* angegeben interpretiert: