

[3.34(4), 2.71(4) Å] for hydrogen bonds and the O—H...O angles also deviate too much from linearity (Table 4). Thus, contrary to the solution studies, it is evident that there exist only intermolecular hydrogen bonds in the crystal. The torsional angle H(6)—O(2)—C(5)—C(4) (16°) indicates that H(6)—O(2) almost eclipses C(4)—C(5).

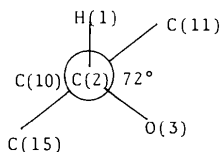


Fig. 5. Newman projection along C(2)—C(10).

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4-Hydroxy-4H-furo[3,2-c]pyran-2(6H)-one (DL-Patulin)

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Abstract. C₇H₆O₄, $M_r = 154.1$, monoclinic, $P2_1/n$, $a = 9.008(2)$, $b = 9.549(2)$, $c = 7.786(2)$ Å, $\beta = 94.80(2)^\circ$, $Z = 4$, $D_m = 1.53(2)$ (floatation), $D_x = 1.535$ g cm⁻³. The structure has been solved by direct methods and refined by least-squares techniques to a final R value of 0.05, based on 1365 reflections. Centrosymmetrically related molecules form dimers via a pair of hydrogen bonds connecting the hydroxyl H atom to the pyran ring O atom. The hydrogen-bond O...O distance is 2.810(2) Å and the OH...O angle is 167(2)°.

Introduction. Crystals of DL-patulin were prepared from the natural product by one of the authors (GW). Details of the isolation and crystallization procedure will be given in a subsequent publication. A pyramidal colorless crystal was selected for film and diffractometer work (maximum dimension 0.2 mm). Precession photographs revealed $2/m$ symmetry. Systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) observed on the films and verified on the diffractometer indicated that the space group is $P2_1/n$. 3013 reflections were measured on a diffractometer out to $\theta = 75^\circ$ with

Cu $K\alpha$ X-radiation ($\lambda = 1.54188$ Å).* The θ - 2θ scan technique was used with a scan range of $(2.0 + 1.0 \tan \theta)^\circ$ and scan speed of 4° min^{-1} . Three standard reflections, measured at regular intervals, showed only statistical fluctuations about the average intensity throughout the course of data collection. The intensities were corrected for Lorentz-polarization effects, but not for absorption ($\mu = 11.2 \text{ cm}^{-1}$). $\sigma(I)$ was estimated by combining a counting statistics term with a factor proportional to scan count: $S^{1.2} + (t_s/t_b)B^{1.2} + 0.01S$, where $S =$ scan count (time t_s) and $B =$ background count (time t_b). Equivalent reflections were then averaged ($R = 0.024$) to yield a data set of 1471 unique reflections of which 93 were systematically extinct. The estimated standard deviation of F_{avg} was calculated from the individual $\sigma(F)$'s and the r.m.s. deviation from the average. A trial model containing all C and O atoms was obtained with *MULTAN* (Germain, Main & Woolfson, 1971). After preliminary refinement, a difference map was calculated and all H atoms in the

* This weighted average wavelength is on the Deslattes & Henins (1973) scale where $\lambda(\text{Cu } K\alpha_1) = 1.5405981$ Å.

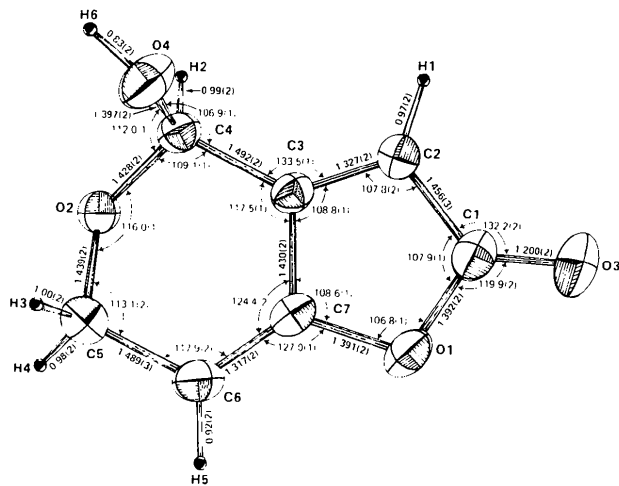


Fig. 1. Bond lengths (Å) and angles (°), and atom numbering of patulin.

molecule were located. A thermal parameter of $U = 0.05 \text{ \AA}^2$ was assigned to each H atom and held fixed. The scattering factors for O and C were from Cromer & Mann (1968). The scattering factors for H were from Stewart, Davidson & Simpson (1965). Anomalous dispersion factors $\Delta f'$ and $\Delta f''$ for O and C atoms were from *International Tables for X-ray Crystallography* (1974).

The model was refined by full-matrix least-squares analysis to a conventional R , based on F , of 0.063 for all reflections. One reflection (006), which apparently was mismeasured, was removed from the data set. The 12 largest reflections, which appeared to be seriously modified by extinction, were omitted from refinement. After further refinement R was 0.050 and R_w $[= \sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ was 0.043. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [o(F_o)]^{-2}$. The average and maximum shift/error for

Table 1. Positional ($\times 10^4$) and thermal ($\text{\AA}^2 \times 10^4$) parameters of the non-hydrogen atoms

Estimated standard deviations are listed in parentheses. The form of the thermal correction is:

$$T = \exp[-2\pi^2(a^*h^2U_{11} + b^*k^2U_{22} + c^*l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	3175 (1)	2811 (1)	3822 (2)	508 (7)	642 (7)	415 (7)	-75 (6)	-71 (5)	-97 (6)
O(2)	4374 (1)	5395 (1)	7855 (1)	495 (7)	374 (5)	465 (7)	11 (5)	-39 (5)	-44 (5)
O(3)	4524 (2)	1056 (1)	2830 (2)	990 (12)	773 (9)	612 (10)	-2 (8)	6 (9)	-320 (8)
O(4)	4335 (2)	3209 (1)	9214 (2)	836 (10)	486 (7)	356 (7)	-121 (6)	-66 (6)	30 (5)
C(1)	4399 (2)	1916 (2)	3930 (2)	610 (11)	507 (9)	456 (11)	-66 (8)	13 (9)	-65 (8)
C(2)	5312 (2)	2245 (2)	5511 (2)	531 (10)	438 (8)	470 (10)	33 (7)	-42 (8)	-49 (7)
C(3)	4658 (2)	3286 (1)	6289 (2)	399 (8)	367 (7)	368 (8)	-45 (6)	-23 (6)	14 (6)
C(4)	4980 (2)	4013 (2)	7975 (2)	452 (9)	385 (8)	397 (9)	3 (7)	-65 (7)	-6 (6)
C(5)	2820 (2)	5494 (2)	7269 (3)	534 (11)	545 (10)	537 (12)	113 (8)	34 (9)	-18 (9)
C(6)	2420 (2)	4680 (2)	5666 (2)	427 (9)	676 (12)	467 (11)	84 (8)	-59 (8)	10 (9)
C(7)	3328 (2)	3673 (2)	5266 (2)	413 (8)	490 (8)	357 (8)	-63 (7)	-32 (7)	-8 (7)

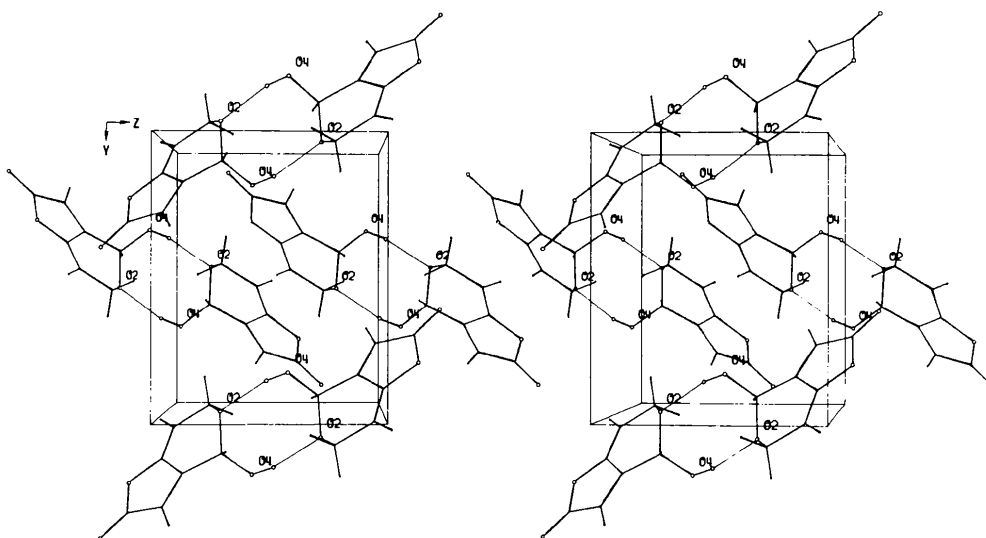


Fig. 2. Stereoscopic packing diagram showing the hydrogen-bonded DL-patulin dimers.

Table 2. *Positional parameters* ($\times 10^3$) *of the hydrogen atoms*

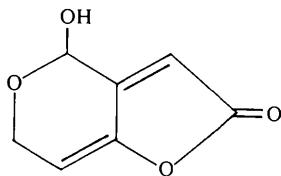
The e.s.d. of each parameter is 2 in the least significant digit.
Thermal parameters for all H atoms were fixed at $U = 0.05 \text{ \AA}^2$.

	x	y	z
H(1)	622	175	590
H(2)	607	417	823
H(3)	228	512	825
H(4)	262	649	705
H(5)	155	489	500
H(6)	472	350	1015

the non-hydrogen parameters were 0.03 and 0.13 respectively.* A final difference electron density map showed no peak greater than 0.2 e \AA^{-3} . Tables 1 and 2 list the atomic parameters. Computer programs used in the refinement were from the X-RAY72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Figs. 1 and 2 were drawn with ORTEP (Johnson, 1965).

Discussion. Patulin is a potent antibiotic and has been found to be toxic to a wide variety of microorganisms, plants, and animals. Reviews by Florey, Chain, Headley, Jennings, Sanders, Abraham & Florey (1949) and by Singh (1966) give the history of the discovery of this important antibiotic. The chemical structure of patulin was elucidated by Woodward & Singh (1949, 1950).

The molecule of patulin with the bond distances, angles and thermal ellipsoids is shown in Fig. 1. The short C—C distances [$C(2) \cdots C(3)$, 1.327(2); and $C(6) \cdots C(7)$, 1.317(2) Å] confirm the system of conjugated double bonds in the formula by Woodward & Singh.



* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32197 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

A least-squares plane through O(3), C(6) and the five atoms of the furan ring shows that these atoms are planar within experimental error ($\pm 0.007 \text{ \AA}$). The hydroxy O atom, O(4), and C(4) are, respectively, 1.46 and 0.10 Å below the plane, and the pyran ring O atom, O(2), is 0.51 Å above the plane.

Since the space group is centrosymmetric, the two possible enantiomorphs of patulin crystallized in a 1:1 ratio. It is possible that the natural product is a mixture of these two. It is more likely, however, that a bond to the asymmetric C(4) atom of the pyran ring broke and reformed during the procedures used to isolate and to crystallize the natural product. Further work is planned to resolve this question and, if possible, to isolate a non-racemic patulin.

The centrosymmetric pairs of D- and L-patulin molecules form dimers as shown in the packing diagrams, Figs. 2 and 3. If one considers O(3) as the head of the molecule, then the dimer is formed by joining the tails of a D- and of an L-patulin molecule. The pyran ring O(2) of a D-patulin molecule is hydrogen bonded to the hydroxyl H atom of an L-molecule and *vice versa*. Thus a pair of equivalent hydrogen bonds is formed, each with the following parameters: $H(6) \cdots O(2)$, 2.00(2), $O(2) \cdots O(4')$, 2.810(2) Å; and $O(4) - H(6) \cdots O(2')$ angle of $167(2)^\circ$. The two patulin molecules illustrated in the center of the cell in Fig. 2 are approximately parallel, as is more clearly shown in Fig. 3. If for one molecule, one calculates a least-squares plane from atomic positions of the five-membered furan ring, then O(2) of the second molecule is 3.08 Å from this plane, and the remaining atoms of the second molecule [except O(4)] range between 3.55 and 3.69 Å from the plane. There are two independent, infinite bands formed by the stacking of the dimers.

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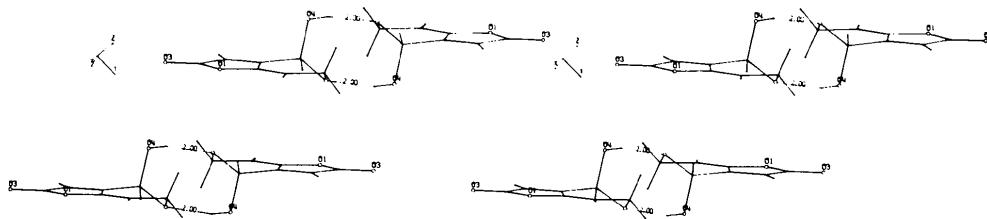


Fig. 3. Stereoscopic view of two DL-patulin dimers related by a center of symmetry. The distance between the dimer pairs is $\sim 3.6 \text{ \AA}$.

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Tri- μ -(trimethylarsine oxide)-hexakis(trimethylarsine oxide)dicalcium(II) Tetraperchlorate — a Dinuclear Calcium Complex

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Abstract. $\{Ca_2[(CH_3)_3AsO]_6\}(ClO_4)_4$, hexagonal, $P6_3/m$, $a = 11.762(1)$, $c = 27.279(2)$ Å; $M_r = 1702.198$, $D_m = 1.71$ (by flotation), $D_x = 1.73$ g cm $^{-3}$, $Z = 2$; $F(000) = 1696$, $\mu(Cu K\alpha) = 91.91$ cm $^{-1}$. Four-circle diffractometer intensity data were refined by the full-matrix least-squares method to give $R = 0.061$ for 1072 data with $F_o^2 \geq 3\sigma(F_o^2)$. The structure consists of Ca atoms each coordinated to six trimethylarsine oxide ligands, three of which bridge to similar adjacent groups forming a dinuclear cationic complex with crystallographically imposed m symmetry. There are three crystallographically distinct perchlorate counter anions, two of which are disordered.

Introduction. Colourless, hexagonal crystals were recrystallized from powder samples (Jameson & Rodley, 1975, 1976) in methanol–triethyl orthoformate solution in the presence of acetonitrile vapour. Weissenberg and precession photography revealed the crystal to be hexagonal. Systematic absences ($00l$: $l = \text{odd}$) are consistent with space groups $P6_3$ and $P6_3/m$. On the basis of the statistical distribution of intensities, $P6_3/m$ was selected and successful refinement verified the choice.

The transparent crystal chosen for data collection had a maximum dimension of about 0.38 mm. Cell dimensions and their e.s.d.'s were determined from least-squares refinement of the setting angles of 12

Table 1. *Final parameters for non-group atoms*

The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Parameters without standard deviations are fixed by symmetry. Variable parameters have been multiplied by 10^4 .

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	$\frac{1}{3}$	$\frac{2}{3}$	1860 (1)	61 (2)	$\beta_{22} = \beta_{11}$	7 (0)	$2\beta_{12} = \beta_{11}$	0	0
As(1)	1205 (1)	3806 (1)	1018 (1)	112 (2)	106 (2)	14 (0)	37 (2)	-9 (1)	-15 (1)
As(2)	4677 (3)	4861 (3)	$\frac{1}{4}$	214 (4)	188 (4)	12 (0)	172 (3)	0	0
O(1)	1673 (8)	4984 (8)	1434 (3)	110 (10)	110 (10)	16 (1)	39 (9)	-7 (3)	-19 (3)
O(2)	3630 (10)	5409 (9)	$\frac{1}{4}$	110 (10)	60 (10)	7 (1)	50 (10)	0	0
C(11)	-230 (30)	2230 (20)	1224 (8)	470 (50)	150 (30)	36 (5)	10 (30)	40 (10)	-30 (10)
C(12)	2590 (20)	3510 (20)	850 (10)	200 (30)	390 (50)	100 (10)	170 (30)	-10 (10)	-120 (20)
C(13)	750 (30)	4250 (30)	430 (7)	720 (80)	430 (50)	24 (4)	390 (60)	-70 (10)	-40 (10)
C(21)	6460 (20)	6370 (30)	$\frac{1}{4}$	90 (30)	470 (60)	24 (5)	170 (40)	0	0
C(22)	4410 (20)	2790 (20)	1929 (5)	490 (50)	300 (40)	18 (3)	320 (40)	0 (10)	-23 (8)
Cl(1)	0	0	0	132 (7)	$\beta_{22} = \beta_{11}$	17 (1)	$2\beta_{12} = \beta_{11}$	0	0
Cl(2)	0	0	$\frac{1}{4}$	350 (20)	$\beta_{22} = \beta_{11}$	49 (4)	$2\beta_{12} = \beta_{11}$	0	0
Cl(3)	$\frac{2}{3}$	$\frac{1}{3}$	783 (7)	230 (10)	$\beta_{22} = \beta_{11}$	58 (4)	$2\beta_{12} = \beta_{11}$	0	0
O(31)	6640 (40)	2220 (30)	700 (10)	780 (80)	680 (90)	160 (20)	470 (80)	30 (30)	-150 (30)
O(32)	$\frac{2}{3}$	$\frac{1}{3}$	1210 (20)	800 (100)	$\beta_{22} = \beta_{11}$	100 (20)	$2\beta_{12} = \beta_{11}$	0	0