t-4-Benzoyloxymethyl-c-4-hydroxy-t-2,t-5-dimethoxy-c-5-methyl-r-3-tetrahydrofuryl Acetate

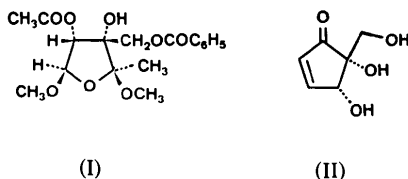By A. Valentina Rivera and George M. Sheldrick*

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Abstract. $C_{17}H_{22}O_8$, $M_r = 354 \cdot 36$, monoclinic, $P2_1/c$, $a = 5 \cdot 822$ (6), $b = 15 \cdot 928$ (6), $c = 19 \cdot 194$ (5) Å, $\beta = 94 \cdot 09$ (1)°, $U = 1775 \cdot 4$ Å³, $Z = 4$, $D_x = 1 \cdot 326$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·85 mm^{-1}. $R = 0 \cdot 040$ for 2018 unique diffractometer data. The five-membered ring adopts an envelope conformation with C(3) out of the plane; the two methoxy groups are *cis*.

Introduction. The title compound (I) was prepared by Marsden (1978) as a potential intermediate in the synthesis of pentenanycin (II), an antibiotic isolated from *Streptomyces eurythermus* (Umino, Takeda, Ito & Okuda, 1974). The crystal structure reported here confirms the structure suggested by Marsden (1978) on the basis of NMR evidence and mode of synthesis.

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CH₃COO   OH                    O
  H─┬─┬─CH₂OCOC₆H₅             ║
  H···┤ ├··CH₃              ┌──OH
  CH₃O  O  OCH₃             │  ''OH
                            └──''OH
    (I)          (II)
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Crystals of (I) were grown from pentane. 2802 data were measured for $5 \le 2\theta \le 112°$ for a crystal $0 \cdot 3 \times 0 \cdot 3 \times 0 \cdot 4$ mm with a Syntex $P2_1$ four-circle diffractometer and graphite-monochromated Cu $K\alpha$ radiation. Equivalents were averaged to give 2018 unique reflexions with $F > 4\sigma(F)$. The structure was solved by multisolution tangent refinement and refined by least squares with complex neutral-atom scattering factors and weights $w = [\sigma^2(F) + 0 \cdot 001F^2]^{-1}$ to $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0 \cdot 047$ and $R = 0 \cdot 040$. H atoms were located in difference syntheses and refined without constraints, except for those bonded to C(16), which were refined as a rigid methyl group (C–H 1·08 Å, H–C–H 109·5°). Individual isotropic temperature factors were assigned to the H atoms; the remaining atoms were anisotropic. Final coordinates and the resulting bond lengths and angles are presented in

Table 1. *Atom coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* (Å² $\times 10^3$)

U_{eq} = one third of the trace of the orthogonalized U_{ij} tensor.

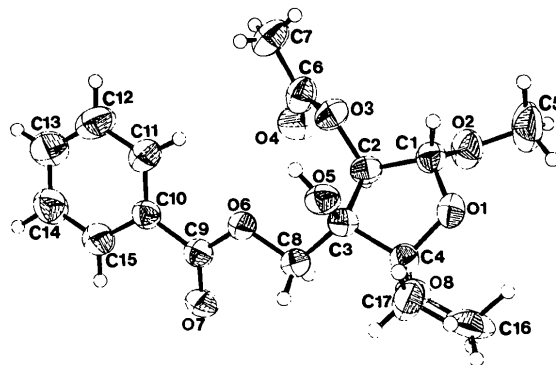|	x	y	z	U_{eq}
O(1)	1192 (2)	2434 (1)	5696 (1)	49 (1)
C(1)	1605 (3)	2084 (1)	5040 (1)	48 (1)
C(2)	174 (3)	2588 (1)	4493 (1)	45 (1)
C(3)	−409 (3)	3398 (1)	4872 (1)	43 (1)
C(4)	−560 (3)	3061 (1)	5621 (1)	45 (1)
C(5)	2455 (6)	704 (2)	5419 (2)	96 (2)
C(6)	722 (5)	2571 (1)	3257 (1)	58 (1)
C(7)	2458 (5)	2764 (2)	2750 (1)	73 (2)
C(8)	−2615 (4)	3831 (1)	4605 (1)	53 (1)
C(9)	−4080 (4)	4519 (1)	3581 (1)	47 (1)
C(10)	−3611 (3)	4841 (1)	2882 (1)	46 (1)
C(11)	−1580 (4)	4693 (2)	2585 (1)	67 (2)
C(12)	−1247 (5)	5008 (2)	1931 (1)	85 (2)
C(13)	−2924 (6)	5476 (2)	1576 (1)	78 (2)
C(14)	−4917 (5)	5639 (2)	1869 (1)	78 (2)
C(15)	−5277 (4)	5323 (2)	2523 (1)	66 (1)
C(16)	−3176 (5)	2253 (2)	6258 (2)	97 (2)
C(17)	−66 (5)	3700 (2)	6188 (1)	65 (1)
O(2)	932 (3)	1240 (1)	4998 (1)	67 (1)
O(3)	1575 (2)	2745 (1)	3917 (1)	51 (1)
O(4)	−1161 (3)	2299 (1)	3125 (1)	88 (1)
O(5)	1470 (2)	3954 (1)	4902 (1)	51 (1)
O(6)	−2276 (2)	4137 (1)	3909 (1)	52 (1)
O(7)	−5915 (3)	4597 (1)	3830 (1)	66 (1)
O(8)	−2746 (2)	2686 (1)	5629 (1)	61 (1)

Fig. 1. The molecule of (I) showing atom labelling and 50% probability thermal ellipsoids for the C and O atoms.

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Table 2. Bond lengths (Å) and angles (°)

O(1)–C(1)	1·413 (3)	O(1)–C(4)	1·427 (3)
C(1)–C(2)	1·523 (5)	C(2)–C(3)	1·531 (5)
C(3)–C(4)	1·543 (5)	C(3)–C(8)	1·514 (5)
C(4)–C(17)	1·504 (5)	C(6)–C(7)	1·485 (5)
C(9)–C(10)	1·479 (4)	C(10)–C(11)	1·369 (4)
C(11)–C(12)	1·378 (5)	C(12)–C(13)	1·370 (5)
C(13)–C(14)	1·350 (5)	C(14)–C(15)	1·382 (5)
C(15)–C(10)	1·382 (4)	C(1)–O(2)	1·401 (3)
C(2)–O(3)	1·441 (3)	C(3)–O(5)	1·406 (3)
C(4)–O(8)	1·407 (3)	C(5)–O(2)	1·438 (4)
C(6)–O(3)	1·356 (3)	C(6)–O(4)	1·190 (4)
C(8)–O(6)	1·449 (3)	C(9)–O(6)	1·332 (3)
C(9)–O(7)	1·208 (4)	C(16)–O(8)	1·428 (4)

O(1)–C(1)–C(2)	106·7 (3)	O(1)–C(1)–O(2)	111·5 (3)
C(2)–C(1)–O(2)	109·2 (3)	C(1)–C(2)–C(3)	104·2 (2)
C(1)–C(2)–O(3)	108·0 (3)	C(3)–C(2)–O(3)	112·0 (3)
C(2)–C(3)–C(4)	100·3 (2)	C(2)–C(3)–O(5)	110·6 (3)
C(4)–C(3)–O(5)	106·1 (2)	C(2)–C(3)–C(8)	115·8 (3)
C(4)–C(3)–C(8)	111·7 (3)	O(5)–C(3)–C(8)	111·5 (3)
O(1)–C(4)–C(3)	104·5 (2)	O(1)–C(4)–O(8)	110·1 (3)
C(3)–C(4)–O(8)	105·6 (2)	O(1)–C(4)–C(17)	107·6 (3)
C(3)–C(4)–C(17)	114·7 (3)	O(8)–C(4)–C(17)	113·9 (3)
O(3)–C(6)–C(7)	110·5 (3)	O(3)–C(6)–O(4)	123·0 (3)
C(7)–C(6)–O(4)	126·5 (3)	C(3)–C(8)–O(6)	107·2 (3)
O(6)–C(9)–O(7)	123·3 (3)	O(6)–C(9)–C(10)	113·4 (3)
O(7)–C(9)–C(10)	123·3 (3)	C(9)–C(10)–C(11)	122·6 (3)
C(9)–C(10)–C(15)	118·5 (3)	C(11)–C(10)–C(15)	118·9 (3)
C(10)–C(11)–C(12)	119·9 (3)	C(11)–C(12)–C(13)	120·6 (4)
C(12)–C(13)–C(14)	120·0 (3)	C(13)–C(14)–C(15)	119·9 (3)
C(10)–C(15)–C(14)	120·6 (3)	C(1)–O(2)–C(5)	112·2 (3)
C(2)–O(3)–C(6)	119·4 (3)	C(8)–O(6)–C(9)	115·8 (3)
C(4)–O(8)–C(16)	115·3 (3)	C(1)–O(1)–C(4)	110·6 (2)

Tables 1 and 2.* Fig. 1 shows the molecule with the atom-numbering scheme.

Discussion. The five-membered ring adopts the envelope conformation with C(3) 0·566 (4) Å out of the plane through O(1), C(1), C(2), and C(4). The bulky benzoyloxymethyl group is *exo* to the ring, and the two methoxy groups are *cis* to one another. The angle at O(1) is close to that in other saturated C_4O rings, but the ring valence angles at the C atoms vary from 100·3 (2) to 106·7 (2)°. There is an intermolecular hydrogen bond [H(5)···O(7′) 2·02 Å, O(5)···O(7′) 2·835 (3) Å, where O(7′) is generated from O(7) by the operation $1 + x, y, z$].

We thank Dr F. Marsden for providing the sample of (I) and the Universidad de Los Andes for a Fellowship to AVR. All calculations were performed with programs written by GMS.

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* A list of structure factors, H-atom coordinates, and anisotropic thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35866 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure de l'Acétamido-1 Fluoro-2 Phényl-1 Cyclohexane cis, obtenu par Fluoroacétamidation Electrochimique du Phényl-1 Cyclohexène

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Abstract. $C_{14}H_{18}FNO$, $M_r = 235\cdot3$, orthorhombic, $Pna2_1$, $a = 9\cdot799$ (1), $b = 16\cdot287$ (2), $c = 7\cdot958$ (1) Å, $V = 1270\cdot0$ (4) Å^3, $Z = 4$, $d_x = 1\cdot23$ Mg m^{-3}, $\mu(\lambda Cu\,K\bar{\alpha}) = 0\cdot72$ mm^{-1}, $F(000) = 504$. Cu $K\bar{\alpha}$ intensities were collected on an automatic four-circle diffractometer and the structure was determined by the direct method and Fourier syntheses. Anisotropic full-matrix least-squares refinement yielded a final R value of 0·030 for the 1117 actually measured reflections. The F atom and the acetamido group are respectively linked in equatorial and axial positions. The structure proves that this electrochemical acetamidation is a *cis* addition. ^{1}H NMR spectra of the *cis* and *trans* isomers are briefly discussed.

Introduction. L'oxydation électrochimique de carbures éthyléniques en solution dans le milieu acétonitrile–sel $(C_2H_5)_4NF$, 3HF (0,3 M) permet d'obtenir des