Discussion. Table 1 lists the coordinates and U_{eq} values for the non-H atoms of (3).* Fig. 1 shows the results of the X-ray analysis and the numbering scheme. There is a *cis* junction between the two six-membered rings (H8a—C8a—C4a—H4a = 0·5°). The bridged six-membered ring is in a normal boat conformation (average absolute value of the four non-planar torsions is 65·2°) while the hydroxylated six-membered ring has a much flatter boat conformation (average absolute value for non-planar torsions is 44·4°). This may be due, in part, to the presence of an intramolecular hydrogen bond with O2 as the donor and O1 as the acceptor (O···O 2·82, H···O 1·89 Å, O—H···O 154·9°). Strain in the molecule is evidenced by the smaller than normal internal ring angles (see Table 2) in the bridged ring system. This is especially true for all the angles in the five-membered ring involving C(9). Packing in this crystal is influenced by the presence of an intermolecular hydrogen bond with O1 as the donor and O2 as the acceptor (O···O 2·80, H···O 1·96 Å, O—H···O 171·8°).

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* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44175 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

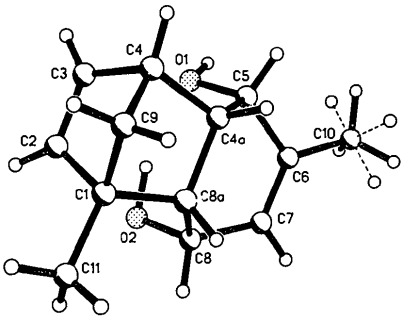

Fig. 1. Results of the X-ray study on (3).

References

CSICSERY, S. M. (1960). *J. Org. Chem.* **25**, 518–521.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MARCHAND, A. P. (1987). *Advances in Theoretically Interesting Molecules*, edited by R. P. THUMMEL, Vol. 1. Greenwich, CN: JAI Press. In the press.

MARCHAND, A. P., LAROE, W. D., SHARMA, G. V. M., SURI, S. C. & REDDY, D. S. (1986). *J. Org. Chem.* **51**, 1622–1625.

MARCHAND, A. P., SURI, S. C., EARLYWINE, A. D., POWELL, D. R. & VAN DER HELM, D. (1984). *J. Org. Chem.* **49**, 670–675.

SHELDRICK, G. M. (1980). *SHELXTL*80: Minicomputer programs for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.

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Structure of a 7α-Methoxy-1-oxacephem: Dichloromethane Solvated (−)-(6*R*,7*R*)-7-{2-[(Difluoromethyl)thio]acetamido}-3-({[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]thio}methyl)-7-methoxy-8-oxo-5-oxa-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic Acid

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Abstract. $C_{15}H_{18}F_2N_6O_7S_2.CH_2Cl_2$, $M_r = 581·39$, monoclinic, $P2_1$, $a = 11·435$ (3), $b = 11·275$ (2), $c = 10·178$ (2) Å, $\beta = 113·52$ (1)°, $V = 1203·2$ (5) Å^3, $Z = 2$, $D_x = 1·605$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·51 mm^{-1}, $F(000) = 596$, $T = 295$ K, $R = 0·028$ for 2580 reflections. The N—C and C=O bonds in the β-lactam amide group are 1·392 (3) and 1·192 (3) Å, respectively. The N atom is displaced by 0·290 (2) Å from the plane of the three attached C atoms.

Introduction. 1-Oxacephems possessing the 1-oxa-1-dethia-3-cephem skeleton are antibiotics which compare favorably with penicillins and cephalosporins. Especially of interest are their 7α-methoxy derivatives which are stable to β-lactamases. One of them,

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latamoxef, is now in clinical use. The structure determination of the title compound, flomoxef, which exhibits more potent antibacterial activity than latamoxef, was undertaken as part of an investigation on the structure–activity relationship for the antibiotics.

Experimental. Platy colorless crystals obtained as a solvate of dichloromethane from acetone–dichloromethane solution. Crystal of dimensions 0·4 × 0·4 × 0·5 mm, Rigaku AFC-5UD diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ scan mode. Cell dimensions calculated from 2θ angles for 25 reflections ($20 < 2\theta < 24°$). Intensities measured up to $2\theta = 54°$ in h 0/14, in k −14/0 and in l −12/11. Three standard reflections monitored every 100 measurements (±1% variation). 2764 unique reflections measured, 83 reflections with $|F_o| \le \sigma(F_o)$ unobserved, no absorption corrections. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located on difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares. Temperature factor of each H atom equal to B_{eq} of the bonded atom. $\sum w|\Delta F|^2$ minimized, $w = [\sigma^2(F_o) + 0{\cdot}00075|F_o|^2]^{-1}$ for

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² ×10²) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O(1)	7570 (1)	8098	6930 (1)	250 (4)
C(2)	8909 (2)	7911 (2)	7366 (2)	246 (5)
C(3)	9720 (2)	8481 (2)	8789 (2)	225 (5)
C(4)	9195 (2)	8772 (2)	9710 (2)	229 (5)
N(5)	7903 (1)	8488 (2)	9326 (2)	238 (4)
C(6)	7217 (2)	7767 (2)	8040 (2)	221 (5)
C(7)	5959 (2)	8360 (2)	7965 (2)	237 (5)
C(8)	6856 (2)	9185 (2)	9189 (2)	256 (5)
O(9)	6724 (2)	10071 (2)	9754 (2)	394 (5)
C(10)	9924 (2)	9297 (2)	11165 (2)	262 (5)
O(11)	10919 (2)	9812 (2)	11479 (2)	379 (5)
O(12)	9345 (2)	9111 (2)	12038 (2)	376 (5)
C(13)	11104 (2)	8599 (2)	9071 (2)	275 (5)
S(14)	11628 (1)	10095 (1)	8890 (1)	335 (2)
C(15)	11324 (2)	10158 (2)	7075 (2)	261 (5)
N(16)	10690 (2)	9401 (2)	6043 (2)	322 (5)
N(17)	10720 (2)	9886 (2)	4837 (2)	370 (6)
N(18)	11332 (2)	10874 (2)	5093 (2)	353 (6)
N(19)	11728 (2)	11066 (2)	6510 (2)	285 (5)
C(20)	12519 (3)	12093 (2)	7207 (3)	359 (7)
C(21)	13906 (2)	11771 (2)	7864 (3)	342 (7)
O(22)	14342 (2)	11349 (2)	6827 (2)	366 (5)
N(23)	5228 (2)	9031 (2)	6700 (2)	260 (4)
C(24)	4702 (2)	8525 (2)	5389 (2)	264 (5)
O(25)	4865 (2)	7482 (2)	5171 (2)	312 (4)
C(26)	3850 (2)	9362 (3)	4219 (2)	329 (6)
S(27)	4006 (1)	9184 (1)	2542 (1)	369 (2)
C(28)	5450 (3)	9981 (2)	2970 (3)	390 (8)
F(29)	6446 (1)	9398 (2)	4021 (2)	510 (6)
F(30)	5722 (3)	9986 (2)	1807 (3)	704 (9)
O(31)	5254 (1)	7528 (2)	8371 (2)	304 (4)
C(32)	4172 (2)	7995 (3)	8558 (3)	417 (8)
Cl(33)	1588 (1)	6939 (1)	4681 (1)	676 (3)
Cl(34)	1561 (1)	6626 (1)	1848 (1)	810 (5)
C(35)	2128 (3)	6104 (3)	3588 (4)	540 (11)

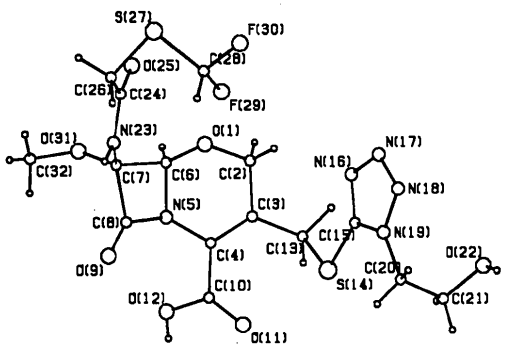

Fig. 1. Perspective view of the molecule with the atom-numbering system.

Table 2. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

O(1)–C(2)	1·430 (3)	C(15)–N(19)	1·343 (3)
O(1)–C(6)	1·394 (3)	N(16)–N(17)	1·357 (3)
C(2)–C(3)	1·516 (3)	N(17)–N(18)	1·286 (3)
C(3)–C(4)	1·340 (3)	N(18)–N(19)	1·346 (3)
C(3)–C(13)	1·497 (3)	N(19)–C(20)	1·466 (4)
C(4)–N(5)	1·406 (3)	C(20)–C(21)	1·499 (5)
C(4)–C(10)	1·501 (3)	C(21)–O(22)	1·417 (4)
N(5)–C(6)	1·473 (3)	N(23)–C(24)	1·352 (3)
N(5)–C(8)	1·392 (3)	C(24)–O(25)	1·225 (3)
C(6)–C(7)	1·560 (3)	C(24)–C(26)	1·527 (4)
C(7)–C(8)	1·565 (3)	C(26)–S(27)	1·797 (4)
C(7)–N(23)	1·439 (3)	S(27)–C(28)	1·775 (4)
C(7)–O(31)	1·402 (3)	C(28)–F(29)	1·379 (4)
C(8)–O(9)	1·192 (3)	C(28)–F(30)	1·339 (5)
C(10)–O(11)	1·202 (3)	O(31)–C(32)	1·426 (4)
C(10)–O(12)	1·320 (3)	Cl(33)–C(35)	1·747 (4)
S(14)–C(15)	1·740 (3)	Cl(34)–C(35)	1·728 (4)
C(15)–N(16)	1·323 (3)		

C(2)–O(1)–C(6)	109·2 (2)	C(4)–C(10)–O(12)	111·8 (2)
O(1)–C(2)–C(3)	113·9 (2)	O(11)–C(10)–O(12)	125·0 (2)
C(2)–C(3)–C(4)	119·9 (2)	S(14)–C(15)–N(16)	129·1 (2)
C(2)–C(3)–C(13)	114·7 (2)	S(14)–C(15)–N(19)	121·9 (2)
C(4)–C(3)–C(13)	125·3 (2)	N(16)–C(15)–N(19)	109·0 (2)
C(3)–C(4)–N(5)	117·7 (2)	C(15)–N(16)–N(17)	104·8 (2)
C(3)–C(4)–C(10)	124·0 (2)	N(16)–N(17)–N(18)	112·0 (2)
N(5)–C(4)–C(10)	118·2 (2)	N(17)–N(18)–N(19)	106·2 (2)
C(4)–N(5)–C(6)	120·0 (2)	C(15)–N(19)–N(18)	108·1 (2)
C(4)–N(5)–C(8)	131·7 (2)	C(15)–N(19)–C(20)	130·2 (2)
C(6)–N(5)–C(8)	95·2 (2)	N(18)–N(19)–C(20)	121·6 (2)
O(1)–C(6)–N(5)	110·4 (2)	N(19)–C(20)–C(21)	111·3 (3)
O(1)–C(6)–C(7)	113·9 (2)	C(20)–C(21)–O(22)	111·9 (3)
N(5)–C(6)–C(7)	87·7 (2)	C(7)–N(23)–C(24)	122·2 (2)
C(6)–C(7)–C(8)	85·2 (2)	N(23)–C(24)–O(25)	123·0 (2)
C(6)–C(7)–N(23)	117·7 (2)	N(23)–C(24)–C(26)	113·8 (2)
C(6)–C(7)–O(31)	109·0 (2)	O(25)–C(24)–C(26)	123·2 (2)
C(8)–C(7)–N(23)	111·2 (2)	C(24)–C(26)–S(27)	113·4 (2)
C(8)–C(7)–O(31)	115·7 (2)	C(26)–S(27)–C(28)	98·4 (2)
N(23)–C(7)–O(31)	114·7 (2)	S(27)–C(28)–F(29)	110·4 (2)
N(5)–C(8)–C(7)	90·5 (2)	S(27)–C(28)–F(30)	107·9 (3)
N(5)–C(8)–O(9)	134·0 (2)	F(29)–C(28)–F(30)	106·1 (3)
C(7)–C(8)–O(9)	135·5 (2)	C(7)–O(31)–C(32)	115·1 (2)
C(4)–C(10)–O(11)	123·2 (2)	Cl(33)–C(35)–Cl(34)	112·7 (2)

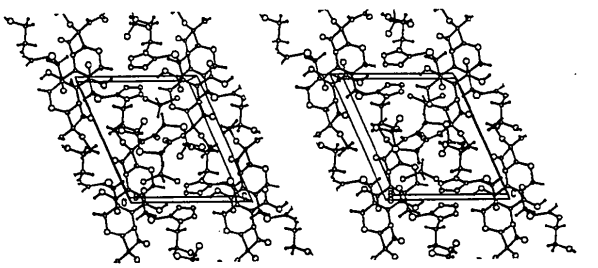

Fig. 2. Stereoscopic view of the crystal structure down the *b* axis.

$w^{1/2}|F_c| \geq 1$ and $w^{1/2}|\Delta F| < 3$, $w = 0$ otherwise. $R = 0{\cdot}028$, $wR = 0{\cdot}037$, $S = 1{\cdot}126$ for 2580 observed reflections ($w \neq 0$). Max. Δ/σ in the final cycle 0·78. No significant peaks in final difference map, highest peak 0·3 e Å^{-3}. Atomic scattering factors calculated by $\sum[a_i \exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ ($i = 1, \cdots, 4$) (*International Tables for X-ray Crystallography*, 1974). Calculations performed by FACOM M-150F computer at Shionogi Research Laboratories.

Discussion. Atomic coordinates and equivalent isotropic temperature factors of non-H atoms are listed in Table 1.* Bond lengths and angles are given in Table 2. The perspective view of the molecule with the atom-numbering system drawn using *PLUTO* (Motherwell & Clegg, 1978) is presented in Fig. 1. The absolute configuration of the molecule was determined on the basis of the *R* configuration of C(6).

A stereoscopic view of the crystal structure is given in Fig. 2. Distances between the molecules and a dichloromethane solvate are longer than the sum of the van der Waals radii. In a layer perpendicular to the *b* axis, there are two intermolecular hydrogen bonds, one between adjacent molecules along the *a* axis, O(22)···N(23)($1+x$, y, z) = 2·825 (3) Å, and the other between those along the *c* axis, O(12)···N(17)(x, y, $1+z$) = 2·789 (3) Å. Another hydrogen bond of O(22)···O(25)($2-x$, $\frac{1}{2}+y$, $1-z$) = 2·839 (3) Å is formed between the layers.

The non-planarity of N(5) is one of the important factors in the investigation of the structure–activity relationship of β-lactam antibiotics. Takasuka, Nishikawa & Tori (1982) proposed the angle θ between the N(5)–C(4) bond and the plane of N(5), C(6) and C(8) as a parameter representing the non-planarity regardless of the relevant bond lengths. For the series 7α*H*-1-oxacephem, 7α-methoxy-1-oxacephem, cephalosporin and 7α-methoxycephalosporin having the same substitutents at the 3, 4 and 7β positions, the wavenumbers of the stretching vibration band of C(8)=O(9), measured in solution, correlate linearly with the cos θ values.

The θ value in flomoxef is 29·4°, which is larger than those of the other 7α-methoxy-1-oxacephems having different substituents at the 3, 4 and 7β positions: 21·8° for diphenylmethyl 7α-methoxy-3-(1-methyl-1*H*-tetrazol-5-ylthio)methyl-7β-phenylacetamido-1-oxa-1-dethia-3-cephem-4-carboxylate (Shiro, Nakai, Onoue & Narisada, 1980), and 18·8 and 16·9° for two independent molecules in an asymmetric unit of latamoxef diammonium salt (Shiro, Nakai, Matsubara & Kikkawa, 1982).

* Lists of structure factors, anisotropic temperature factors of the non-H atoms and coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44135 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

SHIRO, M., NAKAI, H., MATSUBARA, F. & KIKKAWA, I. (1982). *Cryst. Struct. Commun.* **11**, 727–732.

SHIRO, M., NAKAI, H., ONOUE, H. & NARISADA, M. (1980). *Acta Cryst.* B**36**, 3137–3139.

TAKASUKA, M., NISHIKAWA, J. & TORI, K. (1982). *J. Antibiot.* **35**, 1729–1733.

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Structure of 1,5-Di(1-pyrrolidinyl)-4-hexene-1,3-dione

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Abstract. $C_{14}H_{22}N_2O_2$, $M_r = 250$, triclinic, $P\bar{1}$, $a = 7{\cdot}300$ (5), $b = 8{\cdot}790$ (7), $c = 10{\cdot}923$ (7) Å, $\alpha = 96{\cdot}04$ (6), $\beta = 103{\cdot}38$ (7), $\gamma = 90{\cdot}27$ (5)°, $V = 678{\cdot}3$ Å^3, $Z = 2$, $D_x = 1{\cdot}224$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}47$ cm^{-1}, $F(000) = 272$, room temperature. $R = 0{\cdot}056$ for 1829 observed reflections. The molecule consists of two planes inclined at 77 (1)° at the methylene C atom between the carbonyl groups.

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