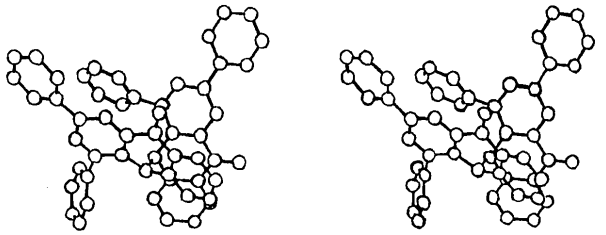

Fig. 2. Stereoview of the single molecule (Motherwell & Clegg, 1978).

(Motherwell & Clegg, 1978) are given in Figs. 1(*b*) and 2, respectively.

The C(47)···O(42) (1 + *x*, *y*, *z*) contact distance is 3·438 (8) Å with C—H 1·00 (7), H···O 2·46 (7) Å, C—H···O 165 (4)°, which is rather long for a C—H···O hydrogen bond. The packing of the molecules in the unit is stabilized by van der Waals forces.

The authors thank Professor S. Ramadas at the Indian Institute of Technology, Madras, for providing the sample, the authorities of the Indian Institute of Science, Bangalore, for extending facilities, and Professor K. Venkatesan and Dr T. N. Guru Row for helpful discussions. The Department of Science and Technology and the Council of Scientific and Industrial Research, India are thanked by VGT for financial assistance.

References

AHMED, F. R. & NEVILLE, G. A. (1982). *Acta Cryst.* B**38**, 2930–2933.

CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY & J. M. ROBERTSON, p. 45. Oxford: Pergamon Press.

DESTRO, R., D'ALFONSO, T. B. & SIMONETTA, M. (1973). *Acta Cryst.* B**29**, 2214–2220.

DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by N. ALLINGER & E. L. ELLIEL, pp. 271–383. New York: John Wiley.

International Tables for X-ray Crystallography (1968). Vol III, 2nd ed. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K., (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, P., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *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.

PADMANABHAN, P. V., JAGANNADHA RAO, K. J., RAMANA, D. V. & RAMADAS, S. (1981). *Heterocycles (Japan)*, **16**, 1–4.

SHIONO, R., (1968). A block-diagonal least-squares program for the IBM 1130. Dept. of Crystallography, Univ. of Pittsburgh, USA.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

THAILAMBAL, V. G. & VASANTHA PATTABHI (1985). *Acta Cryst.* C**41**, 802–804.

THAILAMBAL, V. G., VASANTHA PATTABHI & GABE, E. J. (1986). *Acta Cryst.* C**42**, 1017–1019.

Acta Cryst. (1987). C**43**, 2369–2372

Structure of 2,3-Dihydro-9-hydroxy-2-(1-hydroxy-1-methylethyl)-7*H*-furo-[3,2-*g*][1]benzopyran-7-one Monohydrate*

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(*Received* 21 *April* 1987; *accepted* 24 *July* 1987)

Abstract. $C_{14}H_{14}O_5.H_2O$, $M_r = 280{\cdot}3$, monoclinic, $a = 24{\cdot}629$ (2), $b = 8{\cdot}244$ (1), $c = 6{\cdot}739$ (1) Å, $\beta = 104{\cdot}21$ (1)°, $V = 1326{\cdot}43$ Å^3, $Z = 4$, $D_x = 1{\cdot}403$ (1), $D_m = 1{\cdot}400$ (2) g cm^{-3}, Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å), $\mu = 8{\cdot}9$ cm^{-1}, $T = 293$ K, $F(000) = 592$, $R(F) = 0{\cdot}0441$ for 1038 reflections with $I > 2{\cdot}5\sigma(I)$. The central ring (*B*) makes angles of 2·4 (4) and 3·4 (4)° with the mean planes through the pyran ring (*A*) and the furan ring (*C*) respectively. The molecules are nearly perpendicular to the *c* axis [88·0 (3)°] and the *B* rings of the twofold-related molecules are stacked along the *c* axis with a stacking distance of about 3·4 Å. The protons available from the water molecule and the two hydroxyl groups take part in hydrogen bonding.

Introduction. $C_{14}H_{14}O_5.H_2O$ was extracted from *Atalantia racemosa*, a herb used in Indian medicine. The structure solution was undertaken to determine the three-dimensional structure. Structure (I) has been

* IUPAC name from Professor Lozac'h, former CNOC chairman.

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‡ Contribution No. 708.

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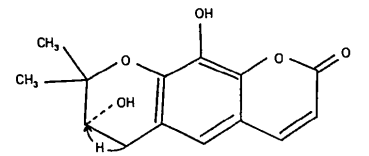
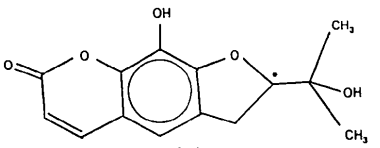
suggested, but the present study confirms (II), a derivative of psoralen, which is used in the photochemotherapy of tumours and skin diseases (Hearst, Stephen, David, Henry & Kenneth, 1984).



(I)



(II)

Experimental. Recrystallized from methanol + ethyl acetate, pale yellow rectangular crystals, 0·3 × 0·4 × 0·5 mm, D_m by flotation, intensity data using Nonius CAD-4 diffractometer, Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation, $\omega/2\theta$ mode, 25 reflections in the range $33 \le \theta \le 54°$ for lattice-parameter measurement and refinement, data corrected for Lp, no absorption correction, $2\theta_{max} = 120°$, $-27 \le h \le 26$; $0 \le k \le 9$; $0 \le l \le 7$, 21,1,1 and $\bar{2}0$,4,1 measured after every 100 reflections, variation in intensity 0·5%, 1143 reflections measured, 1042 unique reflections, $R_{int} = 0{\cdot}014$, 1038 reflections with $I > 2{\cdot}5\sigma(I)$ considered as observed, ambiguity in space-group assignment was solved based on density measurement and intensity distribution, structure solution using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), complete structure obtained after repeated trials: a few cycles of weighted Fourier in *MULTAN*80 revealed the complete structure, refined using *SHELX*76 (Sheldrick, 1976), water molecule was located at $R = 0{\cdot}27$, hydrogens were geometrically fixed and checked against ΔF synthesis, one of the water hydrogens located from the ΔF map showed a high thermal parameter and was hence replaced by one on geometrical considerations as a better position could not be obtained from the ΔF map. The non-hydrogen atoms were refined anisotropically and hydrogens isotropically and the refinement with weighting scheme based on counting statistics converged at $R(F_{obs}) = 0{\cdot}0441$, $wR = 0{\cdot}050$, $(\Delta/\sigma)_{max} = 0{\cdot}37$, $(\Delta/\sigma)_{ave} = 0{\cdot}13$ and goodness of fit for 244 parameters $S = 0{\cdot}6$. $|\Delta\rho|_{max} = \pm 0{\cdot}2$ e Å^{-3}. The presence of an asymmetric carbon [C(14)] indicated that a structure-factor calculation with the inverted coordinates is necessary to decide the absolute configuration of the molecule (Domiano, Nardelli, Balsomo, Macchia & Macchia, 1979). R index for inverted coordinates = 0·0444, showing that the absolute configuration could not be determined uniquely from the present study. The molecule with the initial coordinates has R chirality, which is supported by chemical considerations, though the difference in R factor between the two sets is not very significant. Scattering factors and dispersion coefficients as used in *SHELX*76.

Table 1. *Final positional parameters* (×10⁴) *and equivalent isotropic temperature factors* (×10) *for non-hydrogen atoms with e.s.d.'s in parentheses*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}(Å²)
O(1)	5978 (1)	3695	8323 (3)	35 (1)
C(2)	6242 (1)	5159 (6)	8672 (5)	39 (1)
C(3)	5906 (2)	6591 (5)	8433 (6)	43 (1)
C(4)	5343 (2)	6503 (6)	7917 (6)	40 (1)
C(5)	5065 (1)	4985 (5)	7610 (4)	33 (1)
C(6)	4480 (1)	4801 (6)	7139 (5)	35 (1)
C(7)	4253 (1)	3287 (6)	6944 (5)	34 (1)
C(8)	4594 (1)	1920 (5)	7152 (4)	31 (1)
C(9)	5177 (1)	2020 (5)	7571 (4)	28 (1)
C(10)	5394 (1)	3581 (5)	7815 (4)	30 (1)
O(11)	6754 (1)	5097 (5)	9171 (5)	60 (1)
O(12)	5485 (1)	633 (4)	7800 (4)	36 (7)
C(13)	3654 (1)	2711 (6)	6440 (7)	41 (1)
C(14)	3715 (1)	885 (6)	6725 (6)	36 (1)
O(15)	4307 (1)	502 (4)	6888 (3)	36 (1)
C(16)	3358 (1)	−131 (5)	4979 (5)	35 (1)
C(17)	2738 (1)	193 (7)	4837 (7)	46 (1)
C(18)	3491 (2)	−1916 (6)	5346 (8)	47 (1)
O(19)	3497 (1)	285 (5)	3107 (4)	39 (1)
O*w*	2755 (2)	1968 (6)	214 (6)	76 (1)

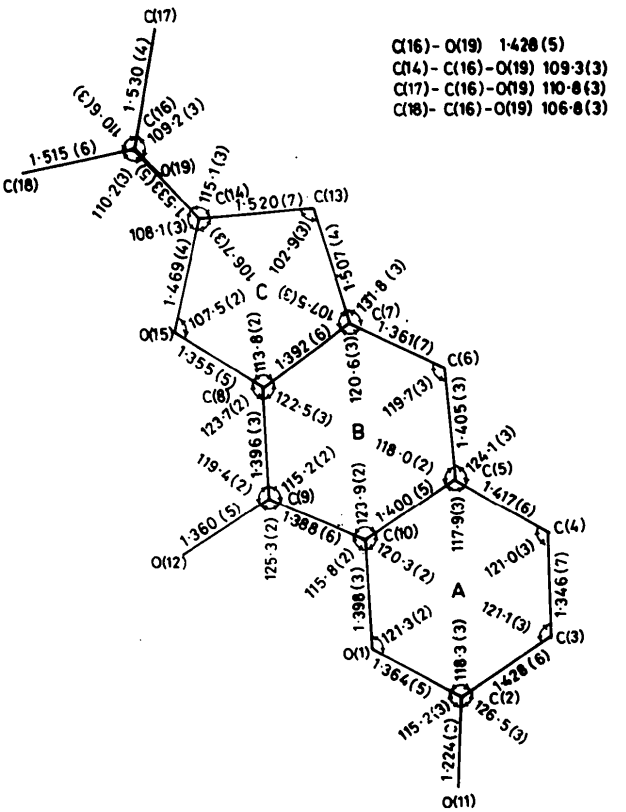


Fig. 1. Bond lengths (Å) and angles (°) involving the non-hydrogen atoms with e.s.d.'s in parentheses.

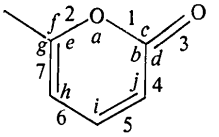
Discussion. The fractional positional parameters for the non-hydrogen atoms are listed in Table 1.* The atom numbering and bond lengths and angles involving the non-hydrogen atoms are represented in Fig. 1. The average e.s.d.'s in bond lengths and angles involving non-hydrogen atoms are 0·005 Å and 0·3° respectively. The bond lengths and angles for similar groups compare well with the values observed in xanthotoxin (Stemple & Watson, 1972). The pyrone-ring geometry agrees well with the values reported in the literature (Table 2). The widening of the angle C(3)–C(2)–O(11), 126·5 (3)°, common in 2-pyrone systems, can be attributed to the lone-pair interactions between O(1) and O(11). The substituents at C(14) and C(16) are in staggered conformation. The furan ring is in an envelope conformation with $\Delta C_s = 0{\cdot}7$ (3) (Duax, Weeks & Rohrer, 1976).

The pyran ring (*A*) ($\chi^2 = 40{\cdot}0$) and the benzene ring (*B*) ($\chi^2 = 51{\cdot}5$) are not strictly planar. The central ring plane (*B*) makes angles of 2·4 (4) and 3·4 (4)° with the mean planes of the pyran ring (*A*) and furan ring (*C*) respectively. The least-squares plane through the furocoumarin group makes an angle of 88·0 (3)° with the *c* axis and the maximum deviation from this plane is −0·163 (4) Å for the C(14) atom.

A stereoview of the packing of the molecules in the unit cell is given in Fig. 2. The molecules are nearly perpendicular to the *c* axis and the *B* rings of the twofold-related molecules are stacked along the *c* axis with a stacking distance of about 3·4 Å.

* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44267 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparison of pyrone geometry*



(*a*) In benzo pyrone systems

(i) Bond lengths (Å)

1	2	3	4	5	6	7	Reference
1·364 (5)	1·398 (3)	1·224 (3)	1·428 (6)	1·346 (7)	1·417 (6)	1·400 (5)	(I) Present work
1·371 (8)	1·383 (8)	1·198 (8)	1·441 (8)	1·338 (8)	1·443 (8)	1·404 (8)	(II) Stemple & Watson (1972)
1·382 (9)	1·385 (9)	1·212 (9)	1·435 (9)	1·346 (9)	1·434 (9)	1·391 (9)	(III) Lai & Marsh (1974)
1·395 (2)	1·366 (2)	1·204 (2)	1·443 (2)	1·329 (3)	1·436 (3)	1·403 (3)	(IV) Shen & Bryan (1975)
1·384 (2)	1·368 (2)	1·207 (2)	1·453 (2)	1·332 (3)	1·433 (3)	1·403 (3)	

(ii) Bond angles (°)

a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	Number
121·3 (2)	118·3 (3)	115·2 (3)	126·5 (3)	120·3 (2)	115·8 (2)	123·9 (2)	117·9 (3)	121·0 (3)	121·3 (3)	(I)
122·1 (5)	117·7 (5)	116·3 (5)	126·0 (5)	122·7 (5)	114·4 (5)	122·9 (5)	117·2 (5)	121·1 (5)	121·2 (5)	(II)
122·4 (4)	117·8 (4)	115·9 (4)	126·3 (4)	119·3 (4)	116·1 (4)	124·6 (4)	119·2 (4)	120·6 (4)	120·5 (4)	(III)
122·1 (2)	116·1 (2)	116·6 (2)	127·3 (2)	121·6 (2)	118·6 (2)	119·8 (2)	116·6 (2)	121·4 (2)	122·1 (2)	
122·1 (2)	117·0 (2)	116·6 (2)	126·4 (2)	120·9 (2)	118·7 (2)	120·4 (2)	117·4 (2)	121·4 (2)	120·9 (2)	(IV)

Compound names:
(I) 2,3-Dihydro-9-hydroxy-2-(1-hydroxy-1-methylethyl)-7*H*-furo[3,2-*g*][1]benzopyran-7-one monohydrate.
(II) 8-Methoxy-3′,2′:6,7-furocoumarin.
(III) Avicennin.
(IV) 2*H*,12*H*-Furo[2,3-*h*:5,4-*h*′]bis[1]benzopyran-2,12-dione.

(*b*) In pyrone group

(i) Bond lengths (Å)

1	2	3	4	5	6	7	Reference
1·394 (7)	1·364 (7)	1·205 (7)	1·438 (8)	1·400 (8)	1·406 (8)	1·348 (8)	(I) Thailambal & Vasantha Pattabhi (1985)
1·398 (8)	1·362 (7)	1·200 (7)	1·438 (9)	1·398 (8)	1·413 (9)	1·321 (9)	(II) Thailambal, Vasantha Pattabhi & Gabe (1986)
1·401 (7)	1·353 (7)	1·203 (7)	1·436 (8)	1·395 (8)	1·419 (8)	1·328 (9)	
1·378 (4)	1·376 (4)	1·233 (4)	1·404 (5)	1·372 (5)	1·427 (5)	1·343 (4)	(IV) Hirata & Suga (1978)
1·390 (3)	1·364 (3)	1·209 (3)	1·419 (3)	1·359 (3)	1·421 (3)	1·334 (3)	(V) Engel & Nowacki (1971)

(ii) Bond angles (°)

a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	Number
123·5 (4)	116·7 (5)	114·8 (4)	128·5 (5)	120·6 (5)	112·0 (4)	127·3 (5)	119·2 (5)	121·6 (5)	118·4 (5)	(I)
123·6 (4)	116·5 (5)	114·6 (5)	129·2 (5)	121·1 (5)	111·5 (5)	127·5 (5)	119·4 (5)	121·3 (5)	118·4 (5)	
122·9 (4)	117·1 (5)	113·7 (4)	129·2 (5)	121·0 (5)	112·1 (5)	126·6 (6)	120·0 (6)	120·6 (5)	118·3 (5)	(II)
122·1 (3)	118·4 (3)	115·5 (3)	126·1 (3)	120·5 (3)	112·0 (3)	127·5 (3)	119·0 (3)	120·6 (3)	119·5 (3)	(III)
121·6 (3)	117·8 (3)	115·3 (3)	126·9 (3)	121·1 (3)	113·7 (3)	125·2 (3)	119·2 (3)	120·5 (3)	119·8 (3)	(IV)

Compound names:
(I) 3-Acetyl-4-hydroxy-6-phenyl-2-pyrone.
(II) 4-Hydroxy-3-(3-hydroxy-1-oxo-3-phenyl-2-propenyl)-6-methyl-2-pyrone.
(III) 4-Methoxy-6-(2,4-dihydroxy-6-methylphenyl)-2-pyrone.
(IV) *trans*-(*p*-Methoxystyryl)-4-methoxy-2-pyrone.

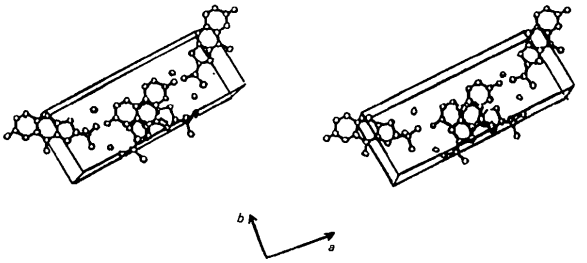


Fig. 2. Stereoview of the packing of the molecules in the unit cell.

The protons available from the water molecule and the two hydroxyl groups take part in hydrogen bonding [C(19)—H(19)—O*w* 2·705 (5), H···*A* 1·93 (5) Å, *D*—H···*A* 168 (5)°; O*w*—H(O*w*)1—O(11) 2·846 (6), H···*A* 2·05 (7) Å, *D*—H···*A* 135 (4)°; O(12)—H(12)—O(19) 2·737 (4), H···*A* 1·93 (3) Å, *D*—H···*A* 151 (2)°; O*w*—H(O*w*)2—O(11) 2·836 (6), H···*A* 2·24 (4) Å *D*—H···*A* 134 (2)°]. The molecules are stabilized by the hydrogen bonds and stacking forces.

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References

DOMIANO, P., NARDELLI, M., BALSAMO, A., MACCHIA, B. & MACCHIA, F. (1979). *Acta Cryst.* B**35**, 1363–1372.

DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). In *Topics in Stereochemistry*, edited by N. L. ALLINGER & E. L. ELLIEL, Vol. 9, pp. 271–383. New York: John Wiley.

ENGEL, P. & NOWACKI, W. (1971). *Z. Kristallogr.* **134**, 180–195.

HEARST, J. E., STEPHEN, T. I., DAVID, K., HENRY, R. & KENNETH, S. (1984). *Q. Rev. Biophys.* **17**, 1–44.

HIRATA, T. & SUGA, T. (1978). *Bull. Chem. Soc. Jpn*, **51**(3), 842–849.

LAI, T. F. & MARSH, R. E. (1974). *Acta Cryst.* B**30**, 1570–1575.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHEN, M. S. & BRYAN, R. F. (1975). *Acta Cryst.* B**31**, 2907–2909.

STEMPLE, N. R. & WATSON, W. H. (1972). *Acta Cryst.* B**28**, 2485–2489.

THAILAMBAL, V. G. & VASANTHA PATTABHI (1985). *Acta Cryst.* C**41**, 802–804.

THAILAMBAL, V. G., VASANTHA PATTABHI & GABE, E. J. (1986). *Acta Cryst.* C**42**, 1017–1019.

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Structures of Two Aza-Steroids: 17β-Hydroxy-4-aza-5β-androst-1-en-3-one (I) and 17β-Acetoxy-3-aza-*A*-homo-4a-androsten-4-one (II)

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Abstract. (I): $C_{18}H_{27}NO_2$, $M_r = 289{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}801$ (2), $b = 11{\cdot}691$ (3), $c = 20{\cdot}134$ (4) Å, $V = 1601$ (1) Å^3, $D_x = 1{\cdot}201$ Mg m^{-3}, $Z = 4$, $F(000) = 632$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 7·2 mm^{-1}, 298 K. (II): $C_{21}H_{31}NO_3$, $M_r = 345{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}562$ (2), $b = 9{\cdot}979$ (2), $c = 25{\cdot}510$ (3) Å, $V = 1925$ (1) Å^3, $D_x = 1{\cdot}192$ Mg m^{-3}, $Z = 4$, $F(000) = 752$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 8·5 mm^{-1}, 298 K. Both structures were solved by direct methods and refined by full-matrix least squares to $R = 0{\cdot}066$ and 0·056, respectively, for 1078 and 882 reflections. Rings *B* and *C* show a chair conformation, while rings *D* show a skew-envelope form. The *A*-ring conformation of (I) is a distorted half-chair, while in (II) C(1), C(3), C(4), C(5) and C(10) atoms are in a plane. The acetate moiety of

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