References

CHU, S. S. C. & CHUNG, B. (1976). *Acta Cryst.* B32, 836–842.
CHU, S. S. C. & VAN DER HELM, D. (1974). *Acta Cryst.* B30, 2489–2490.
CHU, S. S. C. & VAN DER HELM, D. (1975). *Acta Cryst.* B31, 1179–1183.
CHU, S. S. C. & VAN DER HELM, D. (1976). *Acta Cryst.* B32, 1012–1016.
CHU, S. S. C. & VAN DER HELM, D. (1977). *Acta Cryst.* B33, 873–876.
CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* 97, 1354–1358.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
JOVANOVIC, M. V., BIEHL, E. R., DE MEESTER, P. & CHU, S. S. C. (1984). *J. Heterocycl. Chem.* 21, 885–888, 1425–1429, 1793–1800, and references therein.
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.
SCHOMAKER, V. & MARSH, R. E. (1983). *Acta Cryst.* A39, 819–820.
SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Structure of (1S*,2R*)-2-(2-Furoyl)-2,5-dimethylcyclohex-5-en-1-yl Acetate

BY S. D. JOHNSON, P. J. PARSONS† AND M. WEBSTER

Department of Chemistry, The University, Southampton SO9 5NH, England

Abstract. $C_{15}H_{18}O_4$, $M_r = 262.3$, monoclinic, $P2_1/n$, $a = 8.797$ (1), $b = 20.392$ (2), $c = 8.916$ (1) Å, $\beta = 118.33$ (1)°, $V = 1407.9$ (5) Å^3, $Z = 4$, $D_m = 1.22$ (1), $D_x = 1.237$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, μ(Cu $K\alpha$) = 0.65 mm^{-1}, $F(000) = 560$, room temperature, $R = 0.046$ for 1942 observed reflections [$F > 3\sigma(F)$]. The title compound is a key intermediate in a projected trichodermin synthesis and was prepared by an *endo*-selective Diels–Alder reaction. Bond lengths and angles are normal. The formal C—C single bond of the furan ring is 1.412 (3) Å.

Introduction. As part of a programme dealing with the total synthesis of trichothecenes (Godtfredsen & Vangedal, 1964), the title compound (I) was prepared by a Diels–Alder reaction between 1-acetoxy-3-methyl-1,3-butadiene (II) and 1-(2-furanyl)-2-methyl-2-propen-1-one (III). Two likely products were anticipated for this reaction and since (I) is a key intermediate in the proposed route whose stereochemistry was vital, the X-ray structure determination was undertaken.

(I)   (II)   (III)
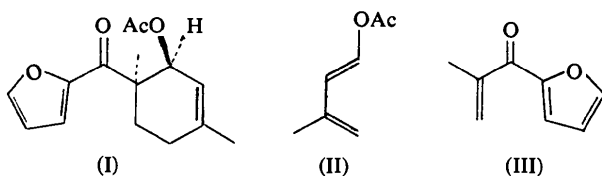
† Author to whom correspondence should be addressed.

Experimental. Air-stable plate-like crystals were obtained from diethyl ether. Following photographic X-ray study, data collected from a crystal, $0.17 \times 0.27 \times 0.62$ mm, D_m by flotation in CCl$_4$/heptane, Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation. Data in the range $3 < \theta < 65°$ with h 0 to 10, k 0 to 23 and l −10 to 10. No decomposition with time was observed for three check reflections; empirical ψ-scan absorption correction (transmission: min. 92%, max. 99%), 1942 reflections with $F > 3\sigma(F)$ from a total of 2396 independent measurements. The structure was solved using *MULTAN80* (Main *et al.*, 1980) and refinement carried out using *SHELX* (Sheldrick, 1976). The O atom of the acyl group was distinguished from the methyl group on the basis of bond lengths, and the O atom of the furan ring identified by bond-length criteria and isotropic thermal parameter refinement. After least-squares refinement using anisotropic thermal parameters the difference electron density synthesis showed the H-atom positions confirming the assignment of O and C. H atoms were introduced into the model with geometrically calculated positions [d(C—H) = 1.00 Å] and with two refined isotropic temperature factors (one for CH$_3$ groups and one for H atoms of CH and CH$_2$ groups). Least-squares refinement (on F) converged to $R = 0.046$, $wR = 0.070$, 183 parameters, $w = 1/[\sigma^2(F) + 0.00055F^2]$, max. shift/e.s.d. = 0.5, residual electron density in the range −0.17 to 0.28 e Å^{-3}. Scattering factors and anomalous-dispersion corrections for O, C

and H taken from *SHELX*. All calculations were carried out on an ICL 2970 computer at Southampton University using the programs *SHELX*, *MULTAN*80 and *ORTEP* (Johnson, 1965).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

$U_{eq} = \frac{1}{3}$ trace U.

	x	y	z	U_{eq}
C(1)	0·8383 (3)	0·1111 (1)	0·8872 (2)	49·2 (9)
C(2)	0·7884 (3)	0·1351 (1)	1·0216 (2)	49·6 (9)
C(3)	0·9177 (3)	0·1878 (1)	1·1310 (3)	56·4 (11)
C(4)	1·1029 (3)	0·1625 (1)	1·2177 (3)	65·8 (12)
C(5)	1·1464 (3)	0·1188 (1)	1·1093 (3)	62·8 (11)
C(6)	1·0267 (3)	0·0974 (1)	0·9598 (3)	57·9 (11)
C(7)	1·3343 (3)	0·1009 (2)	1·1785 (4)	91·5 (17)
C(8)	0·7651 (3)	0·1487 (1)	0·6059 (3)	53·3 (10)
C(9)	0·7263 (4)	0·2080 (1)	0·4944 (3)	72·5 (14)
C(10)	0·7922 (3)	0·0763 (1)	1·1328 (3)	64·0 (12)
C(11)	0·3203 (3)	0·0443 (1)	0·6469 (3)	68·2 (12)
C(12)	0·2006 (3)	0·0868 (1)	0·6327 (3)	69·4 (13)
C(13)	0·2876 (3)	0·1404 (1)	0·7393 (3)	67·4 (13)
C(14)	0·4574 (3)	0·1266 (1)	0·8136 (3)	52·8 (10)
C(15)	0·6058 (3)	0·1631 (1)	0·9420 (3)	51·2 (10)
O(1)	0·4803 (2)	0·0666 (1)	0·7580 (2)	66·5 (8)
O(2)	0·5769 (2)	0·2154 (1)	0·9894 (2)	71·3 (9)
O(3)	0·7876 (2)	0·1647 (1)	0·7605 (2)	51·1 (7)
O(4)	0·7783 (2)	0·0940 (1)	0·5649 (2)	74·7 (9)

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

C(1)–C(2)	1·539 (3)	C(2)–C(10)	1·547 (3)
C(2)–C(3)	1·532 (3)	C(5)–C(7)	1·510 (3)
C(3)–C(4)	1·523 (3)	C(1)–O(3)	1·479 (2)
C(4)–C(5)	1·492 (3)	O(3)–C(8)	1·337 (2)
C(5)–C(6)	1·321 (3)	C(8)–C(9)	1·499 (3)
C(6)–C(1)	1·492 (3)	C(8)–O(4)	1·197 (2)
C(11)–C(12)	1·323 (3)	C(15)–C(2)	1·526 (3)
C(12)–C(13)	1·412 (3)	C(15)–O(2)	1·218 (2)
C(13)–C(14)	1·346 (3)	C(15)–C(14)	1·466 (3)
C(14)–O(1)	1·371 (2)		
O(1)–C(11)	1·359 (3)		

Discussion. In a new synthetic approach to trichodermin (and its analogues) we required the keto acetate (I). Simple retrosynthetic analysis of (I) suggested that the Diels–Alder reaction between the butadiene derivative (II) (Cookson, Cramp & Parsons, 1980) and the unsaturated ketone (III) (Sam & Mozingo, 1969) should yield the desired furan (I). The Diels–Alder reaction could give rise to two possible structures arising from *endo-* and *exo-*addition of (II) to (III). Under the reaction conditions chosen (boiling toluene, 1 d) we isolated one crystalline product shown by the present analysis to be the required *endo* isomer. The atomic parameters are given in Table 1* and bond lengths in Table 2. The atom-numbering scheme and a view of the molecule are shown in Fig. 1.

The furan ring is planar [max. deviation 0·004 (2) Å] with the expected short formal C—C single bond [1·412 (3) Å], and the orientation of the ring O relative to the carbonyl group is *trans* with $\tau[O(1)—C(14)—C(15)—O(2)] = -178·2$ (4)°. Only a few X-ray structures are known of compounds containing the 2-furoyl group, for example 3-(2-furoyl)-4,5-bis(methoxycarbonyl)pyrazole (Aliev, Kartsev, Atovmyan & Voronina, 1982), which shows a similar geometry although in this case the ring O and carbonyl group are *cisoid*. The cyclohexene residue has the expected four atoms coplanar [max. deviation 0·012 (2) Å] with C(2) and C(3) out of this plane and on opposite sides [−0·466 (2) and 0·262 (2) Å, respectively].

* Lists of structure factors, anisotropic thermal parameters, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43209 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
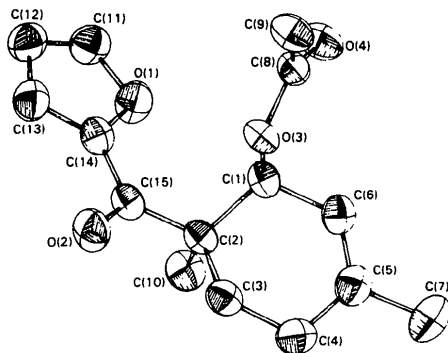

Fig. 1. View of the molecule showing the atom-numbering scheme. Thermal ellipsoids drawn at the 40% probability level; H atoms omitted for clarity.

References

ALIEV, Z. G., KARTSEV, V. G., ATOVMYAN, L. O. & VORONINA, G. N. (1982). *Khim. Geterotsikl. Soedin.* pp. 91–94 (CCDB Refcode BEWLEU).

COOKSON, R. C., CRAMP, M. C. & PARSONS, P. J. (1980). *J. Chem. Soc. Chem. Commun.* pp. 197–198.

GODTFREDSEN, W. O. & VANGEDAL, S. (1964). *Proc. Chem. Soc. London*, pp. 188–189.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

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.

SAM, J. & MOZINGO, J. R. (1969). *J. Pharm. Sci.* **8**, 1030–1032.

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