C208—N203—C202—O201	−177.9 (3)
C204—N203—C202—O215	−177.5 (3)
C208—N203—C202—O215	0.3 (5)
C202—N203—C204—C205	99.5 (4)
C208—N203—C204—C205	−78.5 (4)
C204—N203—C208—C209	171.9 (3)
C202—N203—C208—C209	−5.9 (5)
N203—C204—C205—N206	166.0 (3)
N203—C204—C205—O207	−17.6 (5)
N203—C208—C209—C210	−175.4 (3)
N203—C208—C209—C214	4.5 (4)
C208—C209—C210—C211	−179.3 (3)
C214—C209—C210—C211	0.8 (4)
C208—C209—C214—O215	2.1 (4)
C208—C209—C214—C213	−179.3 (3)
C210—C209—C214—O215	−178.0 (2)
C210—C209—C214—C213	0.6 (4)
C209—C210—C211—C212	−1.6 (5)
C210—C211—C212—C213	1.1 (5)
C211—C212—C213—C214	0.3 (6)
C212—C213—C214—O215	177.5 (3)
C212—C213—C214—C209	−1.1 (5)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	H···A	D—H···A
N106—H161···O107^i	2.104 (48)	166.4 (45)
N106—H162···O101^{ii}	2.162 (46)	167.0 (37)
N206—H261···O207^{iii}	2.032 (48)	166.2 (37)
N206—H262···O201^{iv}	1.978 (44)	163.0 (35)

Symmetry codes: (i) $x+\frac{1}{2}, 1-y, z$; (ii) $-x, 1-y, z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, 2-y, z$; (iv) $-x, 2-y, z+\frac{1}{2}$.

The structure was solved using *SHELXS86* (Sheldrick, 1990) and refined with *SHELXL93* (Sheldrick, 1993). Most of the calculations were performed with the *SHELXL93* package, as was the generation of the Crystallographic Information File (CIF) used for the submission of this paper.

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3-[5-(2-Nitrophenyl)furfurylidene]-2,4-pentanedione

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Abstract

The title compound, $C_{16}H_{13}NO_5$, consists of monomeric units. The whole molecule was tested for planarity. Unlike the 3-nitrophenyl isomer [Lokaj, Vrábel, Sivý, Ilavský & Koreňová (1994). *Acta Cryst.* C50, 1312–1314], the fragment containing the O(1), C(1), C(2) and C(5) atoms, the furylidene ring and the attached nitrophenyl group are not in the same plane. The dihedral angle between the benzene and furan rings is 47.8°.

Comment

The conformation of furan derivatives with an R substituent at position 5 and a —CH=CR_2' substituent at position 2 can be assumed on the basis of previously reported information (Kusá, Polynova, Poray-Koshits, Kováč & Végh, 1979; Kusá, Polynova, Poray-Koshits & Jurásek, 1979; Kusá, Polynova, Poray-Koshits & Kováč, 1979). The conformation depends on the type of R' substituent; electron-acceptor substituents form *trans* and

electron-donor substituents form *cis* conformations with respect to the double bond between the furan and ethylene fragments. In the present molecule, (I), one can predict a *trans* conformation of the vinyl-furan fragment on the basis of the R' substituent type. This was confirmed by the X-ray analysis.

(I)
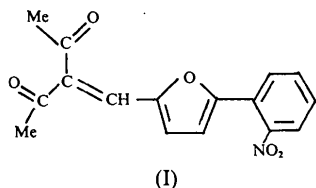
The starting compound (2-nitrophenyl)furalde-hyde was prepared by a published procedure (Krutošíková, Kováč, Frimm, Kováč & Sticzay, 1971). 5-(2-Nitrophenyl)-2-furaldehyde (0.02 mol) was disolved in tetrahydrofuran (25 ml) and then 2,4-pentanedione (0.02 mol) was added. The reaction was catalyzed by anhydrous $CuCl_2$ and the product was extracted by chloroform (3 × 60 ml) and evaporated to dryness. The crude product was recrystallized from ethanol. The molecular structure and the atom numbering of the title compound are shown in Fig. 1.
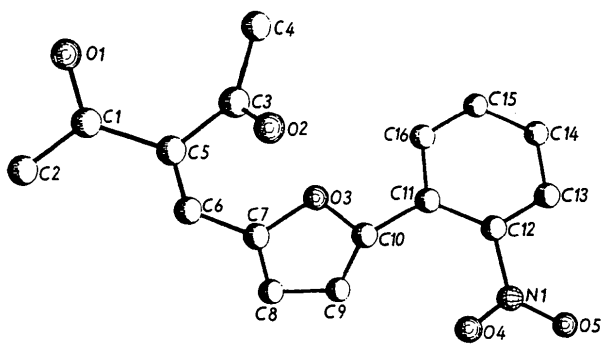

Fig. 1. Perspective drawing of the title compound with atom numbering.

Unlike the 3-nitrophenyl isomer (Lokaj, Vrábel, Sivý, Ilavský & Koreňová, 1994) where the O(1)—C(1)[—C(2)]—C(5) fragment, the furan ring and the nitrophenyl group lie nearly in the same plane, resulting in significant conjugation through the whole molecule, no such planarity was observed in the present molecule. Inserting the nitro group at the *ortho* position of the phenyl ring results in a twisting of the phenyl ring against the furan ring. The angle between the best planes of these two rings is 47.8 (1)°. There is a conjugation along the

O(1)=C(1)—C(5)=C(6)—C(7)=C(8) fragment, as indicated by the planarity of this moiety as well as by the corresponding bond distances. Comparing the C(1)—C(5), C(6)—C(7) and C(7)=C(8) bond lengths with the data (using the 3σ criterion) reported by Allen, Kennard, Watson, Brammer & Orpen (1987), it was found that the C(1)—C(5) bond length agrees well with the C_{sp^3}—C_{sp^3} bond length of Allen *et al.* (1987) [C=C—C(=O)—C 1.464 Å]. The C(6)—C(7) bond length is shortened, whereas the C(7)=C(8) and C(9)=C(10) double-bond lengths agree excellently with the value of 1.341 Å reported by Allen *et al.* (1987) for the C_{sp^2}=C_{sp^2} distance in the furan system. The phenyl ring is approximately planar [maximum deviation of atoms C(11) and C(12) from the least-squares plane is 0.005 (2) Å with an average C—C bond distance of 1.376 (3) Å].

Experimental

Crystal data

$C_{16}H_{13}NO_5$	Mo $K\alpha$ radiation
$M_r = 299.282$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 15
$P\bar{1}$	reflections
$a = 8.243$ (10) Å	$\theta = 4–17°$
$b = 8.717$ (9) Å	$\mu = 0.099$ mm^{-1}
$c = 10.652$ (9) Å	$T = 293$ K
$\alpha = 67.91$ (7)°	Prism
$\beta = 81.73$ (9)°	0.25 × 0.20 × 0.10 mm
$\gamma = 74.09$ (9)°	Orange
$V = 681$ (1) Å^3	Crystal source: crystalliza-
$Z = 2$	tion from CCl_4
$D_x = 1.46$ Mg m^{-3}	
$D_m = 1.43$ (2) Mg m^{-3}	
D_m measured by flotation in	
$ZnSO_4$ solution	

Data collection

XP2$_1$ diffractometer	$\theta_{max} = 27.5°$
$\theta/2\theta$ scans	$h = -10 \rightarrow 10$
Absorption correction:	$k = -10 \rightarrow 10$
none	$l = 0 \rightarrow 13$
3285 measured reflections	2 standard reflections
3153 independent reflections	monitored every 98
1641 observed reflections	reflections
[$I > 1.96\sigma(I)$]	intensity variation: 5%
$R_{int} = 0.026$	

Refinement

Refinement on F	Unit weights applied
$R = 0.054$	$(\Delta/\sigma)_{max} = 0.1$
$wR = 0.051$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$S = 0.84$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
1641 reflections	Atomic scattering factors
199 parameters	from *International Tables*
H-atom parameters not	*for X-ray Crystallography*
refined	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	0.6350 (2)	−0.3605 (2)	0.8980 (2)	4.10 (5)
O(2)	0.4832 (2)	0.0647 (2)	0.7128 (2)	4.23 (6)
O(3)	0.1272 (2)	0.1550 (2)	0.8365 (1)	2.74 (4)
O(4)	0.0337 (2)	0.6269 (2)	0.7431 (2)	4.64 (6)
O(5)	−0.1667 (3)	0.8214 (2)	0.6337 (2)	6.39 (8)
N(1)	−0.0891 (2)	0.6736 (2)	0.6770 (2)	3.80 (6)
C(1)	0.5480 (2)	−0.2948 (2)	0.9744 (2)	2.95 (7)
C(2)	0.5679 (3)	−0.3749 (3)	1.1233 (2)	3.53 (7)
C(3)	0.4229 (3)	−0.0553 (2)	0.7683 (2)	3.01 (7)
C(4)	0.3476 (4)	−0.1297 (3)	0.6925 (2)	4.86 (10)
C(5)	0.4205 (2)	−0.1344 (2)	0.9191 (2)	2.56 (6)
C(6)	0.3175 (2)	−0.0639 (2)	1.0004 (2)	2.72 (6)
C(7)	0.1810 (2)	0.0842 (2)	0.9662 (2)	2.72 (6)
C(8)	0.0908 (3)	0.1765 (3)	1.0404 (2)	3.02 (7)
C(9)	−0.0244 (3)	0.3122 (3)	0.9549 (2)	3.18 (7)
C(10)	0.0011 (2)	0.2954 (2)	0.8332 (2)	2.69 (6)
C(11)	−0.0902 (2)	0.3763 (3)	0.7085 (2)	2.79 (6)
C(12)	−0.1458 (3)	0.5509 (3)	0.6423 (2)	3.16 (6)
C(13)	−0.2463 (3)	0.6169 (3)	0.5327 (2)	4.03 (8)
C(14)	−0.2909 (3)	0.5085 (4)	0.4860 (2)	4.71 (9)
C(15)	−0.2373 (3)	0.3361 (4)	0.5476 (2)	4.47 (9)
C(16)	−0.1374 (3)	0.2711 (3)	0.6574 (2)	3.66 (8)

Table 2. *Selected bond distances* (Å) *and angles* (°)

O(1)—C(1)	1.209 (3)	N(1)—C(12)	1.456 (3)
O(2)—C(3)	1.195 (3)	C(1)—C(2)	1.487 (3)
O(3)—C(7)	1.369 (2)	C(1)—C(5)	1.469 (3)
O(3)—C(10)	1.364 (3)	C(3)—C(4)	1.489 (4)
O(4)—N(1)	1.204 (3)	C(3)—C(5)	1.490 (3)
O(5)—N(1)	1.212 (3)	C(10)—C(11)	1.455 (3)
C(7)—O(3)—C(10)	105.7 (1)	O(1)—C(1)—C(2)	120.8 (2)
O(4)—N(1)—O(5)	122.6 (2)	C(2)—C(1)—C(5)	119.7 (2)
O(5)—N(1)—C(12)	117.5 (2)	O(2)—C(3)—C(5)	119.6 (2)
O(4)—N(1)—C(12)	119.8 (2)	O(2)—C(3)—C(4)	122.4 (2)

Data reduction was performed with the program *XP2*₁ (Pavelčík, 1987). The structure was solved by direct methods and refinement was by block-diagonal least squares. H atoms were found from difference Fourier maps and their coordinates and displacement parameters were fixed. Calculations were performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1984).

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Enantioselective Synthesis of Isoquinoline Alkaloids from Simple Sugar. II. Structure of 1-(6,7-Dimethoxy-3,4-dihydroisoquinolin-1-yl)-1,2,3,4-butanetetrayl Tetraacetate *N*-Oxide

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Abstract

The title compound, $C_{23}H_{29}NO_{11}$, is an important intermediate product in the course of the synthesis of some natural products. Among them are two isoquinoline alkaloids: (*R*)-calycotomine and (*S*)-xylopinine. A single-crystal X-ray study of this compound is reported.

Comment

In the course of our work on the development of an efficient enantioselective synthetic strategy for isoquinoline alkaloids, we described a procedure in which the chiral substrate D-ribonic acid γ-lactone (1) was used (Czarnocki, 1992*a*,*b*). In several steps, compound (1) was transformed into 6,7-dimethoxy-3,4-dihydroisoquinolin-1-yl-(1′,2′,3′,4′-tetraacetoxy)butane (2) (Czarnocki, 1992*a*,*b*, and references therein). Subsequent oxidation of (2) with *m*-chloroperbenzoic acid gave 1-(6,7-dimethoxy-1,2,3,4-tetrahydro-1,2-epoxy-isoquinolinyl)-1,2,3,4-butanetetrayl tetraacetate (3)