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(5R)-5-[(S)-α-Hydroxybenzyl]-5-(L-menthyloxy)-4-(1-pyrrolidinyl)furan-2(5H)-one

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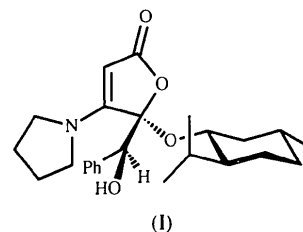
Abstract

The determination of the structure of the title compound, $C_{25}H_{35}NO_4$, confirms the *R* and *S* absolute configurations at the 5 position of the furanone ring and the α position of the hydroxybenzyl substituent, respectively, taking into account the known configuration of the menthyl moiety.

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Comment

Due to their versatility as intermediates in organic synthesis, furan-2(5H)-ones have been the target compounds of several generally applicable synthetic routes. One of the most useful approaches is the reaction of enolate anions generated from furanone derivatives with electrophiles. In this case, the presence of an electron-releasing group such as alkoxy (Honda, Hayakawa, Kondoh, Okuyama & Tsubuki, 1991; Pelter, Al-Bayati, Ayoub, Lewis & Pardasani, 1987) or alkylamino (de Ancos, Fariña, Maestro, Martín & Vicioso, 1991; Nishide, Aramata, Kamanaka & Node, 1993; Schlessinger, Iwanowicz & Springer, 1988; Schlessinger, Mjalli, Adams, Springer & Hoogsteen, 1992) at the 4 position favours the formation of C5-substituted derivatives. With respect to the stereoselectivity of this reaction, several studies were carried out using substrates with a pyrrolidine derivative as chiral auxiliary group at the C4 position. Recently, a new 4-enaminofuranone with the chiral group at the 5 position of the furanone ring, 5-(L-menthyloxy)-4-(1-pyrrolidinyl)furan-2(5H)-one, has been prepared (Martín & Mateo, 1994) and the reaction of the enolate anion of this compound with several electrophiles has been studied (Martín & Mateo, 1995). The determination of the absolute configuration of the main product obtained in the reaction with benzaldehyde, the title compound, (I), has been accomplished by X-ray analysis and the known configuration of the menthyl moiety in the starting material.

(I)

The furanone ring can be considered to be flat, with the mean deviation of the plane for C4 [0.003 (5) Å]. The pyrrolidine ring has an envelope conformation with
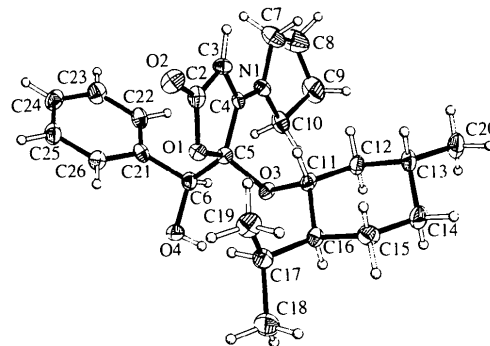

Fig. 1. The molecular structure of the title compound showing 20% probability displacement ellipsoids for non-H atoms.

C9 0.49 (2) Å out of the plane defined by the other four atoms. The angle between these rings is 3.5 (7)°. Inter-molecular hydrogen bonds have been found [C10···O2^i 3.70 (1), H10b···O2^i 2.79 (1) Å, C10—H10b···O2^i 155.2 (2)°; C22···O2^i 3.38 (1), H22···O2^i 2.62 (1) Å, C22—H22···O2^i 139.6 (2)°; symmetry code: (i) x, y+1, z], although none of them involves O4—H41.

Experimental

The crystals were grown by slow evaporation of a hexane solution of the compound prepared according to the procedure described by Martín & Mateo (1995).

Crystal data

C₂₅H₃₅NO₄	Mo $K\alpha$ radiation
$M_r = 413.54$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P1$	reflections
$a = 7.813$ (2) Å	$\theta = 20$–25°
$b = 8.058$ (2) Å	$\mu = 0.078$ mm^{-1}
$c = 10.212$ (2) Å	$T = 273$ (2) K
$\alpha = 92.44$ (3)°	Transparent block
$\beta = 105.51$ (3)°	$0.30 \times 0.27 \times 0.25$ mm
$\gamma = 106.03$ (3)°	Colourless
$V = 590.7$ (2) Å^3	
$Z = 1$	
$D_x = 1.163$ Mg m^{-3}	

Data collection

Rigaku AFC-7R four-circle diffractometer	$\theta_{max} = 22.50°$
	$h = -8 \rightarrow 8$
$2\theta/\omega$ scans	$k = -8 \rightarrow 8$
Absorption correction: none	$l = -10 \rightarrow 10$
	3 standard reflections
3086 measured reflections	monitored every 100
3086 independent reflections	reflections
1701 observed reflections	intensity decay: none
[$I > 2\sigma(I)$]	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0742$	$\Delta\rho_{max} = 0.156$ e Å^{-3}
$wR(F^2) = 0.1683$	$\Delta\rho_{min} = -0.190$ e Å^{-3}
$S = 1.020$	Extinction correction: none
3086 reflections	Atomic scattering factors
275 parameters	from *International Tables*
Only coordinates of H atoms refined	*for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.5699 (7)	0.0825 (6)	0.4519 (5)	0.0418 (14)
C2	0.7203 (13)	0.0609 (12)	0.5479 (9)	0.052 (2)
O2	0.7081 (8)	−0.0769 (7)	0.5956 (6)	0.068 (2)
C3	0.8720 (11)	0.2156 (10)	0.5762 (8)	0.046 (2)
C4	0.8176 (10)	0.3345 (10)	0.4993 (8)	0.038 (2)
C5	0.6204 (11)	0.2554 (10)	0.4145 (8)	0.039 (2)
C6	0.4853 (11)	0.3504 (11)	0.4408 (8)	0.050 (2)
O4	0.2986 (8)	0.2584 (9)	0.3615 (7)	0.068 (2)
N1	0.9220 (9)	0.4963 (9)	0.4960 (7)	0.048 (2)
C7	1.1118 (12)	0.5656 (11)	0.5821 (11)	0.078 (3)
C8	1.1726 (16)	0.7512 (14)	0.5561 (15)	0.123 (5)
C9	1.0548 (18)	0.7573 (14)	0.4176 (14)	0.109 (4)
C10	0.8682 (12)	0.6241 (11)	0.4063 (10)	0.065 (3)
O3	0.5894 (7)	0.2422 (6)	0.2708 (5)	0.0441 (14)
C11	0.6791 (10)	0.1353 (10)	0.2081 (8)	0.045 (2)
C12	0.8267 (11)	0.2536 (10)	0.1591 (8)	0.051 (2)
C13	0.9136 (11)	0.1574 (11)	0.0747 (9)	0.055 (2)
C14	0.7546 (12)	0.0415 (12)	−0.0453 (9)	0.065 (3)
C15	0.6090 (12)	−0.0878 (11)	0.0074 (9)	0.062 (3)
C16	0.5230 (11)	0.0094 (9)	0.0930 (8)	0.046 (2)
C17	0.3679 (11)	−0.1179 (11)	0.1395 (9)	0.059 (2)
C18	0.1921 (12)	−0.1961 (12)	0.0174 (10)	0.089 (3)
C19	0.4299 (12)	−0.2604 (11)	0.2127 (9)	0.070 (3)
C20	1.0584 (13)	0.2820 (12)	0.0220 (10)	0.080 (3)
C21	0.4855 (10)	0.3635 (10)	0.5876 (9)	0.045 (2)
C22	0.5999 (12)	0.5128 (10)	0.6778 (10)	0.057 (3)
C23	0.6000 (13)	0.5274 (13)	0.8135 (10)	0.073 (3)
C24	0.4878 (14)	0.3977 (15)	0.8610 (10)	0.072 (3)
C25	0.3749 (13)	0.2519 (12)	0.7745 (10)	0.065 (3)
C26	0.3756 (11)	0.2340 (10)	0.6386 (8)	0.049 (2)

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.373 (9)	C4—C5	1.492 (10)
O1—C5	1.437 (8)	C5—O3	1.416 (9)
C2—O2	1.221 (9)	C5—C6	1.534 (9)
C2—C3	1.419 (10)	C6—O4	1.433 (9)
C3—C4	1.351 (10)	C6—C21	1.498 (10)
C4—N1	1.341 (9)	O3—C11	1.473 (8)
C2—O1—C5	108.7 (6)	O3—C5—C4	115.8 (7)
O2—C2—O1	120.0 (8)	O1—C5—C4	104.3 (6)
O2—C2—C3	130.3 (9)	O3—C5—C6	104.6 (6)
O1—C2—C3	109.8 (7)	O1—C5—C6	109.3 (6)
C4—C3—C2	108.5 (7)	C4—C5—C6	114.4 (6)
N1—C4—C3	126.5 (7)	O4—C6—C21	106.7 (7)
N1—C4—C5	124.7 (7)	O4—C6—C5	110.2 (6)
C3—C4—C5	108.8 (7)	C21—C6—C5	112.7 (6)
O3—C5—O1	108.2 (6)	C5—O3—C11	118.7 (6)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1992b). Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1288). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1:1 Complex Formed by 2-Picoline N-Oxide and 4-Nitrophenol

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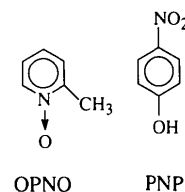
Abstract

The 2-picoline N-oxide and 4-nitrophenol moieties in the title complex, $C_6H_7NO.C_6H_5NO_3$, are held together by an intermolecular O—H···CN hydrogen bond. This crystal structure exhibits partial overlap between the rings of the molecules, in the [110] direction. The complex formed may be described by two planes which contain the 2-picoline N-oxide and 4-nitrophenol molecules, respectively.

Comment

There is a growing interest in the study and development of organic materials that have non-linear properties, as evidenced by the large number of publications on this subject (*e.g.* Pugh, Morley, Nicoud & Twieg, 1987; Prasad & Williams, 1991; Marder, Gorman, Tiemann & Cheng, 1993; Burland, Miller & Walsh, 1994; Kitazawa, Higuchi, Takahashi, Wada & Sasabe, 1995).

The present structure determination is one in a series of investigations of molecular complexes based on 2-picoline N-oxide (OPNO). The crystal structure reported in this work is part of an ongoing study into the effect of substitution on the packing of the complexes formed from OPNO and hydrogen-bond donors. The formation of the adduct from OPNO and 4-nitrophenol (PNP) may help to explore the possible applications of this system in non-linear optics. Since the literature does not contain enough structural information about OPNO, other similar systems have been analysed. One structure that could be compared with our system is that of the picolinic acid N-oxide (Laing & Nicholson, 1971). The formation of similar adducts from 3-picoline N-oxide and fumaric acid, 4-picoline N-oxide and 2-nitrobenzoic acid (Gorres, McAfee & Jacobson, 1975; Moreno-Fuquen, de Almeida Santos & Valderrama, 1995) have been undertaken. The N—O bond length of 1.324 (2) Å in the title structure lies between the values of 1.304 (6) Å, found in the adduct of 3-picoline N-oxide and fumaric acid, and 1.37 Å in the chlorhydrate of pyridinoxide (Tsoucaris, 1961), and is close to the values reported for picolinic acid N-oxide (1.34 Å) and for the adduct of 4-picoline N-oxide and 2-nitrobenzoic acid [1.338 (3) Å]. The C—O bond length of 1.364 (3) Å in the present complex is very close to that in the PNP molecule (1.361 Å; Coppens & Schmidt, 1965). Other internal distances and angles of the PNP molecule of the adduct are comparable with those reported for the free molecule, furthermore distances and angles for the pyridinoxide ring are comparable with those reported previously (Laing & Nicholson, 1971; Gorres, McAfee & Jacobson, 1975; Moreno-Fuquen, de Almeida Santos & Valderrama, 1995).

OPNO   PNP

The OPNO + PNP adduct and its numbering scheme are shown in Fig. 1. The molecular complex is held together by an intermolecular hydrogen bond between the O3 of the PNP and the O4 of the N-oxide group of the OPNO with an O3···O4 distance equal to 2.600 (3) Å. The dihedral angle formed by the planes which essentially contain the rings of the molecules is 87.75 (8)°. The title complex exhibits overlap between the OPNO and PNP molecules in approximately the [110] direction. The mean interplanar distances between