

**(5*S*)-3-Oxo-4-oxa-endo-tricyclo-
[5.2.1.0^{2,6}]dec-8-en-5-yl acetate**

Dianne D. Ellis* and Anthony L. Spek

Bijvoet Centre for Biomolecular Research, Department of Crystal and Structural
Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
Correspondence e-mail: d.d.ellis@chem.uu.nl

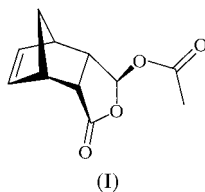
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The molecular structure of C₁₁H₁₂O₄, based on a norbornene core, was established to confirm the configuration of an acetoxy side-chain group in addition to the formation of the *endo* product. The acetoxy side chain lies in an axial position relative to the five-membered fused ring. Bond distances and angles show no unusual features, with all geometric parameters lying within their expected ranges. The overall stereochemistry of the molecule was ascertained from the chiral furanone starting material.

Comment

Strigol derivatives and members of the related sesquiterpene lactone family are known to induce germination of seeds from parasitic weeds. Early synthetic routes to the formation of *endo*-tricyclo *exo*-hydroxy lactones consisted of laborious processes which included the separation of diastereomers and selective recrystallization. A simpler synthetic procedure was achieved by reaction of the racemic alcohol mixture with an acyl donor in the presence of lipase, which acts as a catalyst (Thuring *et al.*, 1996). The synthesis of the title compound, (I), encompasses the optically pure 5-acetoxy-2(*5H*)furanone (van der Deen *et al.*, 1994), the acetyl functionality acting as temporary protection for the hydroxy group.

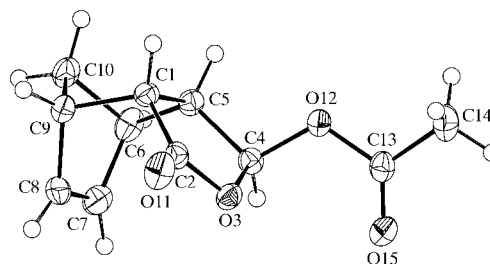


The molecular structure of (I) is shown in Fig. 1, with selected geometric parameters provided in Table 1. The conformation of (I) is based on the standard bicyclo[2.2.1]-heptene (norbornene) core, comprising two five-membered rings, with a third fused system in an *endo* configuration. Under the reaction conditions, there has been retention of

configuration at the carbon centre (C4) and the molecular structure was based on having an *S* configuration here. Thus the configuration at atoms C1, C5, C6 and C9 are *R*, *S*, *R* and *S*.

All three five-membered rings in (I) are in envelope conformations. The C6, C7, C8, C9 and C10 ring has 97% in the *cis* form (Evans & Boeyens, 1989) with puckering parameters of $Q = 0.546(2) \text{ \AA}$, $\varphi = 323.5(2)^\circ$ (calculations from *PLATON*; Spek, 2000), whilst the second ring comprising C1, C5, C6, C10 and C9 has 85% in the *cis* form [$Q = 0.642(2) \text{ \AA}$, $\varphi = 105.34(19)^\circ$]. Both rings have C10 as the 'envelope' atom. The third ring, with atoms O3, C2, C1, C5 and C4, is not as puckered as the other two rings, being more 'twisted' at C4 by 64% [$Q = 0.150(2) \text{ \AA}$, $\varphi = 150.6(7)^\circ$].

Comparison of the bond distances and angles in (I) with those determined for norbornene carboxylic anhydride derivatives (Garbaskas & Buese, 1992; Schonk *et al.*, 1992; Shnulin *et al.*, 1982) show no significant variations associated with acetylation at O12. The three types of C—O bonds within each O=C—O—C unit of (I) are consistent: C2—O11 = 1.194(2) *cf.* C13—O15 = 1.195(2) \AA ; C2—O3 = 1.360(2) *cf.* C13—O12 = 1.369(2) \AA ; and C4—O3 = 1.425(2) *cf.* C4—O12 = 1.425(2) \AA , and all other bond types lie in their expected ranges. The inter-bridgehead angles C10—C6—C5 and C10—C9—C1 of 98.44(15) and 98.99(15) $^\circ$, respectively, are contracted with respect to the tetrahedral value, as is the C6—

**Figure 1**

Displacement ellipsoid plot (*PLATON*; Spek, 2000) of (I) drawn at the 50% probability level.

C10—C9 angle of 93.82(14) $^\circ$. The angles at the non-substituted end of the norbornene fragment are 4 $^\circ$ wider on average than those at the fused end [the C—C—C bond angles being in the range 102.70(15)–108.53(16) $^\circ$].

The acetoxy side chain (O12, C13, C14, O15) at C4 is axial and almost perpendicular to the carboxylate group which forms part of the fused ring (O11, C2, O3, C4); the angle between the two planes is 85.62(16) $^\circ$. The twisting of the acetoxy functionalities is indicated by the torsion angles of $-169.71(17)^\circ$ for O11—C2—O3—C4 and 10.9(3) $^\circ$ for C4—O12—C13—O15, each deviating from the *trans* conformation.

The crystal structure is not stabilized by inter- (or intra-) molecular hydrogen bonds – all contacts to potential donor atoms are quite long: O3 \cdots H10Bⁱ 2.60, O11 \cdots H14Cⁱⁱ 2.55, O12 \cdots H9ⁱⁱⁱ 2.81 and O15 \cdots H6ⁱ 2.69 \AA [symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) *x*, $-1 + y$, *z*; (iii) $-x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$].

Experimental

C₁₁H₁₂O₄ was synthesized from a Diels–Alder reaction of (+)-5-acetoxy-2(5*H*)-furanone (van der Deen *et al.*, 1994) with cyclopentadiene. The compound was recrystallized from a diethyl ether/hexane mixture.

Crystal data

C ₁₁ H ₁₂ O ₄	Mo <i>K</i> α radiation
<i>M_r</i> = 208.21	Cell parameters from 25 reflections
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	$\theta = 9.73\text{--}13.97^\circ$
<i>a</i> = 7.4538 (8) Å	$\mu = 0.106\text{ mm}^{-1}$
<i>b</i> = 7.5568 (7) Å	<i>T</i> = 150 (2) K
<i>c</i> = 17.6385 (13) Å	Plate, colourless
<i>V</i> = 993.52 (16) Å ³	0.5 × 0.5 × 0.5 mm
<i>Z</i> = 4	
<i>D_x</i> = 1.392 Mg m ⁻³	

Data collection

Enraf–Nonius CAD-4T diffractometer	$\theta_{\text{max}} = 27.44^\circ$
$\omega/2\theta$ scans	<i>h</i> = −9 → 9
3710 measured reflections	<i>k</i> = −9 → 7
1334 independent reflections	<i>l</i> = 0 → 22
1213 reflections with <i>I</i> > 2σ(<i>I</i>)	3 standard reflections
<i>R</i> _{int} = 0.023	frequency: 60 min
	intensity decay: 2.2%

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.1472P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.083$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.080	$\Delta\rho_{\text{max}} = 0.17\text{ e \AA}^{-3}$
1334 reflections	$\Delta\rho_{\text{min}} = -0.24\text{ e \AA}^{-3}$
149 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

C2—O11	1.194 (2)	C13—O15	1.195 (2)
C2—O3	1.360 (2)	C13—O12	1.369 (2)
C4—O3	1.425 (2)	C4—O12	1.425 (2)
C10—C6—C5	98.44 (15)	C9—C10—C6	93.82 (14)
C10—C9—C1	98.99 (15)		
O11—C2—O3—C4	−169.71 (17)	C4—O12—C13—O15	10.9 (3)

The data set included some Friedel-related reflections, but due to the absence of anomalous scatterers, the absolute configuration could not be established reliably (Flack & Bernardinelli, 1999). A final value of 0.4 (13) was obtained for the Flack *x* parameter (Flack,

1983). The absolute configuration was therefore set in accordance with the known configuration of the optically pure precursor (+)-5-acetoxy-2(5*H*)-furanone. The estimated number of Friedel pairs measured was 935 (70%), and these reflections were merged in the final refinement cycles. The presence of only one H atom on C7 and C8 was confirmed by inspection of the difference Fourier map. All H atoms except for those on methyl group C14 were placed in idealized positions (0.95–1.00 Å) and constrained to ride on their C atoms with *U*_{iso}(H) = 1.2*U*_{eq}(C). The methyl H atoms on C14 were constrained to an ideal geometry (C—H = 0.98 Å) with *U*_{iso}(H) = 1.5*U*_{eq}(C), and allowed to rotate freely about the C—C bonds.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1119). Services for accessing these data are described at the back of the journal.

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