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Functionalized Hydrocarbons with Condensed Ring Skeletons. IX. A Trioxotricyclo[8.4.0.0^{2,7}]tetradecane

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Abstract. Methyl 1,2-*trans*-1,10-*cis*-2,7-*cis*-7-methyl-6,8,14-trioxotricyclo[8.4.0.0^{2,7}]tetradecane-1-carboxylate, $C_{17}H_{22}O_5$, $M_r = 306{\cdot}36$, monoclinic, $P2_1/c$, $a = 10{\cdot}3072\ (2)$, $b = 14{\cdot}9042\ (3)$, $c = 10{\cdot}5568\ (3)$ Å, $\beta = 109{\cdot}552\ (2)°$, $V = 1528{\cdot}22\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}332$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54056 Å, $\mu = 0{\cdot}76$ mm^{-1}, $F(000) = 665{\cdot}93$, room temperature, final $R = 0{\cdot}037$ for 2500 observed reflections. The structure consists of three angular fused six-membered rings *A*, *B* and *C*. The *AB* ring junction is *cis*, the C1 ester and the C2 proton (IUPAC numbering) are in an *anti* relationship, and the *BC* ring junction is *cis* (abbreviated to *CAC*). Rings *A*, *B* and *C* adopt chair conformations.

Introduction. Quassinoids are a class of degraded triterpenes found mostly in the bitter principles of 'Simaroubaceous' plants growing in central Asia (Polonsky, 1973, 1985). Some members of that family display interesting and potent biological activities and some have antineoplastic properties. In the course of studies directed toward the synthesis of compounds belonging to this family of natural products we prepared β-diketone (3) (Fig. 1) in a stereoselective fashion from the base-catalyzed [4 + 2] cycloaddition of β-ketoester (1) and dienophile (2) followed directly by an acidic decarboxylation–hydrolysis step (Spino & Deslongchamps, 1989). The stereochemistry shown for compound (3) was assigned on the basis of previous studies on similar systems (Deslongchamps & Lavallée, 1988) and was consistent with a high-resolution ^{1}H NMR spectroscopic analysis. We decided to look at the alkylation reaction of β-diketones like (3) and its stereochemistry as a means of introducing the C8 methyl group present in many quassinoids. Only a few examples of the alkylation of systems like compound (3) have so far appeared in the literature (Duthaler & Maienfisch, 1982; Chan & Prasad, 1987). On the basis of stereoelectronic control, we would expect the alkylation of the enolate of (3) to yield, as the major product, the tricyclic compound having the *trans* fused junction between rings *B* and *C*. However, the methyl ester at C1 could direct the attack of the alkylating agent, by way of steric hindrance, to the opposite face of the molecule giving the product with the *cis-BC* ring junction. The alkylation with methyl iodide actually proceeded to 65% yield to give predominantly the *cis-BC* ring junction product (4) along with its *trans* isomer in a 2:1 ratio.† The two isomeric products could easily be separated by column chromatography on silica gel, but their respective structures could not be determined by spectroscopic means. That no epimerization had occurred at C9 (Fig. 2) under the reaction conditions was verified simply by recovering (3), unchanged, after protonation of the potassium enolate generated in an identical manner. We report herein the X-ray diffraction analysis of the major isomer, compound (4), undertaken to determine its relative stereochemistry and, therefore, also that of the minor isomer.

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† In addition, 8% of *O*-alkylated products were isolated.

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Experimental. Crystal 0·30 × 0·30 × 0·30 mm; Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Cu $K\alpha$ radiation; lattice parameters refined from 42 reflections with 2θ range 60–100°; $-12 \le h \le 11$, $0 \le k \le 17$, $0 \le l \le 12$; $2\theta_{max} = 144°$; two standard reflections monitored every 60 min, without significant deviation; 2983 unique measured reflections; 2500 observed with $I_{net} > 2{\cdot}5\sigma I_{net}$; structure solved by direct methods and refined with *NRCVAX* (Gabe, Lee & Le Page, 1985). All non-H atoms were located in the first Fourier E map. After subsequent least-squares refinement, all H atoms were found by two Fourier difference syntheses. All non-H atoms were refined anisotropically. Positional and isotropic thermal parameters for H atoms were refined. The last least-squares cycle was calculated with 44 atoms; 288 parameters using weights based on counting statistics. The residuals for all significant reflections are $R_F = 0{\cdot}037$, $wR = 0{\cdot}028$ and $S = 2{\cdot}589$; max. $\Delta/\sigma = 0{\cdot}016$. In the final difference map, the deepest hole was $-0{\cdot}14$ e Å^{-3} and the highest peak 0·19 e Å^{-3}. The secondary-extinction coefficient was 2·02 (4). Atomic scattering factors used were those incorporated in *NRCVAX*.

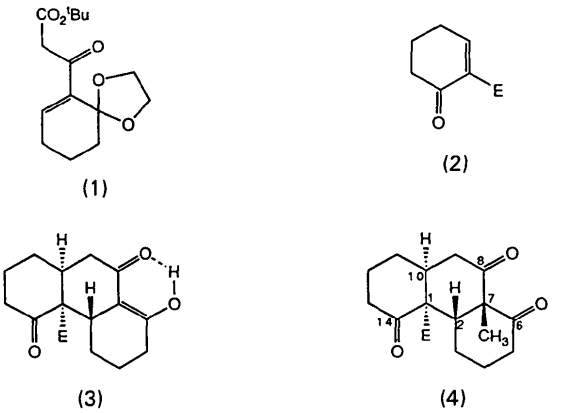

Fig. 1. IUPAC numbering (E = $COOCH_3$).

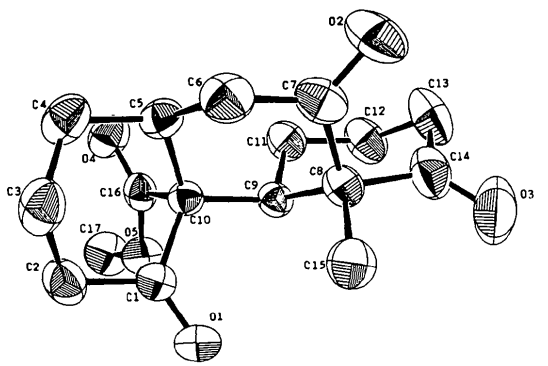

Fig. 2. *ORTEP* perspective view and atom numbering.

Table 1. *Final coordinates and B_{eq} values for non-H atoms, with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
C1	0·61279 (15)	0·34307 (10)	0·14266 (15)	3·19 (7)
C2	0·61442 (21)	0·24569 (12)	0·18097 (20)	4·31 (9)
C3	0·75655 (22)	0·21378 (13)	0·26784 (20)	4·76 (10)
C4	0·80924 (22)	0·27166 (12)	0·39300 (19)	4·49 (9)
C5	0·81704 (16)	0·37130 (11)	0·35971 (16)	3·51 (7)
C6	0·93985 (19)	0·38690 (13)	0·31125 (22)	4·55 (9)
C7	0·95053 (16)	0·48122 (12)	0·26873 (17)	4·10 (8)
C8	0·82183 (15)	0·51758 (11)	0·16211 (15)	3·44 (8)
C9	0·69531 (14)	0·50617 (10)	0·21241 (15)	2·93 (7)
C10	0·68016 (14)	0·40831 (9)	0·26002 (13)	2·80 (6)
C11	0·70072 (19)	0·57448 (11)	0·32332 (18)	3·83 (8)
C12	0·71528 (21)	0·67057 (12)	0·28251 (23)	4·73 (11)
C13	0·84587 (23)	0·68231 (15)	0·2481 (3)	5·84 (13)
C14	0·84713 (17)	0·61762 (13)	0·14015 (21)	4·89 (10)
C15	0·80569 (22)	0·46708 (16)	0·03100 (20)	4·71 (10)
C16	0·57525 (16)	0·41198 (10)	0·33547 (15)	3·23 (7)
C17	0·33810 (23)	0·42618 (19)	0·30798 (25)	5·23 (12)
O1	0·55752 (11)	0·36854 (8)	0·02848 (10)	4·37 (6)
O2	1·05562 (11)	0·52492 (9)	0·31419 (13)	6·07 (7)
O3	0·86624 (15)	0·64203 (9)	0·03832 (15)	7·36 (9)
O4	0·60285 (12)	0·40701 (7)	0·45478 (10)	4·50 (6)
O5	0·44758 (11)	0·42161 (7)	0·24953 (10)	4·06 (6)

Table 2. *Molecular geometry*

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

C1—C2	1·5052 (24)	C8—C14	1·5444 (24)
C1—C10	1·5450 (20)	C8—C15	1·535 (3)
C1—O1	1·2092 (18)	C9—C10	1·5675 (20)
C2—C3	1·521 (3)	C9—C11	1·5384 (22)
C3—C4	1·518 (3)	C10—C16	1·5436 (20)
C4—C5	1·5344 (25)	C11—C12	1·517 (3)
C5—C6	1·534 (3)	C12—C13	1·517 (3)
C5—C10	1·5519 (20)	C13—C14	1·496 (3)
C6—C7	1·491 (3)	C14—O3	1·2119 (24)
C7—C8	1·5234 (22)	C16—O4	1·1972 (18)
C7—O2	1·2164 (20)	C16—O5	1·3328 (19)
C8—C9	1·5732 (21)	C17—O5	1·4577 (21)

(*b*) Valence angles (°) with e.s.d.'s in parentheses

C2—C1—C10	115·45 (13)	C8—C9—C10	113·06 (12)
C2—C1—O1	121·99 (14)	C8—C9—C11	111·24 (12)
C10—C1—O1	122·49 (14)	C10—C9—C11	110·72 (12)
C1—C2—C3	112·66 (15)	C1—C10—C5	112·50 (12)
C2—C3—C4	109·81 (16)	C1—C10—C9	113·25 (11)
C3—C4—C5	112·43 (15)	C1—C10—C16	103·40 (11)
C4—C5—C6	109·60 (15)	C5—C10—C9	112·49 (12)
C4—C5—C10	113·19 (14)	C5—C10—C16	107·31 (12)
C6—C5—C10	112·62 (13)	C9—C10—C16	107·14 (11)

Discussion. Table 1 gives the final atomic parameters with their B_{eq} values.* Fig. 2 shows the atom numbering and an *ORTEP* (Johnson, 1976) perspective view of the tricyclic compound. Bond lengths and angles are given in Tables 2(*a*) and 2(*b*). From

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52922 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the two isolated isomers, (4) corresponds to the major product and is found to be *cis* at the *BC* junction. The three rings of compound (4) can, in principle, exist in two distinct chair-chair-chair conformations owing to its *cis-anti-cis* stereochemistry. In one of these two conformations, however, the methyl ester at C10 experiences two repulsive interactions with the C14 carbonyl and the C11 methylene. The X-ray diffraction analysis indicates that compound (4) therefore prefers to adopt the chair-chair-chair conformation in which only the methyl at C8 experiences interaction with the carbonyl group at C1. In addition this confirms the *cis* stereochemistry of the *AB* ring junction of the starting compound (3).

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Structure of 7,7-Dimethyldihydropyrnopetrocropane

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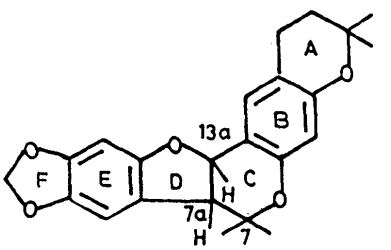
Abstract. 1,2,7a,13a-Tetrahydro-3,3,7,7-tetramethyl-3*H*,7*H*-[1,3]dioxolo[4″,5″:5′,6′]benzofuro[2′,3′:4,3]-pyrano[3,2-*g*][1]benzopyran, $C_{23}H_{24}O_5$, $M_r = 380{\cdot}44$, monoclinic, $P2_1/c$, $a = 6{\cdot}403$ (3), $b = 28{\cdot}081$ (5), $c = 10{\cdot}807$ (4) Å, $\beta = 97{\cdot}56$ (3)°, $V = 1926{\cdot}59$ Å^3, $Z = 4$, $D_x = 1{\cdot}311$ Mg m^{-3}, $\mu = 0{\cdot}66$ mm^{-1}, $F(000) = 808$, λ(Cu $K\alpha$) = 1·5418 Å, $T = 296$ K, final R and wR are 0·0573 and 0·0699 respectively using 2405 observed reflections. The basic benzofurobenzopyran skeleton has a *cis* ring junction with a staggered conformation viewed from C(7) to C(7*a*). Intermolecular distances indicate the possibility of C—H···O interactions.

Introduction. A number of structurally related oxygen heterocyclic compounds, isolated from nature, were reported to be biologically active, showing antifungal and antitumor activity (Vanetten, 1976; Kojima, Fukushima, Ueno & Saiki, 1970). The antifungal activity may depend on the molecular geometry (Perrin & Cruickshank, 1969). From two possible conformations of the benzofurobenzopyran skeleton in the *cis* arrangement (I), the most stable is the staggered one (Pachler & Underwood, 1967).



(I)

In order to compare the structure of the basic benzofurobenzopyran skeleton of this synthesized compound with the related natural products and to correlate the suggested structure–activity (Perrin & Cruickshank, 1969) relationship, a detailed structure analysis by X-ray diffraction methods was undertaken.

Experimental. The title compound was synthesized by $LiPdCl_4$-catalyzed Heck arylation of chromene-

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