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Structure of a Tricyclic Lactone – an Important Intermediate for the Total Synthesis of Dihydromevinolin

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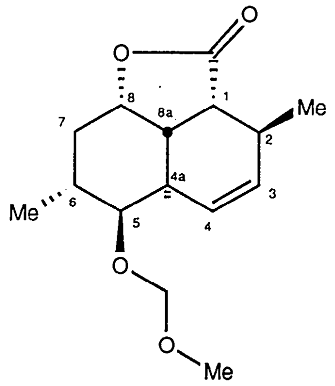
Abstract. (1*R*,2*S*,4a*R*,5*S*,6*R*,8*S*,8a*S*)-5-Methoxymethoxy-2,6-dimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1,8-carbolactone, $C_{15}H_{22}O_4$, $M_r = 266{\cdot}34$, monoclinic, $P2_1$, $a = 9{\cdot}806\,(6)$, $b = 5{\cdot}758\,(3)$, $c = 12{\cdot}879\,(8)$ Å, $\beta = 92{\cdot}87\,(5)°$, $V = 726{\cdot}27$ Å^3, $D_x = 1{\cdot}218$ Mg m^{-3}, $Z = 2$, $\lambda(\mathrm{Cu}\,K\bar{\alpha}) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\,K\bar{\alpha}) = 0{\cdot}674$ mm^{-1}, $F(000) = 288$, $T = 218$ K, $R = 0{\cdot}0458$ for 2633 observed reflections. The title compound, $C_{15}H_{22}O_4$, contains a *trans*-fused hexahydronaphthalene system, with a C=C bond at C(3)—C(4), and with a γ-lactone ring *cis*-fused across C(1)···C(8). The cyclohexane ring exhibits a flattened-chair conformation, the cyclohexene ring has the 1,3-diplanar conformation, and the five-membered γ-lactone has a C(8a)-envelope conformation. The molecule also contains a methoxymethoxy substituent axial at C(5), *trans* to a C(6) methyl group, and another methyl substituent at C(2) *trans* to the C atom of the γ-lactone.

Introduction. During the course of synthetic work aimed at the elaboration of the octahydronaphthalene portion of dihydromevinolin from optically active starting materials, it became necessary to use an intramolecular Diels–Alder reaction. Inspection of models had shown a preference for an *exo*-transition state leading possibly to the desired product. However, in view of the unknown stereochemistry at a secondary alcohol group produced in a previous step, it became imperative to seek definitive evidence for the structure of the Diels–Alder product. We report herein the crystal structure of this tricyclic product, $C_{15}H_{22}O_4$, which is a crucial intermediate in the total synthesis of the antihypercholesteremil agent dihydromevinolin (Albers-Schonberg *et al.*, 1981).



Experimental. Crystals of $C_{15}H_{22}O_4$ were recrystallized from hexane solution. Crystal fragment is a triangular

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prism of dimensions 0·12 × 0·12 × 0·15 mm (edges) × 0·41 mm (height). Unit-cell dimensions from 25 well centered reflections in the range $40 \le 2\theta \le 50^\circ$. Unit-cell dimensions and data collection at 218 K using the Nonius low-temperature attachment. Temperature fluctuations within ±4 K. Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\bar{\alpha}$ radiation, ω–2θ scan, $\Delta\omega = (1\cdot00 + 0\cdot14\tan\theta)^\circ$, $2\theta_{\max} = 140\cdot0^\circ$, $-11 \le h \le 11$, $-6 \le k \le 7$, $-15 \le l \le 15$. Orientation monitored every 200 measurements, intensity checked every hour using seven standard reflections, largest intensity fluctuation 3·0%, 5354 measured reflections, 2715 relections $(hkl, \bar{h}kl, h\bar{k}l, \bar{h}\bar{k}l)$ retained after averaging of equivalent reflections of which 2635 where $I > 1\cdot96\sigma(I)$ retained for structure determination and refinement. Lp correction, no absorption correction.

The structure was solved by direct methods (*MULTAN*80).[*] Full-matrix least-squares refinement based on F, all non-H atoms anisotropic. All H atoms found on difference Fourier synthesis. Function minimized: $\sum w(|F_o| - |F_c|)^2$. In the last refinement cycles, two reflections ($\bar{1}12$ and $\bar{2}23$) were given zero weight as they were suffering from extinction. Final $R = 0\cdot0458$, $wR = 0\cdot0567$ [weights derived from the counting statistics $w = 1/\sigma^2(F)$] and $S = 4\cdot4169$ for 260 parameters. Maximum $\Delta/\sigma = 0\cdot049$, average $\Delta/\sigma = 0\cdot008$, residual electron density fluctuation on the final difference Fourier synthesis $+0\cdot39$ and $-0\cdot35$ e Å^{-3}.

The scattering curves for the non-H atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965).

Discussion. The final atomic coordinates for $C_{15}H_{22}O_4$ are given in Table 1.[†] The atomic numbering adopted is given on the stereoview of the molecule shown in Fig. 1. The bond distances, angles and torsion angles of interest are given in Table 2.

This tricyclic molecule consists of a *trans*-fused hexahydronaphthalene system, with a C=C bond at C(3)—C(4), and with a γ-lactone ring *cis*-fused across C(1)···C(8). The cyclohexane ring exhibits a flattened-chair conformation, the cyclohexene ring has the 1,3-diplanar conformation while the five-membered ring γ-lactone has a C(8a)-envelope conformation.

Table 1. *Final atomic coordinates with their e.s.d.'s* (×10^4) *and* U_{eq} (Å^2×10^4) *for* $C_{15}H_{22}O_4$

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(10)	−440 (2)	2653	3902 (2)	722
O(50)	4729 (2)	−298 (6)	1938 (1)	440
O(60)	6358 (2)	1347 (7)	901 (2)	767
O(80)	310 (2)	−91 (6)	2865 (1)	495
C(1)	1830 (2)	948 (7)	4269 (2)	405
C(2)	2440 (3)	3061 (7)	4851 (2)	457
C(3)	3668 (3)	4023 (7)	4339 (2)	480
C(4)	3961 (3)	3598 (7)	3368 (2)	415
C(4a)	3057 (2)	2020 (6)	2708 (2)	326
C(5)	3590 (2)	1212 (7)	1683 (2)	359
C(6)	2454 (2)	−65 (7)	1045 (2)	418
C(7)	1856 (3)	−2024 (7)	1677 (2)	472
C(8)	1558 (3)	−1489 (6)	2794 (2)	414
C(8a)	2629 (2)	−9 (6)	3379 (2)	337
C(10)	447 (2)	1337 (7)	3703 (2)	482
C(20)	2808 (4)	2489 (10)	5992 (2)	693
C(50)	5612 (3)	−615 (9)	1125 (2)	639
C(60)	1380 (3)	1623 (8)	587 (2)	520
C(70)	7360 (4)	1972 (13)	1702 (3)	930

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with their e.s.d.'s for* $C_{15}H_{22}O_4$

C(1)—C(2)	1·535 (5)	C(1)—C(10)	1·524 (4)
C(2)—C(3)	1·507 (4)	C(10)—O(80)	1·358 (4)
C(3)—C(4)	1·320 (4)	O(80)—C(8)	1·472 (4)
C(4)—C(4a)	1·503 (4)	C(10)—O(10)	1·191 (3)
C(4a)—C(5)	1·517 (3)	C(2)—C(20)	1·531 (4)
C(4a)—C(8a)	1·525 (4)	C(5)—O(50)	1·440 (4)
C(5)—C(6)	1·538 (4)	O(50)—C(50)	1·404 (3)
C(6)—C(7)	1·525 (5)	C(50)—O(60)	1·384 (6)
C(7)—C(8)	1·514 (4)	O(60)—C(70)	1·435 (5)
C(8)—C(8a)	1·522 (4)	C(6)—C(60)	1·530 (5)
C(8a)—C(1)	1·524 (4)		

C(1)—C(2)—C(3)	112·2 (3)	O(80)—C(10)—C(1)	110·0 (3)
C(2)—C(3)—C(4)	124·3 (3)	C(10)—C(1)—C(8a)	99·9 (2)
C(3)—C(4)—C(4a)	119·9 (3)	C(10)—C(1)—C(2)	115·7 (3)
C(4)—C(4a)—C(8a)	108·3 (2)	O(80)—C(8)—C(7)	111·8 (2)
C(4a)—C(8a)—C(1)	108·4 (2)	O(80)—C(10)—O(10)	120·8 (3)
C(8a)—C(1)—C(2)	116·9 (2)	C(1)—C(10)—O(10)	129·2 (3)
C(4a)—C(5)—C(6)	109·9 (2)	C(1)—C(2)—C(20)	111·4 (3)
C(5)—C(6)—C(7)	110·9 (2)	C(3)—C(2)—C(20)	110·1 (3)
C(6)—C(7)—C(8)	117·0 (3)	C(4)—C(4a)—C(5)	117·3 (2)
C(7)—C(8)—C(8a)	115·0 (2)	C(4a)—C(5)—O(50)	106·5 (2)
C(8)—C(8a)—C(4a)	110·6 (2)	C(6)—C(5)—O(50)	111·5 (2)
C(8a)—C(4a)—C(5)	112·0 (2)	C(7)—C(6)—C(60)	113·6 (3)
C(1)—C(8a)—C(8)	101·9 (2)	C(5)—C(6)—C(60)	111·6 (2)
C(8a)—C(8)—O(80)	102·6 (2)	C(5)—O(50)—C(50)	114·1 (3)
C(8)—O(80)—C(10)	109·3 (2)	O(50)—C(50)—O(60)	113·7 (3)
		C(50)—O(60)—C(70)	113·9 (3)

C(1)—C(2)—C(3)—C(4)	18·7 (4)	C(4)—C(4a)—C(5)—O(50)	67·7 (3)
C(2)—C(3)—C(4)—C(4a)	−1·4 (5)	C(4a)—C(5)—O(50)—C(50)	−160·6 (3)
C(3)—C(4)—C(4a)—C(8a)	−40·0 (4)	C(5)—O(50)—C(50)—O(60)	69·5 (4)
C(4)—C(4a)—C(8a)—C(1)	61·3 (3)	O(50)—C(50)—O(60)—C(70)	68·6 (4)
C(4a)—C(8a)—C(1)—C(2)	−46·3 (3)	C(7)—C(6)—C(5)—O(50)	63·8 (3)
C(8a)—C(1)—C(2)—C(3)	7·3 (4)	C(6)—C(5)—O(50)—C(50)	79·6 (3)
C(4a)—C(5)—C(6)—C(7)	−54·0 (3)	C(8)—C(7)—C(6)—C(60)	−82·5 (3)
C(5)—C(6)—C(7)—C(8)	44·1 (4)	C(4a)—C(5)—C(6)—C(60)	73·7 (3)
C(6)—C(7)—C(8)—C(8a)	−40·3 (4)	O(50)—C(5)—C(6)—C(60)	−168·5 (2)
C(7)—C(8)—C(8a)—C(4a)	44·7 (3)	O(80)—C(8)—C(7)—C(6)	76·2 (3)
C(8)—C(8a)—C(4a)—C(5)	−56·8 (3)	C(10)—O(80)—C(8)—C(7)	−147·5 (3)
C(8a)—C(4a)—C(5)—C(6)	62·4 (3)	O(10)—C(10)—O(80)—C(8)	179·0 (3)
C(1)—C(10)—O(80)—C(8)	−·7 (3)	O(10)—C(10)—C(1)—C(8a)	−155·0 (3)
C(10)—O(80)—C(8)—C(8a)	−23·8 (3)	C(10)—C(1)—C(8a)—C(4a)	79·2 (3)
O(80)—C(8)—C(8a)—C(1)	38·2 (3)	C(10)—C(1)—C(2)—C(3)	−109·9 (3)
C(8)—C(8a)—C(1)—C(10)	−37·4 (3)	O(10)—C(10)—C(1)—C(2)	−28·7 (5)
C(8a)—C(1)—C(10)—O(80)	24·7 (3)	C(10)—C(1)—C(2)—C(20)	126·1 (3)
C(8)—C(8a)—C(4a)—C(4)	172·3 (2)	C(8a)—C(1)—C(2)—C(20)	−116·7 (3)
C(1)—C(8a)—C(4a)—C(5)	−167·8 (2)	C(20)—C(2)—C(3)—C(4)	143·5 (3)
C(8a)—C(4a)—C(5)—O(50)	−58·4 (3)		

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[*] The programs used here are modified versions of *NRC*-2, data reduction, *NRC*-10, bond distances and angles and *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *MULTAN*80, multisolution program (Main *et al.*, 1980); *SHELX*, program for structure determination (Sheldrick, 1976) and *ORTEP*, stereodrawings (Johnson, 1965).

[†] Tables of anisotropic temperature factors, structure factors and atomic coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51340 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A survey of the saturated γ-lactones in a variety of molecules reveals a common conformation in which the C_α—CO—O—C_γ group is planar and the β-C atom is at the flap of this envelope conformation. This usual arrangement is found for example in 19-acetylteuspinin (Eguren, Fayos & Perales, 1981), nagilactone A diacetate (Hirotsu, Higuchi, Shimada, Hayashi & Sakan, 1975), (+)- or (±)-*trans*-1β-carboxy-8β-hydroxy-1α,4a,6β-trimethyl-5-oxodecahydronaphthalene lactone (Adinolfi, Benedetti, Di Blasio & Pedone, 1975*a*,*b*). In all these molecules the β-C is displaced from the lactone ring plane by about 0·6 Å. The γ-lactone in $C_{15}H_{22}O_4$ fits this pattern, the β-C atom C(8a) is displaced from the best plane calculated for C(1), C(10), O(10), O(80) and C(8) by 0·620 (3) Å. The C(sp^2)—O single bond in the lactone grouping is, as usual, appreciably shorter than the C(sp^3)—O bond (Riche, 1973): C(10)—O(80) = 1·358 (4) Å while C(8)—O(80) = 1·472 (4) Å. The C(1)—C(10)—O(10) bond angle with a value of 129·2 (3)° is the largest of those found around C(10). The same feature was observed in all the other γ-lactones associated with two six-membered rings (Eguren *et al.*, 1981; Hirotsu *et al.*, 1975; Adinolfi *et al.*, 1975*a*,*b*).

The torsion angles O(80)—C(8)—C(8a)—C(1) and C(10)—C(1)—C(8a)—C(8) with values of 38·2 (3) and −37·4 (3)° indicate the *cis*-fusion of the five-membered ring γ-lactone to the other two rings.

The cyclohexane ring has a chair conformation which is slightly distorted from ideal geometry. Atoms C(8), C(8a), C(6) and C(5) are closely coplanar and atoms C(4a) and C(7) are displaced to opposite sides of the above plane by 0·687 (3) and −0·492 (4) Å respectively. The flattening of the ring at C(7) and C(8) is apparent in the C(5)—C(6)—C(7)—C(8), C(6)—C(7)—C(8)—C(8a) and C(7)—C(8)—C(8a)—C(4a) torsion angles whose values are 44·1 (4), −40·3 (4) and 44·7 (3)° respectively. A slight puckering occurs at C(4a) and C(5) since the C(8a)—C(4a)—C(5)—C(6) torsion angle of 62·4 (3)° is larger than 60°. The deviation from the chair conformation may be mainly attributed to the formation of a lactone ring and to the 1,3-diaxial steric strains between C(60) and O(80). Thus, the C(60)···O(80) distance of 3·315 (4) Å is nearly equal to the sum of the van der Waals radii, although this is larger than one might expect from the Dreiding molecular models. The mean of the valency angles within the cyclohexane ring is 112·6°, ranging from 109·9 (2)° for C(4a)—C(5)—C(6) to 117·0 (3)° for C(6)—C(7)—C(8).

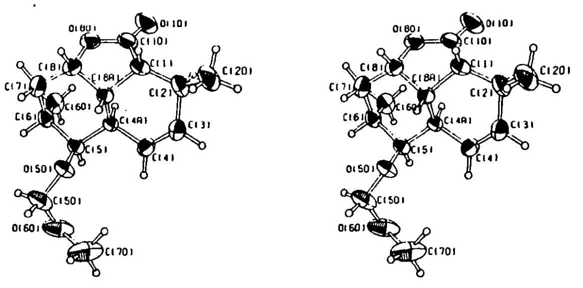

Fig. 1. Stereopair showing the molecular conformation and the atomic numbering of $C_{15}H_{22}O_4$.

The methyl group at C(6) is in the axial position and *trans* to the methoxymethoxy group at C(5). The torsion angle C(60)—C(6)—C(5)—O(50) has a value of −168·5 (2)°. The torsion angles C(5)—O(50)—C(50)—O(60) and O(50)—C(50)—O(60)—C(70) have values of 69·5 (4) and 68·6 (4)° respectively; thus, the methoxymethoxy group may be described by a *gg* conformation.

The cyclohexene ring is *trans*-fused to the cyclohexane ring, *i.e.* the torsion angles C(8)—C(8a)—C(4a)—C(4) and C(1)—C(8a)—C(4a)—C(5) have values of 172·3 (2) and −167·8 (2)° respectively.

The cyclohexene ring usually exhibits a half-chair conformation (monoplane form) in which the C—C=C—C group is planar and the other C atoms of the ring are below and above this plane. Examples of this arrangement are provided by 4-*tert*-butyl-1-cyclohexene-1-carboxylic acid (Gałdecki & Głowka, 1978), by (−)-(4*S*,8*S*)-α-bisabolol-8-(*p*-phenylazo)phenylmethane (Prangé, Babin, Fourneron & Julia, 1979) and by two diastereoisomeric molecules of $C_{12}H_{22}O_3$ (Bélanger-Gariépy, Beaudoin, Hanessian & Brisse, 1989). In each of the above compounds, the cyclohexene adopts the most stable conformation, the monoplane form, as calculated by Bucourt & Hainaut (1965) for this type of ring.

In $C_{15}H_{22}O_4$, on the other hand, the C atoms C(1) and C(8a) are displaced from the best plane [C(2), C(3), C(4), C(4a)], by −0·429 (4) and −0·952 (3) Å respectively. By comparison with the values of torsion angles tabulated for various conformations (Bucourt & Hainaut, 1965), it is found that the 1,3-diplanar form occurs in the cyclohexene part of $C_{15}H_{22}O_4$. The torsion angles differ, on average, by only 3·4° from those computed for this form. This unusual geometry may be due to the strain associated with the two rings: the five-membered ring being *cis*-fused at the C(1) and C(8a) atoms of cyclohexene while the cyclohexane ring is *trans*-fused at the C(8a) and C(4a) atoms of cyclohexene.

Note that the methyl group, C(20), is in an axial position at C(2) of the cyclohexene ring. It is *trans* to C(10) of the γ-lactone, but the torsion angle C(10)—C(1)—C(2)—C(20) of 126·1 (3)° differs greatly from 180°. This could be due to the presence of the lactone bridge between C(1) and C(8).

As a result of all these steric effects, most of the bond angles around the C(sp^3) atoms deviate significantly from the tetrahedral angle. The values range from 99·9 (2)° for C(10)—C(1)—C(8a) to 117·3 (2)° for C(4)—C(4a)—C(5).

There are no intermolecular contacts shorter than 3·35 Å, hence no other interaction but those of the van der Waals type.

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Crystal Structure of 3,8aβ-Diethyl-2,4aβ,6,7-tetramethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone

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Abstract. $C_{18}H_{26}O_2$, $M_r = 274\cdot40$, monoclinic, $P2_1/n$, $a = 21\cdot557\,(3)$, $b = 7\cdot9317\,(4)$, $c = 9\cdot525\,(1)$ Å, $\beta = 95\cdot790\,(7)^\circ$, $V = 1620\cdot3\,(3)$ Å^3, $Z = 4$, $D_x = 1\cdot125$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0\cdot70930$ Å, $\mu = 0\cdot7$ cm^{-1}, $F(000) = 600$, $T = 295$ K, $R = 0\cdot039$ for 1307 reflections. The molecule exists in the solid state in one conformation with the usual twisted geometry [bridgehead torsion angle $= -60\cdot9\,(4)^\circ$], and with the ring-junction methyl and ethyl groups pseudo-axial and pseudo-equatorial, respectively, with respect to the cyclohexene ring. Bond lengths and angles are normal, with no significant asymmetry in the ring skeleton resulting from the asymmetric substitution pattern. The observed photochemical behaviour can be rationalized on the basis of the observed molecular and crystal structure.

Introduction. Solution and solid state photochemical reactions of tetrahydro-1,4-naphthoquinone derivatives [Fig. 1, (1*a*)] proceed by two major reaction pathways (Trotter, 1983): β-hydrogen abstraction by carbonyl oxygen, and γ-hydrogen abstraction by ethylenic C atom. These compounds can exist in two different conformations [Fig. 1, (*A*) and (*B*)], which, for symmetrical quinones such as (1*a*), are enantiomeric and of equal energies. For the related naphthoquin-4-ols the two conformations are diastereomeric, and the lower energy conformation, which is invariably found in the solid state, is that which has the bulkier C4 substituent (usually OH) in the more favourable pseudo-equatorial site of the half-chair six-membered enone ring (Trotter, 1983). For asymmetric naphthoquinones, such as (1*b*) (Fig. 1), the conformers (*A*) and (*B*) are again diastereomeric. (*A*) has the ring-junction methyl (R_1) and ethyl (R_2) groups pseudo-equatorial and pseudo-axial, respectively, with respect to the ene-dione ring (and pseudo-axial and pseudo-equatorial, respectively, with respect to the cyclohexene ring); (*B*) has the opposite orientations. Since methyl and ethyl groups are usually considered to have similar

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