

| | | | | |
|-----|--------------|------------|--------------|-----------|
| C4 | 0.1081 (7) | 0.6680 (3) | -0.0086 (7) | 0.053 (3) |
| C5 | 0.1386 (15) | 0.6444 (6) | -0.2036 (11) | 0.090 (6) |
| C6 | 0.0344 (7) | 0.7196 (3) | -0.1098 (7) | 0.054 (3) |
| C7 | -0.0265 (8) | 0.7775 (3) | -0.0793 (7) | 0.055 (3) |
| C8 | -0.0815 (8) | 0.8473 (3) | 0.1000 (8) | 0.056 (4) |
| C9 | 0.0216 (7) | 0.9113 (3) | 0.1257 (7) | 0.053 (3) |
| C10 | 0.1917 (8) | 0.8966 (4) | 0.2212 (9) | 0.060 (4) |
| C11 | 0.2643 (11) | 0.9672 (5) | 0.2892 (12) | 0.083 (5) |
| C12 | 0.1389 (8) | 0.9998 (4) | 0.3168 (8) | 0.070 (4) |
| C13 | -0.1425 (9) | 1.0014 (3) | 0.1635 (8) | 0.055 (3) |
| C14 | -0.2565 (8) | 1.0996 (3) | 0.2370 (7) | 0.061 (3) |
| C15 | -0.3733 (13) | 1.0563 (5) | 0.2552 (12) | 0.079 (5) |
| C16 | -0.3260 (11) | 1.1365 (5) | 0.0905 (10) | 0.084 (5) |
| C17 | -0.1801 (11) | 1.1508 (4) | 0.3641 (10) | 0.078 (4) |

Table 2. Selected geometric parameters (Å, °)

| | | | |
|----------------|------------|--------------|------------|
| O1—C4 | 1.382 (9) | C1—C7 | 1.417 (11) |
| O1—C5 | 1.414 (13) | C1—C8 | 1.527 (10) |
| O2—C5 | 1.422 (13) | C2—C3 | 1.370 (11) |
| O2—C6 | 1.396 (9) | C3—C4 | 1.365 (12) |
| O3—C2 | 1.382 (10) | C4—C6 | 1.371 (8) |
| O4—C8 | 1.404 (7) | C6—C7 | 1.355 (10) |
| O5—C13 | 1.213 (8) | C8—C9 | 1.522 (9) |
| O6—C13 | 1.354 (8) | C9—C10 | 1.519 (9) |
| O6—C14 | 1.477 (9) | C10—C11 | 1.528 (12) |
| N1—C9 | 1.472 (9) | C11—C12 | 1.515 (15) |
| N1—C12 | 1.456 (8) | C14—C15 | 1.489 (15) |
| N1—C13 | 1.354 (10) | C14—C16 | 1.517 (11) |
| C1—C2 | 1.371 (8) | C14—C17 | 1.525 (10) |
| C4—O1—C5 | 105.1 (5) | C1—C7—C6 | 117.4 (5) |
| C5—O2—C6 | 104.1 (5) | O4—C8—C1 | 107.8 (5) |
| C13—O6—C14 | 121.2 (5) | C1—C8—C9 | 110.9 (6) |
| C12—N1—C13 | 122.5 (5) | O4—C8—C9 | 113.2 (5) |
| C9—N1—C13 | 124.2 (5) | N1—C9—C8 | 116.3 (5) |
| C9—N1—C12 | 112.9 (5) | C8—C9—C10 | 114.0 (5) |
| C7—C1—C8 | 118.7 (5) | N1—C9—C10 | 101.3 (5) |
| C2—C1—C8 | 121.9 (5) | C9—C10—C11 | 106.0 (6) |
| C2—C1—C7 | 119.4 (5) | C10—C11—C12 | 101.5 (7) |
| O3—C2—C1 | 117.4 (5) | N1—C12—C11 | 104.6 (6) |
| C1—C2—C3 | 121.8 (6) | O6—C13—N1 | 109.0 (5) |
| O3—C2—C3 | 120.7 (5) | O5—C13—N1 | 126.4 (5) |
| C2—C3—C4 | 118.2 (6) | O5—C13—O6 | 124.7 (7) |
| O1—C4—C3 | 130.0 (5) | O6—C14—C17 | 101.6 (6) |
| C3—C4—C6 | 120.7 (6) | O6—C14—C16 | 108.9 (6) |
| O1—C4—C6 | 109.2 (5) | O6—C14—C15 | 112.0 (5) |
| O1—C5—O2 | 107.9 (7) | C16—C14—C17 | 112.6 (5) |
| O2—C6—C4 | 109.6 (5) | C15—C14—C17 | 109.9 (7) |
| C4—C6—C7 | 122.3 (6) | C15—C14—C16 | 111.4 (7) |
| O2—C6—C7 | 128.1 (5) | | |
| C14—O6—C13—O5 | 1.8 (11) | C2—C1—C8—O4 | -132.2 (7) |
| C13—O6—C14—C15 | 58.9 (9) | C7—C1—C8—C9 | -75.6 (8) |
| C13—O6—C14—C16 | -64.8 (8) | C2—C1—C8—C9 | 103.4 (8) |
| C13—O6—C14—C17 | 176.2 (6) | C7—C1—C2—O3 | 178.8 (6) |
| C14—O6—C13—N1 | -178.5 (5) | C8—C1—C2—O3 | -0.2 (10) |
| C12—N1—C13—O5 | 175.6 (7) | O3—C2—C3—C4 | -177.2 (6) |
| C9—N1—C13—O5 | 3.3 (11) | O4—C8—C9—N1 | 75.8 (7) |
| C12—N1—C13—O6 | -4.1 (9) | C1—C8—C9—N1 | -162.9 (6) |
| C9—N1—C13—O6 | -176.4 (5) | C1—C8—C9—C10 | -45.5 (8) |
| C13—N1—C9—C8 | -52.4 (9) | O4—C8—C9—C10 | -166.8 (6) |
| C7—C1—C8—O4 | 48.8 (8) | | |

The relatively low number of reflections is probably due to both the small dimensions and the quality of the crystal. H atoms were located in a difference Fourier map and refined isotropically. The model with the opposite configuration and the same data set produced an unchanged *R* factor making it unnecessary to apply the Hamilton (1965) test. The atomic coordinates and Fig. 1 correspond to the configuration of the title compound, which is known from the starting material.

All calculations were performed on an IBM PS2/80 personal computer using the *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreotti, 1987) package.

Data collection: Belletti, Cantoni & Pasquinelli (1988). Cell refinement: Belletti *et al.* (1988). Data reduction: *DI-*

FAU (Belletti *et al.*, 1988). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Software used to prepare material for publication: *CRYSRULER* (Rizzoli *et al.*, 1987).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Intramolecular Diels–Alder Adduct in the Hydroxy- β -ionone Series

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Abstract

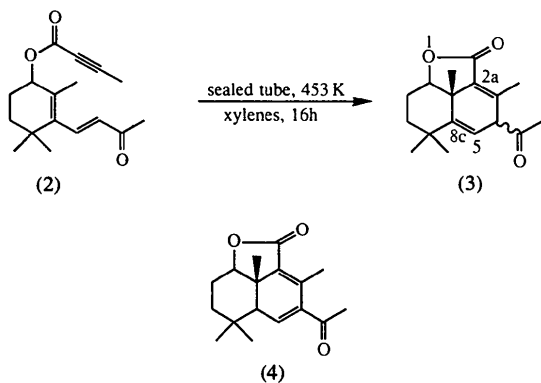
The title compound, (2 α ,6,7,8,8 α ,8 β)-4-acetyl-3,6,6,8 β -tetramethyl-2 α ,6,7,8,8 α ,8 β -hexahydro-2*H*-naphtho-[8,8 α ,1-*bc*]furan-2-one, C₁₇H₂₂O₃, was synthesized by the intramolecular reaction of a butynoate ester of hydroxy- β -ionone. Ring *A* adopts the most stable chair

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conformation, ${}_1C^4$, with atoms C7 and C8b lying at distances of -0.63 (1) and 0.50 (1) Å, respectively, from the least-squares plane composed of atoms C8, C8a, C8c and C6. The furan ring adopts an E^5 envelope conformation. Atom C8b occupies the flap position and lies at a distance of 0.58 (1) Å from the least-squares plane made up of the remainder of the atoms in the ring.

Comment

In the course of studies directed towards the efficient construction of the *A/B* ring system of the polyoxygenated labdanyl diterpenoid forskolin (Colombo, Zinczuk & Rúveda, 1992), we examined the intramolecular Diels–Alder reaction of the butynoate ester (2) of hydroxy- β -ionone and now report the X-ray crystal structure analysis of the major adduct, (1). Contrary to expectations and inconclusive ¹H and ¹³C NMR spectra, this adduct had neither the *pro forma* structure (3) nor the more conjugated rearranged structure (4).



Thermolysis of the acetylenic ester (2) at 453 K (sealed tube, xylene, 16 h) afforded, after chromatography on silica, a colorless crystalline adduct (60% yield, m.p. 393–395 K). Analytical and spectral data were not inconsistent with structure (3). However, subsequent treatment of the adduct with 3-chloroperoxybenzoic acid provided a product whose spectral data clearly indicated epoxidation had occurred somewhere other than the anticipated C5=C8c double bond. Although this does not eliminate structure (3), an explanation of this surprising result clearly required a more detailed examination of the structure of the cycloadduct.

A displacement ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1990) of the molecule with the atom-labeling scheme is given in Fig. 1. The two double bonds in ring *B* are twisted with respect to each other, as evidenced by the torsion angle C3–C4–C5–C8c of -15.2 (2)°. The acetyl group is also twisted out of the plane of ring *B*; torsion angle C3–C4–C11–O3 is -22.1 (2)°. A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed several structures with the same three-ring system (Magnus, Walker, Jenkins & Menear, 1986; Datta,

Franck, Tripathy, Quigley, Huang, Chen & Sihaed, 1990), but none with two double bonds in ring *B*. Four structures had one double bond in ring *B* in the equivalent position of C5=C8c. In all of these four structures, the *A* rings and the furan rings exhibited conformations similar to those of compound (1).

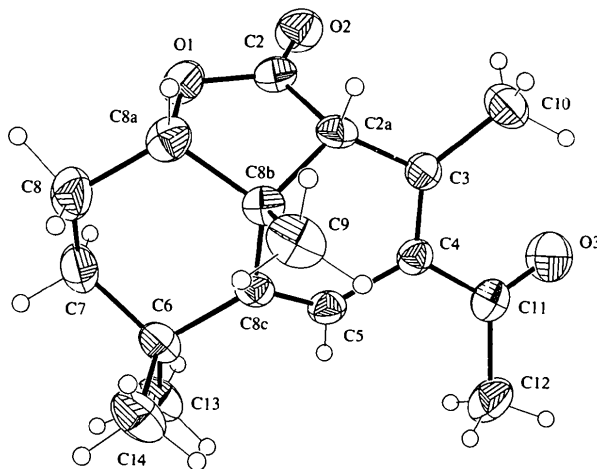


Fig. 1. Molecular structure of (1), plotted with 50% probability ellipsoids, showing the atom-numbering scheme.

Experimental

Multiple crystallizations of the cycloadduct (see *Comment*) from methylene chloride/hexanes provided suitable crystals for structure analysis.

Crystal data

C₁₇H₂₂O₃
M_r = 274.35
 Orthorhombic
*P*2₁2₁2₁
a = 8.649 (1) Å
b = 10.794 (1) Å
c = 15.936 (2) Å
V = 1487.7 (3) Å³
Z = 4
D_x = 1.225 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 32 reflections
 θ = 10–11°
 μ = 0.08 mm⁻¹
T = 293 K
 Plate
 0.49 × 0.42 × 0.17 mm
 Colorless

Data collection

Siemens *P3m/V* diffractometer
 ω scans
 Absorption correction: analytical
 T_{\min} = 0.964, T_{\max} = 0.986
 1960 measured reflections
 1960 independent reflections

1517 observed reflections
 $[F > 4\sigma(F)]$
 θ_{\max} = 25°
h = 0 → 11
k = 0 → 14
l = 0 → 20
 4 standard reflections monitored every 100 reflections
 intensity decay: 1%

Refinement

Refinement on *F*
R = 0.0516

$w = 1/[\sigma^2(F) + 0.0004F^2]$
 $(\Delta/\sigma)_{\max} = 0.0001$

$wR = 0.053$
 $S = 1.62$
 1517 reflections
 269 parameters
 All H-atom parameters refined

$\Delta\rho_{\max} = 0.2 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.2 \text{ e } \text{Å}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | U_{eq} |
|-----|------------|------------|------------|-----------------|
| O1 | 0.6586 (3) | 0.2952 (2) | 0.3367 (2) | 0.0497 (8) |
| O2 | 0.6043 (3) | 0.1472 (2) | 0.4290 (2) | 0.0583 (9) |
| O3 | 0.4789 (4) | 0.3309 (3) | 0.7122 (2) | 0.0712 (11) |
| C2 | 0.6585 (4) | 0.2470 (3) | 0.4147 (2) | 0.0420 (10) |
| C2a | 0.7332 (4) | 0.3381 (3) | 0.4746 (2) | 0.0361 (10) |
| C3 | 0.6665 (4) | 0.3319 (3) | 0.5611 (2) | 0.0359 (9) |
| C4 | 0.5500 (4) | 0.4108 (3) | 0.5787 (2) | 0.0355 (9) |
| C5 | 0.4930 (4) | 0.4950 (3) | 0.5132 (2) | 0.0374 (10) |
| C6 | 0.4989 (4) | 0.6041 (3) | 0.3736 (2) | 0.0452 (11) |
| C7 | 0.5128 (5) | 0.5364 (4) | 0.2894 (2) | 0.0541 (13) |
| C8 | 0.6739 (5) | 0.4943 (4) | 0.2690 (3) | 0.0585 (14) |
| C8a | 0.7420 (4) | 0.4137 (3) | 0.3364 (2) | 0.0460 (11) |
| C8b | 0.7247 (4) | 0.4617 (3) | 0.4272 (2) | 0.0374 (9) |
| C8c | 0.5669 (4) | 0.5204 (3) | 0.4418 (2) | 0.0365 (9) |
| C9 | 0.8592 (5) | 0.5467 (4) | 0.4524 (3) | 0.0555 (14) |
| C10 | 0.7327 (6) | 0.2355 (5) | 0.6177 (3) | 0.057 (2) |
| C11 | 0.4745 (4) | 0.4167 (3) | 0.6630 (2) | 0.0437 (10) |
| C12 | 0.3961 (7) | 0.5347 (5) | 0.6877 (3) | 0.067 (2) |
| C13 | 0.3280 (5) | 0.6333 (4) | 0.3892 (3) | 0.0573 (15) |
| C14 | 0.5833 (7) | 0.7295 (4) | 0.3693 (4) | 0.066 (2) |

Table 2. Selected geometric parameters (Å , $^\circ$)

| | | | |
|------------|-----------|-------------|-----------|
| C2—O1 | 1.347 (4) | C8c—C5 | 1.334 (5) |
| C8a—O1 | 1.468 (4) | C7—C6 | 1.533 (5) |
| C2—O2 | 1.196 (4) | C8c—C6 | 1.530 (5) |
| C11—O3 | 1.214 (4) | C13—C6 | 1.532 (6) |
| C2a—C2 | 1.516 (5) | C14—C6 | 1.540 (6) |
| C3—C2a | 1.495 (4) | C8—C7 | 1.501 (6) |
| C8b—C2a | 1.535 (4) | C8a—C8 | 1.503 (6) |
| C4—C3 | 1.348 (4) | C8b—C8a | 1.545 (5) |
| C10—C3 | 1.492 (6) | C8c—C8b | 1.522 (4) |
| C5—C4 | 1.469 (4) | C9—C8b | 1.535 (5) |
| C11—C4 | 1.495 (5) | C12—C11 | 1.496 (6) |
| C2—O1—C8a | 109.9 (3) | C14—C6—C7 | 110.0 (3) |
| C2a—C2—O1 | 109.3 (3) | C8—C7—C6 | 114.0 (3) |
| C2a—C2—O2 | 129.1 (3) | C8a—C8—C7 | 112.6 (3) |
| O1—C2—O2 | 121.6 (3) | C8b—C8a—O1 | 104.0 (3) |
| C3—C2a—C8b | 118.3 (3) | C8b—C8a—C8 | 115.9 (3) |
| C3—C2a—C2 | 112.8 (3) | O1—C8a—C8 | 108.3 (3) |
| C8b—C2a—C2 | 103.5 (3) | C8c—C8b—C9 | 113.0 (3) |
| C4—C3—C10 | 127.0 (3) | C8c—C8b—C2a | 109.2 (3) |
| C4—C3—C2a | 116.9 (3) | C8c—C8b—C8a | 111.7 (3) |
| C10—C3—C2a | 116.1 (3) | C9—C8b—C2a | 110.8 (3) |
| C5—C4—C11 | 117.7 (3) | C9—C8b—C8a | 111.9 (3) |
| C5—C4—C3 | 119.6 (3) | C2a—C8b—C8a | 99.5 (2) |
| C11—C4—C3 | 122.7 (3) | C5—C8c—C6 | 122.9 (3) |
| C8c—C5—C4 | 124.9 (3) | C5—C8c—C8b | 118.3 (3) |
| C7—C6—C8c | 108.1 (3) | C6—C8c—C8b | 118.8 (3) |
| C7—C6—C13 | 108.4 (3) | C12—C11—O3 | 119.6 (3) |
| C8c—C6—C13 | 112.2 (3) | C12—C11—C4 | 118.1 (3) |
| C8c—C6—C14 | 111.6 (3) | O3—C11—C4 | 122.3 (3) |
| C13—C6—C14 | 106.5 (3) | | |

The ω -scan width was symmetrical over 1.2% about the $K\alpha_{1,2}$ maximum and the background was offset 1.0 and -1.0 in ω from the $K\alpha_{1,2}$ maximum. The scan speed was a variable $3-6^\circ \text{ min}^{-1}$ (depending upon intensity). The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Programs used: *SHELXTL-Plus* (Sheldrick, 1990) for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics; *SHELX76* (Sheldrick, 1976) for structure refinement (full-matrix least squares); *FUER* (Larson, 1982) for geometric and parameter tables.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: BK1064). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tripotassium Phosphoglycolate Dihydrate and Tris(cyclohexylammonium) Phosphoglycolate Trihydrate

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Abstract

The structures of the potassium and cyclohexylammonium salts of the phosphoglycolate trianion, $3\text{K}^+ \cdot \text{C}_2\text{H}_2\text{O}_6\text{P}^{3-} \cdot 2\text{H}_2\text{O}$ and $3\text{C}_6\text{H}_{14}\text{N}^+ \cdot \text{C}_2\text{H}_2\text{O}_6\text{P}^{3-} \cdot 3\text{H}_2\text{O}$, respectively, have been determined by X-ray analysis. The respective ester P—O bond lengths are 1.642 (2) and 1.628 (3) Å.