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# 4-(3α-Hydroxy-4α-methoxycarbonyl-8aβ-methyl-1,6-dioxo-2a,3,4,5,6,7,8,8a-octahydroacenaphth-3-yl)-2-butanone Ethylene Acetal

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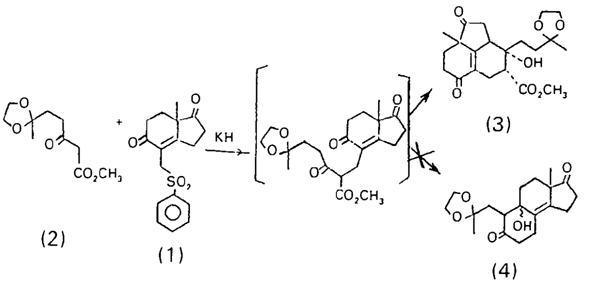
**Abstract.** $C_{21}H_{28}O_7$, $M_r = 392{\cdot}5$, monoclinic, $P2_1$, $a = 12{\cdot}190\,(2)$, $b = 6{\cdot}488\,(2)$, $c = 12{\cdot}702\,(2)$ Å, $\beta = 102{\cdot}33\,(1)°$, $V = 981{\cdot}3\,(2)$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}328\,(2)$, $D_m$(flotation) = 1·32 (1) g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}93$ cm$^{-1}$, $F(000) = 420$, $T = 295\,(1)$ K, final $R_F = 3{\cdot}8\%$ and $wR_F = 4{\cdot}4\%$ for 858 unique reflections. There are no unusual bond distances. The $sp^3$ atoms have angles ranging from 101·8 to 114·4°; the largest deviations occur at the atoms associated with the cyclopentane moiety and are influenced by the *exo* double bonds. There is an intermolecular O—H···O hydrogen bond [O···O 2·909 (5) Å] resulting in the formation of a polymeric chain around the twofold screw axis.

**Introduction.** In view of the potent fertility-regulating properties of dinordrin and the availability of a flexible synthetic scheme, several dinor steroids related to dinordrin have been prepared (Nassim, Schlemper & Crabbé, 1983, and references therein). In continuing the search for compounds with further-improved biological properties and applying the same general route, synthesis of a precursor to a new dinordrin analog was attempted. However, instead of the desired product (4), the octahydroacenaphthene derivative (3) was obtained in 58% yield. Although the formation of this product was not at all surprising, the high yield was unexpected and, because of the structural similarities with the desired product, use of routine spectroscopic techniques ($^1$H NMR, IR and UV) for an unambiguous structural identification of the product (3) proved insufficient. Therefore, in order to determine the structure, an X-ray analysis was undertaken.



**Experimental.** Crystals were obtained by recrystallization from ethyl acetate–hexane. Needles 0·2 × 0·2 × 0·4 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. 24 reflections ($2\theta = 13$–$32°$) used for lattice parameters. No absorption correction ($\psi$ scans indicated less than 2% range). *hkl* range: $h = -11$ to 11, $k = -3$ to 6, $l = 0$ to 12. 1494 *hkl* with $2° < 2\theta < 40°$; $\theta$–$2\theta$ scan technique. 3 standards measured every 2 h of X-ray exposure (1% deviation). 1022 unique reflections, $R_{\text{int}}$ (merging) = 1·8%. 164 unobserved reflections [$I < 2\sigma(I)$]. The majority of non-hydrogen atoms were located using *MULTAN* (Germain, Main & Woolfson, 1971); the remainder of the non-hydrogen atoms and all of the H atoms were located with subsequent Fourier syntheses. Positional parameters and anisotropic temperature factors were refined for all non-hydrogen atoms. No parameters were refined for the H atoms; isotropic temperature factors for H atoms were fixed at 4·0 Å$^2$. $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = (\sigma^2_{\text{counting}} + 0{\cdot}05F_o^2)/4F_o^2$. $R = 3{\cdot}8\%$, $wR = 4{\cdot}4\%$, $S = 1{\cdot}32$. Reversal of the direction of the polar axis did not change the $R$ factors even in the third significant figure. In last cycle $(\Delta/\sigma)_{\max} = 0{\cdot}02$. $\rho$(max.) and $\rho$(min.) on final difference Fourier map 0·15 and −0·20 e Å$^{-3}$. Scattering factors including $f'$ and $f''$ values from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction. Computations on PDP 11/34 computer using Enraf–Nonius (1983) *SDP-Plus* programs.

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**Discussion.** The non-hydrogen-atom positional parameters are listed in Table 1.[*]

Table 1. *Positional and equivalent isotropic thermal parameters of the non-hydrogen atoms and their estimated standard deviations*

$B_{eq} = \frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

| | *x* | *y* | *z* | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 0·5220 (3) | 0·8148 | 0·1631 (3) | 5·1 (1) |
| O(3) | 0·2659 (3) | 0·6545 (6) | 0·3891 (3) | 2·92 (8) |
| O(6) | 0·5216 (3) | 0·0517 (7) | 0·4674 (3) | 4·1 (1) |
| O(*E*1) | 0·1388 (3) | 0·3270 (9) | 0·5053 (3) | 5·1 (1) |
| O(*E*2) | 0·0068 (3) | 0·2888 (7) | 0·3542 (3) | 4·0 (1) |
| O(*K*1) | −0·1419 (3) | 0·6399 (6) | 0·2005 (3) | 3·85 (9) |
| O(*K*2) | −0·0710 (3) | 0·8817 (6) | 0·1038 (3) | 3·69 (9) |
| C(1) | 0·4595 (4) | 0·6871 (9) | 0·1864 (4) | 3·0 (1) |
| C(2) | 0·3381 (5) | 0·725 (1) | 0·1903 (4) | 3·8 (1) |
| C(3) | 0·2137 (4) | 0·5353 (9) | 0·2989 (4) | 2·3 (1) |
| C(4) | 0·1950 (4) | 0·310 (1) | 0·3346 (4) | 2·6 (1) |
| C(5) | 0·3050 (4) | 0·2077 (8) | 0·3924 (4) | 2·4 (1) |
| C(6) | 0·5113 (4) | 0·1686 (9) | 0·3901 (4) | 2·7 (1) |
| C(7) | 0·6101 (4) | 0·224 (1) | 0·3432 (4) | 3·6 (1) |
| C(8) | 0·6018 (4) | 0·440 (1) | 0·2946 (4) | 3·8 (1) |
| C(5a) | 0·4014 (4) | 0·2565 (8) | 0·3415 (4) | 2·0 (1) |
| C(8a) | 0·4910 (4) | 0·4648 (9) | 0·2135 (4) | 2·6 (1) |
| C(2a) | 0·2902 (4) | 0·5209 (9) | 0·2167 (4) | 2·5 (1) |
| C(8b) | 0·3928 (4) | 0·3912 (8) | 0·2605 (4) | 2·1 (1) |
| C(*B*1) | 0·1059 (4) | 0·6525 (9) | 0·2521 (4) | 2·8 (1) |
| C(*B*2) | 0·0317 (4) | 0·565 (1) | 0·1483 (4) | 3·2 (1) |
| C(*B*3) | −0·0819 (4) | 0·665 (1) | 0·1168 (4) | 2·9 (1) |
| C(*B*4) | −0·1483 (5) | 0·572 (1) | 0·0128 (5) | 5·0 (2) |
| C(*E*1) | 0·1128 (4) | 0·310 (1) | 0·4092 (4) | 3·2 (1) |
| C(*E*2) | −0·0815 (4) | 0·311 (1) | 0·4121 (5) | 5·2 (2) |
| C(*K*1) | −0·1780 (5) | 0·835 (1) | 0·2269 (5) | 5·8 (2) |
| C(*K*2) | −0·1534 (5) | 0·978 (1) | 0·1486 (5) | 5·2 (2) |
| C(*M*1) | 0·4928 (5) | 0·352 (1) | 0·1056 (4) | 4·0 (1) |

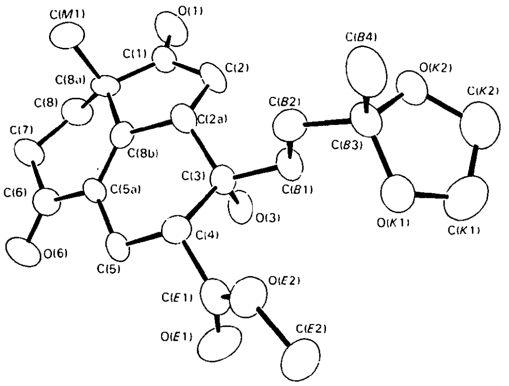

Fig. 1. A view of the molecule showing the thermal ellipsoids (50% probability level) and the atom labeling.

The structure analyzed here (Fig. 1) reveals that the initial substitution reaction between sulfone (1) and the enolate of the *β*-keto ester (2) is followed by an aldol-type condensation at the C(2a)–C(3) region to afford the tricyclic compound (3). The bond distances and angles for the non-hydrogen atoms are listed in Table 2. There are no unusual distances or angles. The angles at the $sp^3$ atoms of the tricyclic system range from 101·8 (5) to 114·4 (4)° with the largest deviations from the tetrahedral value of 109·5° occurring at C(8a) and C(2a). The major factor affecting the geometry of these atoms is their association with the five-membered-ring moiety containing two *exo* double bonds. The 101·8 (5)° angle at C(8a) is flanked by the two $sp^2$-hybridized atoms C(1) and C(8b) which force C(8a) into a distorted form. The strain at C(2a), although to a lesser degree, is caused by similar effects. The latter is at the α-position to C(8b) and at the *β*-position to C(1) and acquires a geometry with angles

Table 2. *Bond distances* (Å) *and angles* (°) *for the non-hydrogen atoms*

Numbers in parentheses are estimated standard deviations in the least significant digits.

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·291 (6) | C(4)–C(5) | 1·535 (7) |
| O(3)–C(3) | 1·416 (6) | C(4)–C(*E*1) | 1·519 (8) |
| O(6)–C(6) | 1·229 (6) | C(5)–C(5a) | 1·491 (7) |
| O(*E*1)–C(*E*1) | 1·199 (6) | C(6)–C(7) | 1·498 (8) |
| O(*E*2)–C(*E*1) | 1·338 (6) | C(6)–C(5a) | 1·466 (7) |
| O(*E*2)–C(*E*2) | 1·434 (6) | C(7)–C(8) | 1·529 (9) |
| O(*K*1)–C(*B*3) | 1·422 (6) | C(8)–C(8a) | 1·522 (7) |
| O(*K*1)–C(*K*1) | 1·401 (9) | C(5a)–C(8b) | 1·337 (6) |
| O(*K*2)–C(*B*3) | 1·428 (7) | C(8a)–C(8b) | 1·524 (7) |
| O(*K*2)–C(*K*2) | 1·402 (8) | C(8a)–C(*M*1) | 1·558 (8) |
| C(1)–C(2) | 1·512 (8) | C(2a)–C(8b) | 1·512 (7) |
| C(1)–C(8a) | 1·513 (8) | C(*B*1)–C(*B*2) | 1·538 (8) |
| C(2)–C(2a) | 1·516 (8) | C(*B*2)–C(*B*3) | 1·582 (8) |
| C(3)–C(4) | 1·553 (8) | C(*B*3)–C(*B*4) | 1·519 (8) |
| C(3)–C(2a) | 1·544 (7) | C(*K*1)–C(*K*2) | 1·440 (10) |
| C(3)–C(*B*1) | 1·525 (7) | | |

| | | | |
|---|---|---|---|
| C(*E*1)–O(*E*2)–C(*E*2) | 118·0 (5) | C(1)–C(8a)–C(8) | 113·4 (5) |
| C(*B*3)–O(*K*1)–C(*K*1) | 108·4 (5) | C(1)–C(8a)–C(8b) | 101·8 (5) |
| C(*B*3)–O(*K*2)–C(*K*2) | 107·5 (5) | C(1)–C(8a)–C(*M*1) | 107·3 (4) |
| O(1)–C(1)–C(2) | 124·9 (6) | C(8)–C(8a)–C(8b) | 111·1 (4) |
| O(1)–C(1)–C(8a) | 124·5 (5) | C(8)–C(8a)–C(*M*1) | 111·6 (5) |
| C(2)–C(1)–C(8a) | 110·6 (5) | C(8b)–C(8a)–C(*M*1) | 111·0 (4) |
| C(1)–C(2)–C(2a) | 106·8 (5) | C(2)–C(2a)–C(3) | 114·4 (4) |
| O(3)–C(3)–C(4) | 110·1 (4) | C(2)–C(2a)–C(8b) | 103·9 (4) |
| O(3)–C(3)–C(2a) | 110·4 (4) | C(3)–C(2a)–C(8b) | 118·9 (4) |
| O(3)–C(3)–C(*B*1) | 104·1 (4) | C(5a)–C(8b)–C(8a) | 124·5 (4) |
| C(4)–C(3)–C(2a) | 106·6 (4) | C(5a)–C(8b)–C(2a) | 124·7 (5) |
| C(4)–C(3)–C(*B*1) | 114·4 (4) | C(8a)–C(8b)–C(2a) | 109·8 (5) |
| C(2a)–C(3)–C(*B*1) | 111·2 (4) | C(3)–C(*B*1)–C(*B*2) | 116·8 (4) |
| C(3)–C(4)–C(5) | 112·1 (4) | C(*B*1)–C(*B*2)–C(*B*3) | 114·2 (5) |
| C(3)–C(4)–C(*E*1) | 109·7 (5) | O(*K*1)–C(*B*3)–O(*K*2) | 105·8 (5) |
| C(5)–C(4)–C(*E*1) | 103·1 (4) | O(*K*1)–C(*B*3)–C(*B*2) | 110·2 (4) |
| C(4)–C(5)–C(5a) | 112·9 (4) | O(*K*1)–C(*B*3)–C(*B*4) | 110·0 (5) |
| O(6)–C(6)–C(7) | 120·9 (5) | O(*K*2)–C(*B*3)–C(*B*2) | 118·5 (5) |
| O(6)–C(6)–C(5a) | 120·5 (5) | O(*K*2)–C(*B*3)–C(*B*4) | 109·6 (5) |
| C(7)–C(6)–C(5a) | 118·7 (5) | C(*B*2)–C(*B*3)–C(*B*4) | 110·6 (5) |
| C(6)–C(7)–C(8) | 113·0 (5) | O(*E*1)–C(*E*1)–O(*E*2) | 123·9 (5) |
| C(7)–C(8)–C(8a) | 110·0 (5) | O(*E*1)–C(*E*1)–C(4) | 124·7 (5) |
| C(5)–C(5a)–C(6) | 117·9 (4) | O(*E*2)–C(*E*1)–C(4) | 111·5 (5) |
| C(5)–C(5a)–C(8b) | 122·2 (4) | O(*K*1)–C(*K*1)–C(*K*2) | 107·2 (5) |
| C(6)–C(5a)–C(8b) | 119·6 (5) | O(*K*2)–C(*K*2)–C(*K*1) | 103·4 (6) |

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[*] Lists of anisotropic thermal parameters, H-atom positions, bond distances and angles involving H atoms and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42356 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of 103·9 (4)° inside the five-membered ring and 114·4 (4)° outside. A second $sp^3$ atom having an angle of 114·4 (4)$^c$ is C(3) which indicates a moderate strain due, apparently, to steric reasons. The major angular deviations in the $sp^2$ atoms are observed at C(1) [110·6 (5)°] and C(8b) [109·8 (5)°] which are also due to their involvement in the five-membered ring. The α,β-unsaturated keto system in the molecules assumes a near-ideal coplanar arrangement as evidenced by the least-squares plane of O(6), C(6), C(7), C(5a), C(8b), C(7), C(5), and C(2a) [maximum deviation 0·090 (6) Å for C(2a)]. Both unsaturated six-membered rings have near-ideal sofa conformations (Duax, Weeks & Rohrer, 1976) with C(8) 0·63 Å from one five-atom plane and C(3) 0·71 Å from the other. The five-membered C ring has the envelope conformation with C(8b) 0·39 Å from the four-atom plane while the other five-membered ring has the half-chair conformation with O(*K*2) 0·19 Å above the three-atom plane and C(*K*2) 0·17 Å below. The closest contact between two molecules is through the hydrogen bond at H(O3): the O(3)···O(6) distance is 2·909 (5) Å and the angle at H(O3) is 158·1 (5)°. The hydrogen bonding results in a polymeric chain around the twofold screw axis.

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# Structure of (*S*)-*N*-[Methyl(phenyl)phosphinothioyl]camphorimide

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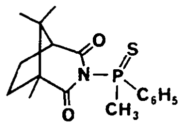
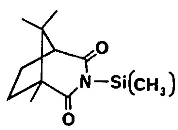
**Abstract.** $C_{17}H_{22}NO_2PS$, $M_r = 335{\cdot}40$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}5279\,(34)$, $b = 20{\cdot}4614\,(38)$, $c = 6{\cdot}9103\,(11)$ Å, $V = 1771{\cdot}4$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}31\,(1)$, $D_x = 1{\cdot}26$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}69$ cm$^{-1}$, $F(000) = 712$, $T = 295\,(2)$ K, $R(wR) = 0{\cdot}0410\,(0{\cdot}0437)$ for 1627 observed independent reflections $[F > 2{\cdot}5\sigma(F)]$, goodness-of-fit = 1·039. The material was obtained as a mixture of diastereoisomers by condensing (+)-*N*-(trimethylsilyl)camphorimide (2) with chloro(methyl)phenylphosphine (3), followed by sulfuration with elemental sulfur. The higher-melting less-soluble (−) diastereoisomer produced crystals suitable for X-ray studies. The absolute configuration at phosphorus was inferred to be *S* from the known absolute configuration of (+)-camphor [Oonk (1965). PhD thesis, Univ. of Utrecht]. The imide group is not planar; the N atom lies out of the plane of the C=O groups. It is also out of the plane of the P and imide C atoms.

**Introduction.** As part of a program designed to prepare chiral sulfur and phosphorus compounds (Harpp, Vines, Montillier & Chan, 1976), we synthesized *N*-[methyl(phenyl)phosphinothioyl]camphorimide (1). We felt that it might serve as a general reagent from which to construct a variety of chiral $P^{IV}$ derivatives by displacement with various nucleophiles. A number of these synthetic transformations have been successful and will be reported elsewhere.



(1)



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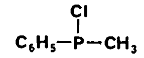

$$C_6H_5-\overset{\displaystyle Cl}{\overset{|}{P}}-CH_3$$

(3)

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