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Synthesis of Hydrophenanthrene Natural Products. Structure of a 17-Nordehydropimarane Derived from Dehydroabietic Acid*

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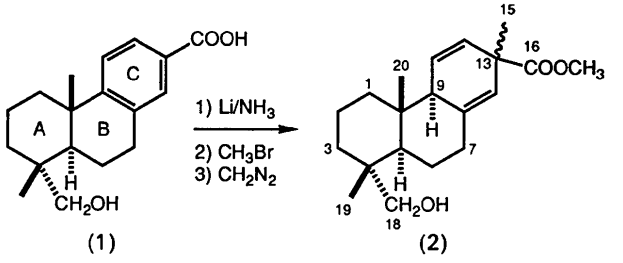
Abstract. $C_{20}H_{30}O_3$, $M_r = 318{\cdot}46$, triclinic, $P\bar{1}$, $a = 7{\cdot}108$ (1), $b = 7{\cdot}362$ (5), $c = 9{\cdot}112$ (2) Å, $\alpha = 96{\cdot}21$ (4), $\beta = 89{\cdot}85$ (1), $\gamma = 106{\cdot}31$ (2)°, $V = 454{\cdot}8$ Å^3, $Z = 1$, $D_x = 1{\cdot}16$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}82$ cm^{-1}, $F(000) = 174$, $T = 293$ K, final $R = 0{\cdot}046$ for 852 observed [$F_o \geq 5\sigma(F_o)$] reflections. The structure reveals a *trans* relationship between the hydrogen at C(9) and the methyl group C(20) as well as an *R* absolute stereochemistry at C(13). Intermolecular hydrogen-bonded chains along the unit-cell edge **c** characterize the crystal lattice.

Introduction. Our interest in the chemistry and biology of hydrophenanthrene natural products has prompted us to investigate the conversion of dehydroabietic acid to diterpenes which may be represented by the pimarane skeleton. Dehydroabietic acid, an abundant abietane diterpene and the major constituent of commercial rosin, has been used previously as a synthon (Ohsawa, Ohtsuka, Nakata, Akita & Shimagaki, 1976; Buchbauer & Kolbe, 1985) but to date has not been transformed to a pimarane natural product. A reductive alkylation of the aromatic *C* ring of 13-carboxydeisopropyldehydroabietanol, (1), was seen as the key step in this transformation. In one step from a 13-carboxy derivative (Ohta, 1956) we envisioned, after alkylation with methyl bromide (see below), the creation of two features prerequisite for transformation to the pimarane skeleton: a quaternary methyl at C(13) and the necessary *trans–anti ABC* ring juncture formed after introduction of the hydrogen at C(9)



(1) (2)

* The *Chemical Abstracts* name is: [2*R*-(2α,4aβ,4bα,8β,8aβ)]-2,4a,4b,5,6,7,8,8a,9,10-decahydro-8-(hydroxymethyl)-2,4b,8-trimethyl-2-phenanthrenecarboxylic acid methyl ester. For the remainder of this paper the more common steroid numbering scheme, as indicated in the reaction scheme, will be used.

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from the α face of the molecule. While it was anticipated that the approach of the newly introduced hydrogen at C(9) should be controlled by the bulky methyl groups on the 'top' face of the molecule we did not see any possibility of controlling the stereochemistry at C(13). Nevertheless, the anticipated isomeric products would provide intermediates for conversion to pimarane and sandarocopimarane natural products, differing only in the stereochemistry at C(13). Some recent reports have appeared of novel pimarane diterpenes with interesting biological activities (De Kimpe, Schamp, Van Puyvelde, Dubé, Chagnon-Dubé, Borremans, Anteunis, Declercq, Germain & Van Meerssche, 1982; Van Puyvelde, Nyirankuliza, Panebianco, Boily, Geizer, Sebikali, De Kimpe & Schamp, 1986; Van Puyvelde, Lefebvre, Mugabo, De Kimpe & Schamp, 1987; Van Puyvelde, De Kimpe, Ayobangira, Costa, Nshimyumuzika, Boily, Hakizamungu & Schamp, 1988). These reductive alkylation intermediates will provide materials for stereospecific conversion to these and other similar natural substances of potential medicinal interest. Herein we describe the X-ray crystal structure for (2), the methyl ester of one of the reductive alkylation products isolated from a mixture of two isomers. This, the crystalline of the two isomers, is the direct precursor to the primarane family of diterpenes, the methoxycarbonyl group after conversion to a vinyl group will provide the necessary stereochemistry at C(13).

Experimental. The title compound was obtained as a single isomer in 43% yield following chromatography of the methyl esters of a 1:1 mixture of isomers arising from a reductive alkylation of 13-carboxydeisopropyldehydroabietanol. Crystals (m.p. 389–391 K) suitable for X-ray analysis were obtained after recrystallization from acetone/water. The spectral and analytical data for this compound were consistent with the X-ray structure.* D_m not determined. Colorless fragment, 0·18 × 0·18 × 0·20 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, ω–2θ scans. Cell constants from setting angles of 25 reflections ($\theta >$ 15°). Corrections for Lorentz polarization were made, but not for absorption. $2\theta_{max} = 50°$; h 0 to 8, k −8 to 8, l −10 to 10. Three standard reflections (300, 030, 003) observed every 3600 s of data collection time, variation ± 2%. 1598 reflections measured, 852 independent observed reflections [$F_o \geq 5\sigma(F_o)$]. Structure solved using *SHELXS* (Sheldrick, 1985). Least-squares refinement with isotropic thermal parameters led to $R = 0{\cdot}113$. O(1) was resolved into two disordered positions. Each was refined in alternate least-squares cycles with occupancy of 50%. Despite the unusual space group no additional symmetry is present to warrant choosing a higher symmetry space group. The geometrically constrained H atoms were placed in calculated positions 0·95 Å from the bonded C atoms and allowed to ride on that atom with B fixed at 5·5 Å^2. The alcoholic H atom was located from a difference Fourier map and included with fixed contributions ($B = 5{\cdot}5$ Å^2). The methyl H atoms were located from a difference Fourier map and included with fixed contributions ($B = 5{\cdot}5$ Å^2). Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV); structure refined with *SHELX*76 (Sheldrick, 1976), $\sum w(|F_o| - |F_c|)^2$ minimized, weights $= [\sigma(F_o)^2 + 0{\cdot}00002F_o^2]^{-1}$, 217 parameters varied. $R = 0{\cdot}046$, $wR = 0{\cdot}048$, $S = 0{\cdot}70$. Δ/σ in final least-squares refinement cycle $< 0{\cdot}01$, $\Delta\rho < 0{\cdot}1$ e Å^{-3} in final difference map.

Discussion. Fractional coordinates and B_{eq} values are given in Table 1,* bond distances and angles in Table 2, and an *ORTEP* drawing (Johnson, 1976) showing absolute stereochemistry in Fig. 1. A cell plot is provided in Fig. 2.

As required in our conversion the hydrogen at C(9) is of the α orientation providing the *trans* stereochemical disposition of H(9)C(9) and C(20). The H(9)C(9)—C(9)—C(10)—C(20) torsion angle of −177·5° is in accord with this finding. This provides the necessary *trans–anti ABC* ring juncture common to the pimarane diterpene skeleton. The X-ray structure also shows the almost planar nature of the *ABC* ring system and the C(20) methyl group which shields the top face of the molecule leading to the introduction of the hydrogen at C(9) from the least hindered α face of the molecule as anticipated. O(1) was resolved into two disordered positions as a 1:1 mixture, probably as a result of distortions in the cell and hydrogen bonding involving O(1) in the crystal lattice. The *ORTEP* diagram reveals an R absolute stereochemistry at C(13) by comparison with known stereochemistry of the natural product dehydroabietic acid. The carboxyl group at C(13) is shown to be of stereochemistry which will result in production

* Physical data: IR (KBr) 3538, 1710, 1248, 1111 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5·80 (brd, 1H, J = 10 Hz), 5·75 (dd, 1H, J = 10, 3 Hz), 5·44 (brs, 1H), 3·66 (s, 3H), 3·42 (d, 1H, J = 10 Hz), 2·30 (brs, 1H), 2·29 (ddd, 1H, J = 13, 5, 2 Hz), 2·06 (ddd, 1H, J = 13, 13, 5 Hz), 1·76–1·68 (brd, 1H, J = 15 Hz), 1·66–1·29 (m, 8H), 1·28 (s, 3H), 1·25–1·16 (m, 1H), 0·75 (s, 3H), 0·71 (s, 3H). High-resolution mass spectroscopy: calculated for $C_{20}H_{30}O_3$, 318·2193; observed, 318·2199.

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes results and final fractional coordinates for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53791 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters for* $C_{20}H_{30}O_3$

	x	y	z	B_{eq}(Å^2)*
O(1)†	0·304 (2)	0·150 (2)	0·471 (2)	5·59
O(1)'†	0·307 (2)	0·228 (2)	0·500 (2)	4·54
O(2)	0·601 (1)	0·286 (1)	0·403 (1)	4·79
O(3)	−0·057 (1)	−0·088 (1)	−0·4755 (9)	4·16
C(1)	−0·226 (1)	−0·052 (1)	0·003 (1)	3·64
C(2)	−0·325 (1)	−0·250 (1)	−0·069 (1)	4·08
C(3)	−0·263 (1)	−0·276 (1)	−0·228 (1)	3·48
C(4)	−0·042 (1)	−0·238 (1)	−0·247 (1)	2·95
C(5)	0·062 (1)	−0·040 (1)	−0·1627 (9)	2·54
C(6)	0·288 (1)	0·016 (1)	−0·172 (1)	3·03
C(7)	0·376 (1)	0·227 (1)	−0·117 (1)	2·99
C(8)	0·307 (1)	0·275 (1)	0·033 (1)	2·63
C(9)	0·088 (1)	0·219 (1)	0·043 (1)	2·81
C(10)	0·0000	0·0000	0·0000	2·78
C(11)	0·025 (2)	0·293 (1)	0·189 (1)	4·04
C(12)	0·144 (1)	0·375 (1)	0·302 (1)	4·00
C(13)	0·363 (2)	0·405 (1)	0·299 (1)	3·26
C(14)	0·427 (1)	0·353 (1)	0·148 (1)	2·80
C(15)	0·417 (2)	0·282 (1)	0·406 (1)	3·23
C(16)	0·665 (2)	0·169 (1)	0·495 (1)	5·25
C(17)	0·473 (2)	0·615 (1)	0·353 (1)	4·45
C(18)	0·027 (2)	−0·402 (1)	−0·198 (1)	4·82
C(19)	−0·005 (1)	−0·234 (1)	−0·412 (1)	3·80
C(20)	0·074 (1)	−0·106 (1)	0·114 (1)	3·52

* $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

† Atoms refined at 50% occupancy.

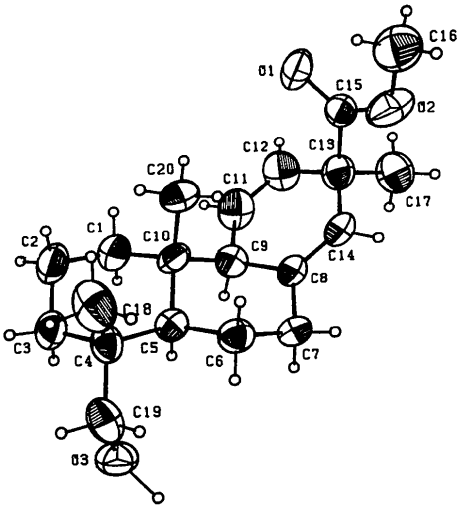

Fig. 1. Thermal-ellipsoid plot of the title compound showing the atom-numbering scheme. H-atom radii are arbitrarily reduced.

Table 2. *Bond distances* (Å) *and angles* (°) *for* $C_{20}H_{30}O_3$

O(1)—C(15)	1·27 (2)	O(1)'—C(15)	1·18 (2)
O(2)—C(15)	1·30 (1)	O(2)—C(16)	1·42 (2)
O(3)—C(19)	1·41 (1)	C(1)—C(2)	1·51 (1)
C(1)—C(10)	1·545 (9)	C(2)—C(3)	1·52 (1)
C(3)—C(4)	1·53 (1)	C(4)—C(5)	1·55 (1)
C(4)—C(18)	1·53 (2)	C(4)—C(19)	1·53 (1)
C(5)—C(6)	1·54 (1)	C(5)—C(10)	1·566 (8)
C(6)—C(7)	1·53 (1)	C(7)—C(8)	1·49 (1)
C(8)—C(9)	1·49 (1)	C(8)—C(14)	1·33 (1)
C(9)—C(10)	1·564 (8)	C(9)—C(11)	1·50 (1)
C(10)—C(20)	1·54 (1)	C(11)—C(12)	1·31 (1)
C(12)—C(13)	1·51 (1)	C(13)—C(14)	1·50 (1)
C(13)—C(15)	1·53 (2)	C(13)—C(17)	1·55 (1)

C(15)—O(2)—C(16)	117·6 (9)	C(2)—C(1)—C(10)	113·1 (8)
C(1)—C(2)—C(3)	111·0 (8)	C(2)—C(3)—C(4)	114·5 (8)
C(3)—C(4)—C(5)	108·4 (8)	C(3)—C(4)—C(18)	110·2 (8)
C(5)—C(4)—C(18)	114·4 (8)	C(3)—C(4)—C(19)	106·8 (8)
C(5)—C(4)—C(19)	109·7 (7)	C(18)—C(4)—C(19)	107·0 (8)
C(4)—C(5)—C(6)	113·5 (8)	C(4)—C(5)—C(10)	116·8 (6)
C(6)—C(5)—C(10)	110·6 (6)	C(5)—C(6)—C(7)	110·3 (8)
C(6)—C(7)—C(8)	111·5 (7)	C(7)—C(8)—C(9)	113·6 (7)
C(7)—C(8)—C(14)	123·1 (8)	C(9)—C(8)—C(14)	123·3 (8)
C(8)—C(9)—C(10)	110·8 (7)	C(8)—C(9)—C(11)	111·6 (7)
C(10)—C(9)—C(11)	114·5 (7)	C(1)—C(10)—C(5)	108·7 (5)
C(1)—C(10)—C(9)	109·6 (5)	C(5)—C(10)—C(9)	105·4 (4)
C(1)—C(10)—C(20)	108·9 (5)	C(5)—C(10)—C(20)	115·4 (5)
C(9)—C(10)—C(20)	108·6 (5)	C(9)—C(11)—C(12)	125 (1)
C(11)—C(12)—C(13)	123·1 (9)	C(12)—C(13)—C(14)	111·8 (8)
C(12)—C(13)—C(15)	108·1 (8)	C(14)—C(13)—C(15)	109·3 (9)
C(12)—C(13)—C(17)	110·4 (9)	C(14)—C(13)—C(17)	109·9 (8)
C(15)—C(13)—C(17)	107·2 (8)	C(8)—C(14)—C(13)	124·4 (9)
O(1)—C(15)—O(2)	116 (1)	O(1)'—C(15)—O(2)	126 (1)
O(1)—C(15)—C(13)	129 (1)	O(1)'—C(15)—C(13)	119 (1)
O(2)—C(15)—C(13)	113·1 (8)	O(3)—C(19)—C(4)	114·6 (9)

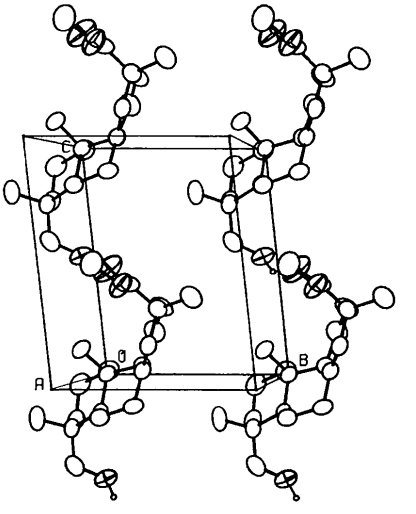

Fig. 2. Cell plot of the title compound.

of the pimarane diterpene skeleton following chemical conversion to a vinyl group. As a result, the other isomer from the reductive alkylation reaction, isolated as a pure oil and shown by NMR studies to differ only in the stereochemistry at C(13), is assigned as possessing the *S* absolute stereochemistry at this position, the direct precursor to the sandarocopimarane series of diterpenes.

The atoms C(8), C(9), C(11), C(12), C(13) and C(14) define a planar *C* ring to within 0·068 Å; the angles around the olefinic carbons, C(8), C(11), C(12) and C(14), are all slightly greater than the expected 120°, reflecting this slight distortion from planarity. All other bond lengths and angles are normal.

The intermolecular contacts of the crystal lattice are dominated by a head-to-tail hydrogen-bonded arrangement of molecules along the unit-cell edge **c**.

The intermolecular hydrogen-bond distances O(1)···H(1)O(3) and O(1′)···H(1)O(3) are 1·70 and 2·04 Å, for the two disordered positions, respectively. The corresponding O(1)···O(3) and O(1′)···O(3) distances are 2·75 and 2·98 Å while the C(15)···H(1) O(3) close contact is 2·82 Å.

Conversion of this reductive alkylation product to natural products of possible medicinal interest is currently under way to demonstrate the utility of this reductive alkylation technique.

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Structure of *trans,endo*-1-Phenyl-2-(4-methoxyphenyl)decahydroquinolin-4-one

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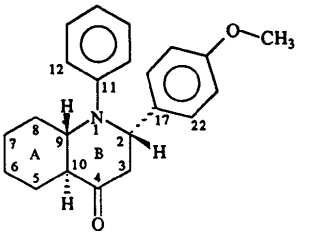
Abstract. $C_{22}H_{25}NO_2$, $M_r = 335{\cdot}45$, monoclinic, $P2_1/c$, $a = 15{\cdot}306$ (7), $b = 6{\cdot}779$ (6), $c = 18{\cdot}004$ (6) Å, $\beta = 91{\cdot}29$ (2)°, $V = 1867$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}193$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 7{\cdot}06$ mm^{-1}, $F(000) = 720$, room temperature, final $R = 0{\cdot}061$ for 1106 observed reflections [$I > 3\sigma(I)$]. Both the cyclohexane ring and the heterocycle adopt a chair conformation. The N-atom geometry is tetrahedral rather than square planar. The X-ray data provide precise information in good agreement with previously obtained data by ^{1}H NMR.

Introduction. The determination of the structure of the decahydroquinolin-4-one is necessary to understand its reactivity. For the *trans*-ring-fused 1-phenyl-2-(*p*-methoxyphenyl)decahydroquinolin-4-one, the ^{1}H NMR data permit the determination of the *trans* relationship between C(9)—H(9) and C(10)—H(10) bonds both of which occupy an axial position in the cyclohexane ring and moreover indicate a quasi-equatorial or equatorial position for the C(2) phenyl group depending on the *B* ring conformation.

Unambiguous assignment of its structure has to be obtained from a single-crystal X-ray structure analysis.



(1)

The preparation and the study of the reactivity of this compound will be reported further.

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