Structure of 4α-Carbomethoxy-15α-cyano-4β-methyl-5α,13α-androstane

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Abstract. $C_{23}H_{35}NO_2$, $M_r = 357 \cdot 5$, orthorhombic, $P2_12_12_1$, $a = 7 \cdot 825$ (1), $b = 14 \cdot 976$ (2), $c = 17 \cdot 702$ (3) Å, $V = 2074 \cdot 4$ Å^3, $Z = 4$, $D_x = 1 \cdot 14$ g cm^{-3}, $\lambda(\text{Cu} K\alpha) = 1 \cdot 54178$ Å, $\mu = 5 \cdot 6$ cm^{-1}, $F(000) = 784$, room temperature, final $R = 0 \cdot 038$ for 1182 observed reflections. The bond lengths and angles are normal. The A/B and B/C junctions are *trans* whereas the C/D junction is *cis* with the D ring directed towards the β face of the molecule.

Introduction. The resin acids extracted from the conifer rosins are useful for the synthesis of biologically active compounds. With their tricyclic backbones, they can be considered as potential intermediates for the elaboration of steroid derivatives. A few attempts in this field have been made, starting mainly from abietic or dehydroabietic acids (Steindl & Haslinger, 1985; Curini, Coccia, Ceccherelli, Halls, Porter & Wenkert, 1984; Wenkert *et al.*, 1982; Tahara, Shimayaki, Itoh, Yoshiroto & Masayuki, 1975; Wirthlin, Wehrli & Jegger, 1974; Wheeler & Witt, 1972). In the present work we start with the methyl pimarate (*a*) to provide the basis for the steroid skeleton. During the process the title compound (*b*) was isolated and the present X-ray analysis was undertaken to establish its structure.

(*a*) (*b*)
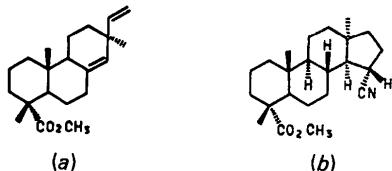
Experimental. The title compound crystallized at room temperature from a methanol solution. Crystal dimensions $0 \cdot 1 \times 0 \cdot 1 \times 0 \cdot 3$ mm. Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, graphite mono-

chromator. Lattice parameters from least-squares adjustments to setting angles of 25 reflections with $21 < 2\theta < 42°$. Corrections for Lorentz and polarization effects; no corrections for absorption or secondary extinction; ω–2θ scans. Scan width $(1 \cdot 0 + 0 \cdot 14 \tan\theta)°$. $\theta_{max} = 65°$. Range of hkl h: $0 \to 9$; k: $0 \to 17$; l: $0 \to 20$. Intensity variation of three standard reflections $< 3\%$. 2033 unique reflections measured; 1121 with $I > 3\sigma(I)$ considered observed. Solution by direct methods (*MITHRIL*: Gilmore, 1984). Refinement on F by block-diagonal least squares, anisotropic thermal parameters for C, N and O, isotropic for H atoms (located in ΔF map). $R = 0 \cdot 038$, $wR = 0 \cdot 039$; $w = 1/\sigma^2(F_o)$ based on counting statistics; $S = 1 \cdot 12$; $\Delta/\sigma(\text{max.}) = 0 \cdot 02$. Max. and min. heights in final $\Delta\rho$ map $+0 \cdot 31$ and $-0 \cdot 27$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974) for non-H and from Stewart, Davidson & Simpson (1965) for H. Local programs *CRISAFFI* and *CRISUTIL*; Mini-6/92 Bull.

Discussion. A projection of the molecular structure with numbering of atoms is shown in Fig. 1.* Final atomic parameters are listed in Table 1. Bond lengths and angles are listed in Table 2 together with the main torsion angles relevant to the conformation of the molecular backbone.

The intramolecular geometry of the structure is essentially normal. The A, B and C rings all have chair conformations and are slightly flattened in that the torsional angles are less than 60°. This flattening is often observed in steroids belonging to the androstan

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family (Weeks, Cooper & Norton, 1971; Precigoux, Busetta, Courseille & Hospital, 1972; Precigoux & Fornies-Marquina, 1973). The *D* ring has a slightly distorted half-chair conformation (Bucourt, 1964). The *A/B* and *B/C* junctions are *trans* whereas the *C/D* junction is *cis* (Fig. 2). In the packing, there is only one intermolecular O···C distance less than the sum of the van der Waals radii: O(44)(*x,y,z*)—C(16)(*x* + 1, *y*, *z*) = 3·284 (5) Å.

The authors are indebted to M. Saux who made the experimental X-ray measurements.
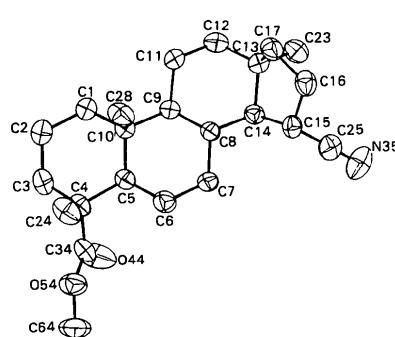
Fig. 1. View of the title compound illustrating atom labelling. Thermal ellipsoids scaled to 50% probability.

Table 1. *Final atomic coordinates* (×10⁴) *and* B_{eq} *values with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	*y*	*z*	$B_{eq}(\text{Å}^2)$
C(1)	7665 (6)	448 (2)	3161 (2)	4·3 (2)
C(2)	8796 (6)	509 (3)	3866 (2)	5·4 (3)
C(3)	9949 (5)	1322 (3)	3843 (2)	4·8 (2)
C(4)	8938 (5)	2205 (2)	3755 (2)	3·6 (2)
C(5)	7715 (5)	2108 (2)	3059 (2)	3·0 (2)
C(6)	6736 (5)	2971 (2)	2889 (2)	3·9 (2)
C(7)	5917 (5)	2912 (2)	2107 (2)	3·7 (2)
C(8)	4764 (5)	2090 (2)	2025 (2)	2·9 (2)
C(9)	5746 (5)	1231 (2)	2225 (2)	3·0 (2)
C(10)	6540 (2)	1269 (2)	3042 (2)	3·2 (2)
C(11)	4592 (5)	426 (2)	2096 (2)	3·9 (2)
C(12)	4015 (6)	375 (2)	1274 (2)	4·2 (2)
C(13)	3068 (5)	1206 (2)	999 (2)	3·4 (2)
C(14)	4020 (5)	2075 (2)	1217 (2)	3·0 (2)
C(15)	2613 (5)	2811 (2)	1156 (2)	3·4 (2)
C(16)	867 (5)	2321 (3)	1179 (2)	4·1 (2)
C(17)	1299 (5)	1348 (3)	1352 (2)	4·2 (2)
C(20)	5088 (5)	1287 (3)	3637 (2)	4·6 (2)
C(23)	2880 (6)	1141 (3)	128 (2)	4·5 (2)
C(24)	8048 (6)	2467 (3)	4500 (2)	5·1 (2)
C(25)	2784 (5)	3380 (2)	478 (2)	4·1 (2)
C(34)	10258 (5)	2895 (3)	3536 (2)	3·7 (2)
N(35)	2912 (5)	3814 (2)	−41 (2)	6·1 (2)
O(44)	11099 (4)	2884 (2)	2969 (2)	6·8 (2)
O(54)	10491 (4)	3534 (2)	4049 (1)	4·9 (2)
C(64)	11820 (7)	4184 (3)	3882 (3)	·6·4 (3)

Table 2. *Bond distances* (Å), *bond angles* (°) *and main torsion angles* (°)

Averaged e.s.d.'s are respectively 0·005 Å, 0·3 and 0·7°.

C(1)—C(2)	1·532	C(9)—C(11)	1·524
C(1)—C(10)	1·527	C(10)—C(20)	1·549
C(2)—C(3)	1·515	C(11)—C(12)	1·526
C(3)—C(4)	1·549	C(12)—C(13)	1·527
C(4)—C(5)	1·567	C(13)—C(14)	1·549
C(4)—C(24)	1·541	C(13)—C(17)	1·534
C(4)—C(34)	1·513	C(13)—C(23)	1·553
C(5)—C(6)	1·533	C(14)—C(15)	1·561
C(5)—C(10)	1·556	C(15)—C(16)	1·552
C(6)—C(7)	1·529	C(16)—C(17)	1·528
C(7)—C(8)	1·533	C(25)—N(35)	1·130
C(8)—C(9)	1·540	C(34)—O(44)	1·201
C(8)—C(14)	1·545	C(34)—O(54)	1·332
C(9)—C(10)	1·576	O(54)—C(64)	1·455

C(2)—C(1)—C(10)	113·4	C(5)—C(10)—C(20)	114·0
C(1)—C(2)—C(3)	111·7	C(9)—C(10)—C(20)	109·6
C(2)—C(3)—C(4)	112·6	C(9)—C(11)—C(12)	110·9
C(3)—C(4)—C(5)	108·2	C(11)—C(12)—C(13)	114·0
C(3)—C(4)—C(24)	111·3	C(12)—C(13)—C(14)	111·9
C(3)—C(4)—C(34)	105·1	C(12)—C(13)—C(17)	114·9
C(5)—C(4)—C(24)	114·8	C(12)—C(13)—C(17)	114·9
C(5)—C(4)—C(34)	106·1	C(12)—C(13)—C(23)	108·2
C(24)—C(4)—C(34)	110·7	C(14)—C(13)—C(17)	102·5
C(4)—C(5)—C(6)	112·4	C(14)—C(13)—C(23)	110·2
C(4)—C(5)—C(10)	116·7	C(17)—C(13)—C(23)	109·1
C(6)—C(5)—C(10)	112·5	C(8)—C(14)—C(13)	115·1
C(5)—C(6)—C(7)	109·8	C(8)—C(14)—C(15)	108·7
C(6)—C(7)—C(8)	112·2	C(13)—C(14)—C(15)	103·7
C(7)—C(8)—C(9)	110·9	C(14)—C(15)—C(16)	106·6
C(7)—C(8)—C(14)	108·7	C(14)—C(15)—C(25)	113·5
C(9)—C(8)—C(14)	112·9	C(16)—C(15)—C(25)	111·9
C(8)—C(9)—C(10)	112·2	C(15)—C(16)—C(17)	105·2
C(8)—C(9)—C(11)	109·4	C(13)—C(17)—C(16)	104·5
C(10)—C(9)—C(11)	113·6	C(15)—C(25)—N(35)	179·9
C(1)—C(10)—C(5)	107·9	C(4)—C(34)—O(44)	125·4
C(1)—C(10)—C(9)	108·9	C(4)—C(34)—O(54)	114·2
C(1)—C(10)—C(20)	110·1	O(44)—C(34)—O(54)	120·4
C(5)—C(10)—C(9)	106·3	C(34)—O(54)—C(64)	116·1

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C(10)—C(1)—C(2)—C(3)	−57·8	C(14)—C(8)—C(9)—C(11)	−54·7
C(1)—C(2)—C(3)—C(4)	56·9	C(8)—C(9)—C(11)—C(12)	59·7
C(2)—C(3)—C(4)—C(5)	−52·3	C(9)—C(11)—C(12)—C(13)	−57·7
C(3)—C(4)—C(5)—C(10)	51·7	C(11)—C(12)—C(13)—C(14)	47·5
C(4)—C(5)—C(10)—C(1)	−52·0	C(12)—C(13)—C(14)—C(8)	−42·1
C(5)—C(10)—C(1)—C(2)	53·0	C(13)—C(14)—C(8)—C(9)	46·9
C(10)—C(5)—C(6)—C(7)	−59·6	C(17)—C(13)—C(14)—C(15)	−37·0
C(5)—C(6)—C(7)—C(8)	55·5	C(13)—C(14)—C(15)—C(16)	18·6
C(6)—C(7)—C(8)—C(9)	−54·4	C(14)—C(15)—C(16)—C(17)	7·0
C(7)—C(8)—C(9)—C(10)	56·1	C(15)—C(16)—C(17)—C(13)	−30·4
C(8)—C(9)—C(10)—C(5)	−57·3	C(16)—C(17)—C(13)—C(14)	42·2
C(9)—C(10)—C(5)—C(6)	59·3		
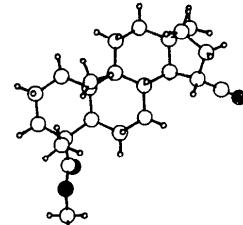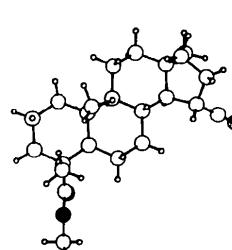
Fig. 2. Stereodrawing of the molecule.

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Structure of 4-Phthalimido-*N*-(1,3-thiazol-2-yl)benzenesulfonamide

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Abstract. $C_{17}H_{11}N_3O_4S_2$, $M_r = 385 \cdot 4$, monoclinic, $P2_1/c$, $a = 7 \cdot 955$ (2), $b = 6 \cdot 501$ (1), $c = 35 \cdot 859$ (8) Å, $\beta = 116 \cdot 92$ (2)°, $V = 1653 \cdot 5$ (5) Å^3, $Z = 4$, $D_m = 1 \cdot 560$, $D_x = 1 \cdot 548$ Mg m^{-3}, λ(Cu $K\alpha$) = $1 \cdot 5418$ Å, $\mu = 3 \cdot 13$ mm^{-1}, $F(000) = 792$, $T = 293$ K, final $R = 0 \cdot 061$ for 2116 observed reflections. The molecule exists as an *imido* tautomer with deprotonation of the sulfonamide nitrogen and protonation of the thiazole nitrogen. Centrosymmetrically related pairs of molecules dimerize through hydrogen bonds of the type N—H···O and N—H···N. The thiazole and the phthalimide rings form stacks amongst themselves.

Introduction. Sulfonamides and their derivatives are well known antibacterial drugs. The present compound is a substituted sulfonamide with the substituents a thiazole at the sulfonamide nitrogen, N(1), and a phthalimide ring at the *para* position of the phenyl ring, and is used in the treatment of intestinal infections. The main advantage of this drug is that it does not build up in the blood because of its rapid excretion and poor absorption and hence large doses can be administered without danger of toxic effects. The X-ray structural study of the present compound has been carried out in continuation of our studies (Basak, Mazumdar & Chaudhuri, 1982, 1983, 1984; Basak, Chaudhuri & Mazumdar, 1984) of the substituted sulfonamides in order to obtain detailed structural information and also to study the effects of substituents on the molecular

geometry and the change in conformations with the ultimate aim of obtaining a better insight into the activity of these compounds.

Experimental. Transparent, slightly yellowish rectangular crystals from a mixture of acetone and water (1:1), density by flotation (benzene–bromoform), symmetry from oscillation and Weissenberg photographs, $P2_1/c$ (absences: 0*k*0, *k* odd; *h0l*, *l* odd), crystal size: $0 \cdot 23 \times 0 \cdot 18 \times 0 \cdot 15$ mm, 5051 equivalent reflections collected, Enraf–Nonius CAD-4 diffractometer, moving crystal/moving counter technique, $2 \leq 2\theta \leq 150°$, -8 to 8 (*h*), 0 to 7 (*k*), -40 to 40 (*l*). Cell parameters from 32 high-angle reflections ($23 \leq \theta \leq 39°$), $\bar{3},0,12$ used as intensity standard, average count (= 1361) with σ(calc.) = 106 (7·8%), 2130 reflections were non-zero after merging ($R = 0 \cdot 0909$) with $I \geq 2 \cdot 5\sigma(I)$. No absorption corrections were applied. Structure solved by direct methods using *SHELX76* (Sheldrick, 1976) with E's $\geq 1 \cdot 475$. Anisotropic full-matrix least-squares refinement based on F with H's (from ΔF synthesis) isotropic gave $R = 0 \cdot 068$.

Further refinement, after omitting 14 reflections with $(F_o - F_c)/\sigma \geq 3 \cdot 0$ (poor agreement probably due to poor quality of the crystals or extinction), gave final $R = 0 \cdot 061$, $wR = 0 \cdot 063$, $R_G = 0 \cdot 079$, $S = 2 \cdot 028$, with $w = 1/\sigma^2(|F_o|) + 0 \cdot 008512(F)^2$. In the final cycle, maximum shift/σ is 0·1, average shift/$\sigma < 0 \cdot 04$; peak heights in final ΔF map from $-0 \cdot 28$ to $0 \cdot 32$ e Å^{-3}.