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## Structure of a New Triterpene Oxide, 3-Filicanone

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**Abstract.** 21-Isopropyl-4 $\beta$ ,5 $\beta$ ,9 $\beta$ ,13 $\alpha$ ,14 $\beta$ ,17 $\alpha$ -hexamethylperhydrocyclopenta[*a*]chrysen-3-one C<sub>30</sub>H<sub>50</sub>O, monoclinic, *P*2<sub>1</sub>, *a* = 13.538 (6), *b* = 6.342 (3), *c* = 14.797 (7) Å,  $\beta$  = 96.04 (15)°, *V* = 1263.3 Å<sup>3</sup>, *D<sub>c</sub>* = 1.12 g cm<sup>-3</sup>, *Z* = 2, m.p. = 521–522 K, *F*(000) = 576, *M<sub>r</sub>* = 426.7,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å; *R* = 0.09 for 1703 measured reflections (791 observed). The structure has been solved by direct methods and refined by full-matrix least-squares procedures with isotropic *B* values. The molecule has a C(3) oxygen and consists of four six-membered rings and one five-membered ring, all *trans* fused and giving a stretched, long form of the molecule. There are five axial methyl groups in positions 5,9,13,14,17 and one equatorial in position 4. The five-membered ring has an isopropyl substituent at C(21). The name accordingly is 3-filicanone. The interatomic distances and angles are of normal values. Non-bonded interaction between methyl groups in 1,3 positions causes some bending and slight twisting along the major axis of the molecule.

**Introduction.** The title compound, believed to be a friedelin-type triterpene isolated from the stem bark of *Strychnos dolichothyrsa*, was selected for a three-dimensional X-ray study to elucidate the molecular constitution. The crystals were kindly supplied by Dr R. Verpoorte from Gorleus Laboratories at the State University of Leiden. The molecular formula was established as C<sub>30</sub>H<sub>50</sub>O by means of high-resolution mass spectrometry (Verpoorte, 1978). The single-crystal X-ray structure determination shows that the structure of this triterpene is a '3-keto-oxide'.

A well formed, transparent, non-twinned, prismatic *b* crystal was used for data collection on a Picker automatic four-circle diffractometer. Intensities were measured for 1796 reflections ( $2\theta_{\max}$  = 45.0°) using

graphite-monochromatized Mo *K* $\alpha$  radiation and the  $\omega/2\theta$  scan technique. Twice the normal background counting time was chosen (60 s) to minimize the influence of fluctuations in the background, and hence give as good standard deviations for the weakest reflections as possible. Three reflections were monitored periodically to ensure a common scale, and the intensities varied by less than 2% during the data collection. Reflections with  $I < 2\sigma(I)$  were considered unobserved, giving a total of 791 observed reflections after data work-up. The low number of observed reflections is caused by the small size of the crystal (0.3 × 0.12 × 0.08 mm) which had to be selected because of severe twinning in most of the crystals. The intensities of all reflections were placed on an absolute scale, and normalized structure factors were derived. All calculations were performed on a Cyber 74 computer using standard programs (Groth, 1973).

The scattering factors for C and O were taken from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson (1965). No absorption correction was applied.

Phase angles for the individual  $E_{hkl}$ 's were derived from the structure-factor magnitudes by means of a multiresolution tangent-formula approach, *MULTAN* (Germain, Main & Woolfson, 1971). The calculated figures of merit, however, did not make a good discrimination possible. The molecule was initially supposed to consist of five six-membered rings and to be highly symmetrical and the solution was not straightforward. When it was realized that the molecule consisted of four six-membered rings and one substituted five-membered ring and the direction of the longest axis of the molecule in the cell was determined, a solution was eventually found and refined smoothly to a conventional *R* value of 0.11. The positions for all

H atoms excluding those of the methyl groups were calculated, and the parameters compared well with positive regions in the difference map. The methyl H atoms were then calculated based on staggered arrangements about the C—C bonds. This arrangement is, however, not the correct one as the space for 1,3 axial methyl groups 24,25, 25,27 and 26,28 is a limiting factor. The methyl substituents lead to a crowded molecular arrangement and some strain is introduced into the ring system to prevent the shortest contacts. Trial and error led to an arrangement which gives non-bonded H—H distances about 1.9 Å. The structure was refined by full-matrix least-squares procedures using isotropic temperature factors only, because of the limited number of observed reflections. The final *R* value was 0.09. Final positional and thermal parameters for the non-H atoms are given in Table 1.\* Bond distances and angles determined are given in Fig. 1. Standard deviations in the bond lengths and angles are 0.02 Å and 1.5° not including H atoms.

\* Lists of structure factors and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36627 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional* ( $\times 10^4$ ) *and isotropic thermal parameters for the non-H atoms*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
C(1)	9796 (11)	4556	8031 (10)	3.5 (4)
C(2)	10149 (11)	6098 (38)	8815 (10)	4.5 (4)
C(3)	9407 (13)	6320 (39)	9481 (12)	4.9 (4)
C(4)	8383 (11)	7105 (30)	9012 (10)	3.5 (4)
C(5)	7988 (12)	5401 (41)	8289 (11)	3.0 (5)
C(6)	6985 (12)	6210 (38)	7817 (10)	3.3 (4)
C(7)	6631 (11)	4953 (38)	6914 (10)	3.7 (4)
C(8)	7447 (12)	5099 (37)	6271 (11)	3.4 (4)
C(9)	8415 (13)	3982 (43)	6700 (12)	3.2 (5)
C(10)	8768 (12)	5135 (39)	7597 (11)	3.2 (5)
C(11)	9250 (12)	4017 (38)	6062 (11)	3.9 (5)
C(12)	8890 (13)	3523 (41)	5064 (11)	4.4 (5)
C(13)	7999 (12)	4848 (37)	4675 (11)	2.0 (4)
C(14)	7107 (8)	4416 (29)	5277 (8)	2.3 (3)
C(15)	6192 (12)	5663 (37)	4866 (11)	3.7 (5)
C(16)	5871 (12)	5276 (39)	3841 (11)	3.2 (5)
C(17)	6760 (11)	5429 (36)	3246 (10)	3.6 (4)
C(18)	7635 (12)	4233 (35)	3732 (10)	2.6 (4)
C(19)	8345 (13)	4068 (42)	2956 (12)	2.8 (5)
C(20)	7645 (12)	3689 (40)	2116 (11)	3.8 (5)
C(21)	6590 (14)	4062 (40)	2372 (13)	3.7 (5)
C(22)	5881 (12)	4834 (37)	1527 (10)	4.6 (4)
C(23)	7670 (12)	7575 (46)	9714 (11)	4.2 (4)
C(24)	7836 (11)	3296 (35)	8817 (10)	4.0 (4)
C(25)	8273 (12)	1641 (36)	6892 (10)	4.2 (4)
C(26)	8337 (12)	7225 (36)	4732 (11)	3.2 (4)
C(27)	6758 (11)	2117 (37)	5238 (9)	3.7 (4)
C(28)	6900 (11)	7738 (38)	2950 (10)	4.1 (4)
C(29)	4883 (12)	5500 (38)	1729 (11)	4.9 (5)
C(30)	5750 (14)	3121 (44)	766 (13)	6.5 (6)
O	9540 (13)	5939 (37)	10302 (11)	5.5 (4)

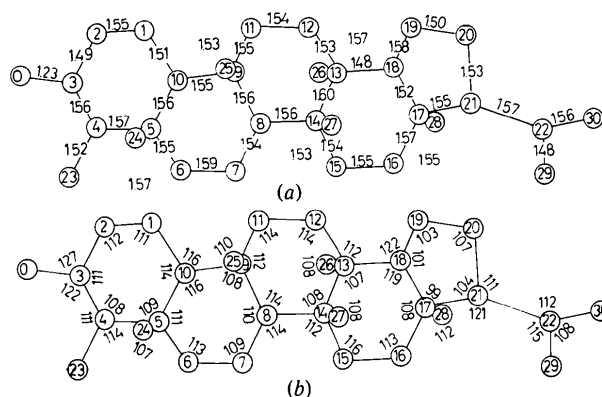


Fig. 1. 3-Filicanone, atomic numbering and (a) interatomic distances (Å), (b) angles (°).

**Discussion.** The crystal structure of 3-filicanone consists of discrete molecules, one of which is shown in Fig. 1 which also gives the identities of the atoms. The most significant aspect of the structure is the substituted five-membered ring and the methyl positions. As far as the author knows, the natural occurrence of this compound has not been reported earlier. The molecule consists of four six-membered rings and one five-membered ring, all *trans* fused. All six-membered rings possess more or less deformed chair conformations whereas the five-membered ring has a twisted envelope conformation, with C(17) 0.86 (2) Å out of the plane on the same side as C(28). As can be seen in Fig. 1, the C—C single bonds are of normal values, from 1.48 (2) to 1.60 (2) Å, the mean value being 1.54 Å. Due to the high standard deviations in the present work none of the differences found is significant. The internal angles of the six-membered rings range from 106.5 (1.5) to 118.7 (1.5)°, giving a mean value of 111.3°. The only angle significantly different from the rest is C(13)—C(18)—C(17) of 119 (1.5)° at the junction of the five- and six-membered rings. The angles in the five-membered ring range from 99.0 (1.5) to 107.3 (1.5)° with a mean value of 102.8°. The C—C—C angles involving methyl groups show a significant difference whether the angle involves a bond common to two rings or not, the mean value of the first type being 113.8 (1.5)° in contrast to 108.3 (1.5)°. This is probably one effect of non-bonded repulsion between the methyl groups. The triterpenoid nucleus distorts further to maximize the separation of these groups. The distortion involves a twist about the long axis of the molecule and bending in opposite directions at the two ends of the molecule. This effect is shown in Fig. 2 which is a view of the molecule parallel to the least-squares plane through C(1) to C(21) inclusive. Similar distortion is found in the structure of gym-nemagenin (Hoge & Nordman, 1974) and in echinocystic acid diacetate (Carlisle, Lindley & Perales, 1976). There is a planar arrangement around

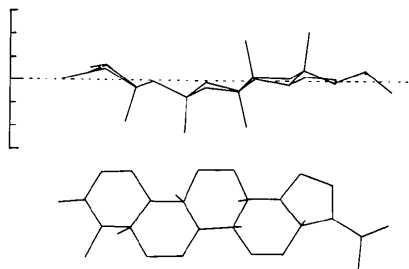


Fig. 2. Molecular deformation of 3-filicanone (scale divisions in Å).

C(3), and C(23) is 0.18 (2) Å out of the plane. The C(3)—O distance is 1.23 (2) Å, and thus of normal length.

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## Structure of (4*S*)-2,4-Dimethyl-1,2-dihydropyrazino[2,1-*b*]quinazoline-3(4*H*),6-dione

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**Abstract.** C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 17.443 (5), *b* = 11.650 (4), *c* = 5.784 (1) Å, *Z* = 4, *d<sub>m</sub>* = 1.456, *d<sub>c</sub>* = 1.429 Mg m<sup>-3</sup>, *F*(000) = 512, μ(Cu *K*α) = 0.843 mm<sup>-1</sup>. The *R* index is 0.040 for 1358 significant reflections. The structure is stabilized by C—H...O interactions. The *N*-methylated *cis* peptide group which forms part of a six-membered ring is non-planar. The torsion angle about the peptide bond is -6.1 (4)° and the peptide bond length is 1.337 (3) Å.

**Introduction.** *N*-Methylated peptides occur in cyclic antibiotics where they introduce significant conformational changes. The structure analysis of the present compound has been undertaken with a view to studying (i) the effect of *N*-methylation on the geometry of the amide group and (ii) the packing of the molecules where the amide proton, which can normally participate in hydrogen bonding, is absent. NMR studies (Rajappa & Advani, 1974) have earlier indicated the presence of an axial methyl group in this compound.

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The title compound, a tricyclic quinazolone (Fig. 1), was derived from *cyclo*(-Sar-L-Ala-) (Rajappa & Advani, 1974) and was crystallized from ethyl acetate/hexane solutions. The unit-cell dimensions were initially obtained from photographs and then refined by least-squares calculation based on 25 reflections on a Nonius CAD-4 diffractometer. Intensity data were collected in the ω-2θ scan mode using monochromated Cu *K*α radiation (λ = 1.5418 Å) with a crystal of dimensions 0.6 × 0.2 × 0.1 mm. Of the

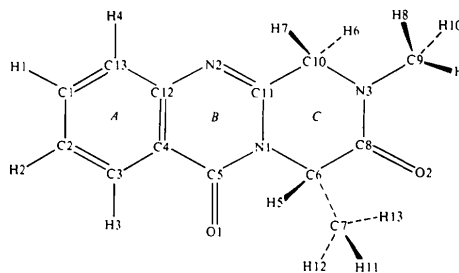


Fig. 1. The numbering of the atoms.

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