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# CRYSTAL AND MOLECULAR STRUCTURE OF THE SESQUITERPENE KETONE 9α-HYDROXYMUROLA-4-ONE

Yu. V. Gatilov, V. A. Khan, and Zh. V. Dubovenko

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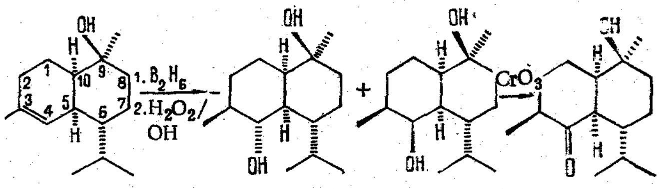
In a study of the structure and absolute configuration of bicyclic sesquiterpenoids of the cadalene series, some of their keto derivatives have been synthesized, and the optical activities of these derivatives have been studied by the ORD and CD methods [1]. However, the use of the octant rule for this set of ketones has led to ambiguous results, since their spatial structure has not been reliably established.

In the present paper we give results of an x-ray structural investigation of the ketone (IV) synthesized from (+)-δ-cadinol (I) and having mp 92-93°C.



I II III IV

Under the conditions of the oxidation of diols and, particularly, of the subsequent isolation of the ketone (IV) on sorbents, epimerization at two asymmetric carbon atoms C(3) and C(5) is possible on sorbents.

The structure of the molecule of the ketone (IV) is shown in Figure 1. The mean bond lengths and valence angles of two independent molecules having the same conformations are given below.

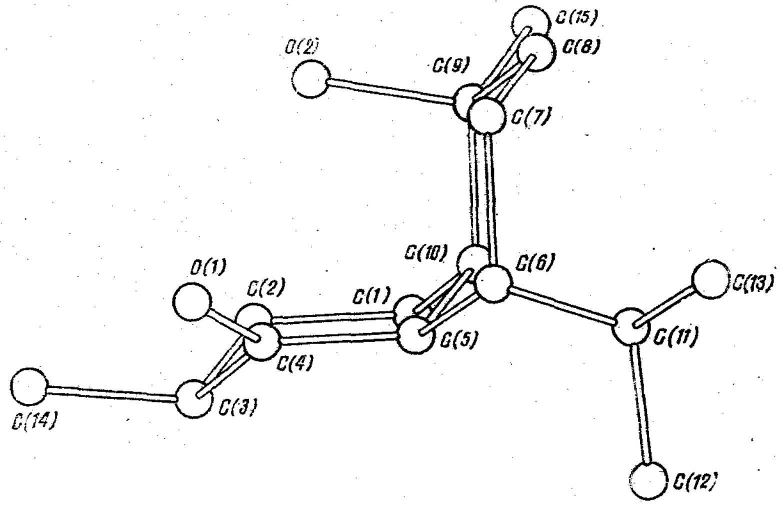


Fig. 1. Crystal structure of the sesquiterpenoid 9α-hydroxy-murola-4-one.

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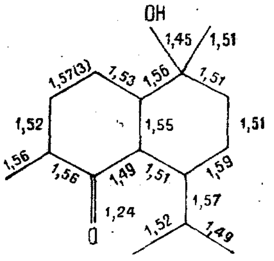

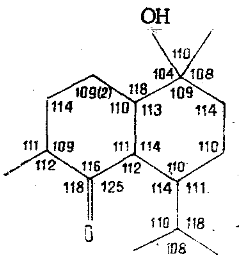

The geometry of the molecule is the usual one. The configurations in the initial diols (II) and (III) are retained at all the asymmetric centers. We also investigated the crystal and molecular structures of the diols (II) and (III) by x-ray structural analysis.* The conformation of the ketone molecule is "steroid-like" with axial isopropyl and hydroxy groups. The axial position of the isopropyl group makes a small contribution of the strain energy [2], and the OH···C(2), 2.90 Å, and OH···C(4), 2.85 Å, interactions are also weaker. Inversion of the conformation of the ketone into the "nonsteroid-like" form would lead to appreciable C(14)···C(6) 1,3-diaxial interaction. Consequently, retention of the "steroid-like" conformation of the ketone even in solution may be expected. This is not contradicted by the ORD results. According to the octant rule, ketone (IV) in the "steroid-like" conformation should have an appreciable negative, and in the "nonsteroid-like" conformation a very weak Cotton effect of the sign of which is difficult to determine. Measurements in heptane and methanol [1] showed negative Cotton effects (A = —11.02 and A = —7.74, respectively).

In the crystal, with the aid of hydrogen bonds the molecules form two independent infinite chains oriented along screw axes. The corresponding distances are 2.88 and 2.90 Å. Short contacts between the two chains are C(12)···C(12'), 3.63 Å, and C(13)···(13'), 3.70 Å.

## EXPERIMENTAL

Ketone (IV) was obtained by the scheme given above [1].

The x-ray structural experiment was carried out on a "Sinteks $P2_1$" diffractometer in molybdenum radiation with a graphite monochromator. The crystals belong to the monoclinic system with $a$ = 7.863(3), b = 9.826(4), c = 18.982(9) Å, β = 90.53(3)°, z = 4, space group $P2_1$. The intensities were measured by the $2\theta/\omega$ scanning method up to $2\theta < 40$. The calculations made use of 918 independent reflections with $I > 3\sigma$. Absorption was not taken into

TABLE 1. Coordinates ($\times 10^3$) of the Atoms of the Ketone Molecule

| Atom | $x$ | $y$ | $z$ | $B_{iso}$ | Atom | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|---|---|---|---|---|
| Molecule A | | | | | Molecule B | | | | |
| C (1) | 072 (2) | 01 (0) | 372 (1) | 5,7 | C (1) | 620 (2) | 642 (2) | 130 (1) | 4,6 |
| C (2) | 038 (2) | 483 (3) | 454 (1) | 4,9 | C (2) | 69 (2) | 652 (3) | 052 (1) | 6,0 |
| C (3) | 062 (2) | 614 (3) | 494 (1) | 4,2 | C (3) | 566 (2) | 516 (3) | 010 (1) | 6,7 |
| C (4) | 238 (2) | 673 (3) | 477 (1) | 3, | C (4) | 735 (2) | 432 (3) | 028 (1) | 6,6 |
| C (5) | 281 (2) | 687 (3) | 402 (1) | 2,6 | C (5) | 780 (2) | 423 (3) | 105 (1) | 3,0 |
| C (6) | 448 (3) | 75 (2) | 389 (1) | 3, | C (6) | 939 (3) | 336 (3) | 115 (1) | 4,1 |
| C (7) | 603 (2) | 650 (3) | 407 (1) | 4,9 | C (7) | 1102 (3) | 424 (3) | 098 (1) | 6,6 |
| C (8) | 570 (2) | 520 (3) | 359 (1) | 6,0 | C (8) | 1107 (3) | 555 (3) | 133 (1) | 4,3 |
| C (9) | 402 (2) | 445 (3) | 377 (1) | 3,3 | C (9) | 956 (3) | 642 (3) | 121 (1) | 6,1 |
| C (10) | 258 (2) | 547 (3) | 362 (1) | 3,7 | C (10) | 785 (3) | 563 (3) | 138 (1) | 6,2 |
| C (11) | 474 (3) | 818 (3) | 315 (1) | 5,8 | C (11) | 946 (3) | 275 (3) | 193 (1) | 4,7 |
| C (12) | 326 (3) | 911 (3) | 295 (1) | 7,7 | C (12) | 1086 (3) | 167 (3) | 198 (1) | 10.4 |
| C (13) | 630 (3) | 887 (4) | 295 (1) | 9,0 | C (13) | 782 (3) | 210 (4) | 217 (1) | 9,1 |
| C (14) | 038 (3) | 594 (3) | 575 (1) | 6,0 | C (14) | 546 (3) | 540 (3) | —064 (1) | 6,4 |
| C (15) | 402 (3) | 313 (3) | 337 (1) | 5,1 | C (15) | 977 (3) | 771 (3) | 165 (1) | 6,5 |
| O (1) | 329 (1) | 724 (2) | 528 (1) | ,4 | O (1) | 804 (2) | 376 (2) | —020 (1) | 6,3 |
| O (2) | 392 (1) | 415 (2) | 451 (1) | 5,8 | O (2) | 939 (1) | 669 (2) | 045 (1) | 5,8 |

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*The results will be published in the "Zhurnal Strukturnoi Khimii" ["Journal of Structural Chemistry"].

account. Numerous attempts to determine the structure by the direct method using the MULTAN program were unsuccessful. A Debye correction was introduced for the known geometry of the molecule [3]. To evaluate the significance of the variants of the phases of the reflection we used the NQEST criterion [4] (94 quartets with $E_{main} = 1.6$, $E_{cross} = 0.56$, and $B_{min} = 0.5$). Among the 64 variants of the phases that were calculated for 204 $E > 1.4$, the best had NQEST = −0.03 and did not lead to resolution. Then we calculated 128 variants of the phases, among which there was one correct variant with NQEST = −0.13. The use of magic numbers by the methods of Lessinger and Margulis [5] enabled us to find the correct variant from only 60 calculated varients. The refinement of the structure found was carried out in the isotropic and anisotropic full-matrix approximations to $R = 0.087$ and $R_w = 0.072$, where $w = 1/\sigma(F)^2$. The coordinates of the atoms are given in Table 1.

## SUMMARY

The crystal and molecular structure of a ketone (9α-hydroxymurola-4-one) synthesized from δ-cadinol has been investigated. Under the conditions of its production and isolation, the ketone retains the configurations of the asymmetric centers.

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# STRUCTURE OF FERTENIN

G. V. Sagitdinova, A. I. Saidkhodzhaev,
and V. M. Malikov

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Continuing a study of the phenolic components of *Ferula tenuisecta* Eug. Kor. [1-5] we have isolated a new substance with the composition $C_{22}H_{30}O_5$, mp 209-211°C (decomp.), $[\alpha]_D^{22}$ +125° (c 0.8; ethanol), which we have called fertenin (I).

UV spectrum: $\lambda_{max}$ 260 nm (log ε 3.80). This maximum underwent a bathochromic shift when the spectrum was taken with the addition of alkali, which is due to the presence of a phenolic hydroxy group.

IR spectrum, $\nu_{max}$, cm$^{-1}$: 3200-3600 (hydroxy group); 1685 (ester carbonyl conjugated with an aromatic nucleus); 1610, 1590, 1520 (aromatic nucleus); 1290, 1070, 856 (oxide ring) [6].

The mass spectrum of fertenin was characteristic for the spectra of esters of sesquiterpene alcohols [4, 7] and had the peaks of ions with m/e 331 $(M - C_3H_7)^+$, 236 $(M - C_7H_6O_3)^+$, 218 $(M - C_7H_6O_3 - H_2O)^+$, 203 $(M - C_7H_6O_3 - H_2O - CH_3)^+$, 193 $(M - C_7H_6O_3 - C_3H_7)^+$, 175 $(M - C_7H_6O_3 - C_3H_7 - H_2O)^+$, and 138 $(C_7H_6O_3)^+$.

The PMR spectrum of fertenin shows the signals of methyl groups in the form of two three-proton doublets at 0.81 and 0.89 ppm with J = 5 Hz; of methyls on carbon atoms bearing oxygen at 1.24 (s, 3 H), and 1.31 ppm (s, 3 H) [6]; of an epoxide proton at 2.91 ppm (d, J = 10 Hz, 1 H); and of olefinic protons at 5.39 and 5.61 ppm (d, J = 10 Hz, 1 H each). On the signal

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