290 sh, 309, 351. PMR spectrum in deuteropyridine (ppm); 7.92 (d, 9 Hz, H-2',6'); 7.20 (d, 9 Hz, H-3'5'); 6.77 (s, H-3); 2.50 (s, 8-CH_3); 2.44 (s, 6-CH_3).

The Triacetate of (V). PMR spectrum in $CDCl_3$ (ppm): 7.90 (H-2',6'), 7.30 (H-3',5'), 6.72 (H-3), 2.27 (8-CH_3), 2.10 (6-CH_3), 2.42 (s, CH_3CO), 2.35 (s, $2CH_3CO$).

CONCLUSION

The spectral properties of a number of C-methylflavones have been studied.

It has been shown that, in contrast to literature statements, the 6-C-methyl group has the same influence on the UV spectra as 6-O-substitution in producing a shift with $AlCl_3/HCl$.

In the mass spectra of the flavonoids, the production of intense $(M - 15)^+$ ions is usually connected with the presence of a 6-OCH_3 or an 8-OCH_3 group. For the 6,8-di-C-methylflavones, similar ions are characteristic in the presence of a 7-OCH_3 group.

LITERATURE CITED

1. J. B. Harborne, T. J. Mabry, and H. Mabry, The Flavonoids, Chapman and Hall, London (1975).
2. S. A. Medvedeva, C. Z. Ivanova, N. A. Tyukavkina, and G. G. Zapesochnaya, Khim. Prir. Soedin., 650 (1977).
3. D. H. S. Horn, Z. H. Kranz, and J. A. Lamberton, Aust. J. Chem., 17, 464 (1964).
4. J. A. Lamberton, Aust. J. Chem., 17, 692 (1964).
5. W. E. Hillis and K. Isoi, Phytochemistry, 4, 541 (1965).
6. G. G. Zapesochnaya and T. T. Pangarova, Compt. Rend. Acad. Bulg. Sci., 33, No. 7, 933 (1980).
7. J. A. Mears and T. J. Mabry, Phytochemistry, 11, 411 (1972).

X-RAY STRUCTURAL STUDY OF SESQUITERPENE ESTERS FROM PLANTS OF THE GENUS *Ferula*.

I. CRYSTALLINE AND MOLECULAR STRUCTURES OF THE CAROTANE ESTER LAPIDOLIN

B. Tashkhodzhaev, M. K. Makhmudov, L. A. Golovina,
A. I. Saidkhodzhaev, M. R. Yagudaev,
and V. M. Malikov

UDC 547.992:547.37+548.737

An x-ray structural study has been made of the carotane ester lapidolin: diffractometer: Mo K_α radiation, 1601 reflections, direct method, R factor 0.099. The spatial structure of the lapidolin molecule has been determined. The orientation of the ester group in position 10 has been found.

Structure (I) has been proposed on the basis of spectral characteristics and chemical transformations for lapidolin, $C_{24}H_{26}O_8$ — a carotane ester isolated from the roots of *Ferula lapidosa* [1].

A comparative analysis of the PMR spectra of lapidolin and compounds close to it in structure, lapidolinol (II), lapidolinin (III), has enabled the most probable orientations of the substituents and the type of linkage of the rings to be determined. Conclusions relating to the stereochemistry of lapidolin have been made on the basis of the following facts. The characteristic pattern of the splitting of the signal at C(6) with its neighbors (m: 5.32 ppm; $W_{1/2}$ = 24 Hz) shows the axial orientation of H(6) and the α-pseudoequatorial orientation of the angeloyl residue geminal to the proton, with the trans-linkage of the cyclopentane and the cycloheptane rings [2]. The presence in the spectrum of (I) of two doublets (2.8 and 4.87 ppm) is the result of the interaction of the epoxide proton with the vicinal

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 309-314, May-June, 1984. Original article submitted April 21, 1983.

0009-3130/84/2003-0287$08.50

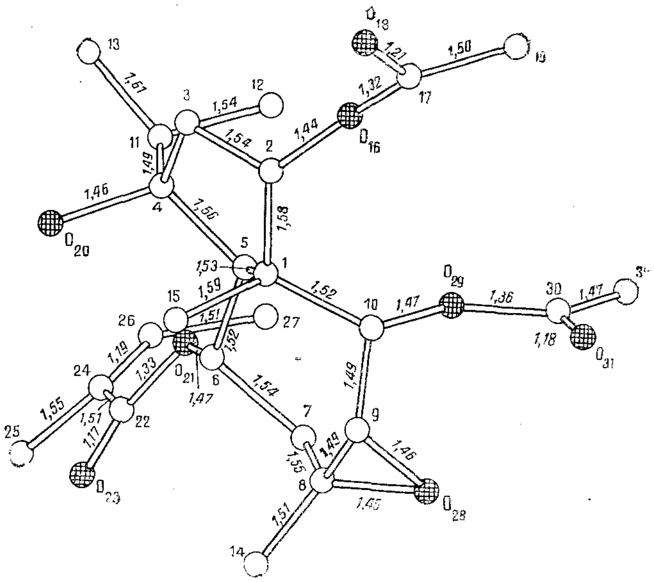


Fig. 1. Geometry of the lapidolin molecule.

TABLE 1. Coefficients of the Equations Ax + By + Cr = 0 of the Main Planar Fragments of the Molecule of (I) and the Deviations of the Atoms (δ) from the Planes

Plane	Atom	δ, Å	A	B	C	D
Five-membered ring	C (1)* C (2) C (3) C (4) C (5)	—0,60 —0,03 0,04 —0,04 0,03	—12,58	7,55	—5,34	3,66
Seven-membered ring	C (1) C (10) C (7) C (6) C (9)* C (8)* C (5)*	—0,01 0,01 —0,01 0,01 —1,04 —1,14 0,74	—10,75	8,22	—6,68	5,25
Ester group at C(2)	C (2) O (16) C (17) O (18) C (19)	—0,01 0,02 —0,02 0,01 0,00	—0,71	8,52	—7,39	7,50
Ester group at C(6)	C (6) O (21) C (22) O (23) C (24)	0,03 —0,04 —0,00 —0,01 0,02	—12,09	3,51	5,58	0,80
Ester group at C(10)	C (10) O (29) C (30) O (31) C (32)	0,02 —0,03 0,00 —0,01 0,02	—2,48	4,15	9,81	4,42

---

*These atoms were not included in the calculation of the equations of the planes.

gem-acyl proton at C(10). The value of the spin—spin coupling constant (SSCC) of these protons (J = 6 Hz) shows the α position of the oxide ring (by analogy with lapiferin) [3]. The configuration of the C(10)—OAc ester group still remains ambiguous, i.e., analysis of the molecular model shows that the SSCC of the H(9) and H(10) protons does not depend on the orientation of this bond. The relative position of the isopropyl radical was determined in the following way. When the PMR spectra of lapidolin and lapidolinin (III), which are based on the same alcohol — lapidolinol (II) — are compared, it can be seen that the replacement

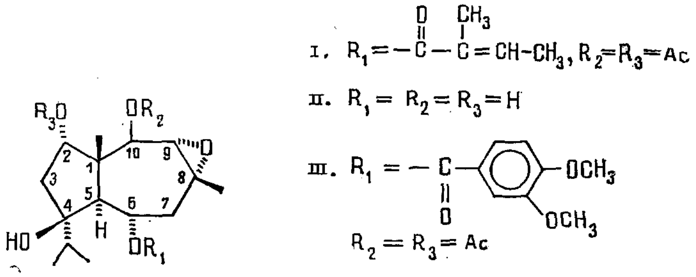
TABLE 2. Valence Angles (ω, degrees) of the Molecule of (I)

Angle	ω	Angle	ω	Angle	ω	Angle	ω
2—1—5	103,0	5—4—20	110,3	14—8—28	116,3	6—21—22	115,0
2—1—10	112,2	11—4—20	108.1	8—9—10	123,8	21—22—23	126 3
2—1—15	103,1	1—5—4	105,3	8—9—28	58,9	21—22—24	113.2
5—1—10	115,3	1—5—6	113,5	10—9—28	120,3	23—22—24	120,5
5—1—15	115,3	4—5—6	116,0	1—10—9	112.2	22—24—25	113,6
10—1—15	107.2	5—6—7	112,6	1—10—29	106,7	22—24—26	127,3
1—2—3	103,8	5—6—21	107,5	9—10—29	109,5	25—24—26	119.2
1—2—16	108,1	7—6—21	106,0	4—11—12	115,5	24—26—27	122.6
3—2—16	110,4	6—7—8	113.2	4—11—13	113,4	8—28—29	61 5
2—3—4	108.7	7—8—9	117,9	12—11—13	105,9	10—29—30	116 3
3—4—5	104.7	7—8—14	115,8	2—16—17	117,3	29—30—31	122,5
3—4—11	112,5	7—8—28	112,5	16—17—18	123,8	29—30—32	113 8
3—4—20	105,9	9—8—14	121,8	16—17—19	112.6	31—30—32	123,7
3—4—11	114,9	9—8—28	59,7	18—17—19	123,5		

TABLE 3. Coordinates (× 10^4) and Isotropic Thermal Parameters of the Atoms of the (I) Molecule

Atom	x/a	y/b	z/c	Bj Å^{-2}
C (1)	2510 (8)	10673 (10)	1224 (12)	6,72
C (2)	2504 (8)	10982 (10)	2707 (11)	5,19
C (3)	1677 (9)	9960 (9)	3348 (10)	7.13
C (4)	1460 (8)	9047 (9)	2433 (10)	4.35
C (5)	2277 (7)	9547 (7)	1319 (10)	4,24
C (6)	1984 (7)	8976 (7)	14 (10)	3,96
C (7)	2896 (8)	9418 (9)	—959 (11)	5,57
C (8)	3049 (7)	10402 (7)	—1685 (9)	5,79
C (9)	3407 (7)	11368 (7)	—912 (8)	5,96
C (10)	3521 (8)	11420 (8)	534 (12)	5,11
C (11)	1476 (7)	8175 (8)	3137 (9)	6.52
C (12)	2540 (12)	8418 (10)	3684 (12)	7,85
C (13)	682 (13)	7737 (10)	4348 (11)	11,62
C (14)	2439 (8)	10208 (10)	—2931 (9)	9,32
C (15)	1617 (7)	10820 (7)	586 (10)	6,41
O (16)	3515 (6)	11305 (7)	3250 (8)	7,22
C (17)	3881 (8)	12066 (8)	4111 (10)	6,84
O (18)	3393 (8)	12455 (8)	4526 (12)	8,44
C (19)	4951 (9)	12365 (8)	4566 (13)	8,48
O (20)	416 (5)	8664 (7)	1921 (8)	7,70
O (21)	1720 (6)	7898 (5)	263 (7)	5,17
C (22)	1139 (8)	7222 (10)	—646 (14)	4,98
O (23)	763 (7)	7392 (9)	—1550 (11)	7,32
C (24)	964 (12)	6140 (10)	—410 (15)	8 90
C (25)	156 (10)	5308 (18)	—1351 (34)	17,51
C (26)	1379 (23)	5386 (17)	382 (39)	20,21
C (27)	2515 (36)	6546 (28)	719 (31)	17,77
O (28)	4126 (6)	11217 (7)	—1728 (8)	8,73
O (29)	4287 (5)	11122 (5)	917 (7)	5,03
C (30)	5298 (8)	11871 (9)	817 (9)	8,09
O (31)	5557 (6)	12737 (7)	531 (12)	9,90
C (32)	6030 (8)	11511 (10)	1145 (10)	8,23

of the aliphatic acid residue at C(6) by an aromatic acid residue leads to a paramagnetic shift of the doublet of one of the isopropylmethyl groups by 0.12 ppm (from 0.85 to 0.97 ppm). This indicates identical orientation of the acyl residue at C(6) and of the isopropyl group [4]. Consequently, the latter has the α-pseudoequatorial orientation. Thus, it follows from what has been said above that the following is the most probable relative configuration for lapidolinol [5]:



I. $R_1 = -\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH-CH_3, R_2=R_3=Ac$

II. $R_1 = R_2 = R_3 = H$

III. $R_1 = -\underset{\underset{O}{\|}}{C}-C_6H_3(OCH_3)_2$

$R_2 = R_3 = Ac$

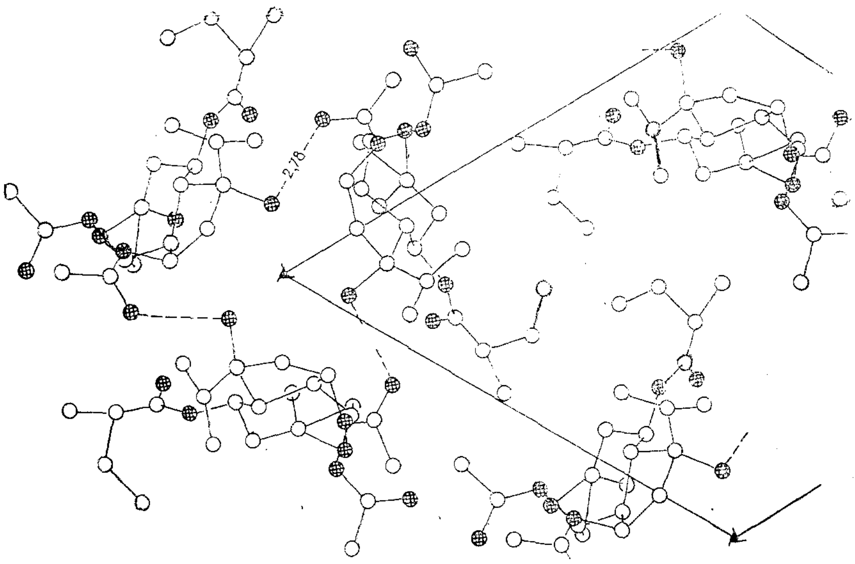


Fig. 2. Packing of the lapidolin molecules.

In order to determine the spatial structure of lapidolin (I) unambiguously, we performed an x-ray structural investigation. We give its results in the present paper.

It can be seen from Fig. 1 that the five- and seven-membered rings have the trans-linkage with the following orientations of the substituents: The ester groups attached in positions 2, 6, and 10 and the epoxy group at position 8,9 are α-oriented and the methyl groups in positions 1 and 8 and the OH group in position 4 are β-oriented. On the whole, the linkage of the two rings and the orientation of the substituents in lapidolin coincides with that which is observed in p-bromobenzoyllaserol [6].

The C(1-5) five-membered ring in (I) has the C(1) β-envelope conformation: The departure of the C(1) atom from the plant of the other four amounts to 0.60 Å (Table 1). The seven-membered ring in (I), in contrast to what is observed in laserol, has the chair conformation (in laserol, the ring is present in the boat form): The C(1), C(10), C(6) and C(7) atoms lie in a single plane with an accuracy of 0.01 Å and the distances by which the C(9), C(8), and C(5) atoms depart from this plane are −1.04, −1.24, and 0.74 Å. The ester groups are planar to within an accuracy of 0.04 Å (see Table 1). However, the butenyl part of the ester group at C(6) is twisted somewhat relative to the plane of the C(6), O(21), C(22), O(23), and C(24) atoms (20°), which shows some disturbance of the conjugation of this section. The butenyl unit is itself distorted: The torsional angle of the C(25)—C(24)=C(26)—C(27) fragment is 38°.

No anomalies are observed in the valence distances and angles (see Fig. 1 and Table 2). The mean square deviations of the determination of the lengths of the bonds do not exceed 0.022 Å, with the exception of the distances in the butenyl unit. Because the lability of this unit [the C(25), C(26), and C(27) atoms have large temperature factors (see Table 3)] the standard deviations in the determination in the lengths of the valence bonds in it amounted to 0.05 Å and the corresponding valence angles at the C(24) and C(26) atoms were determined with an error of 2.4°, although in the determinations of the other angles it was no worse than 1.2°. The values of the valence angles and distances found for the (I) molecule are, on the whole, close to those observed in related compounds (see, for example, [6, 7, 8]).

The packing of the molecules of (I) as projected on the plane of the *a* and b axes is shown in Fig. 2. The molecules, transformed by 3_1 screw axes, are linked by intermolecular hydrogen bonds and form an infinite chain directed along the c crystallographic axis. An intermolecular hydrogen bond exists between the O(20)H...O(18) atoms.

EXPERIMENTAL

Lapidolin crystals grown from solution in ethanol were first investigated by the photographic method: The parameters of the elementary cell and the space group were determined from precession photographs. Then these parameters were refined on a "Syntex" diffractometer using Mo Kα radiation: $a = b = 14.850(7)$, $c = 10.226(4)$ Å, $D_{calc} = 1.160$ g/cm³, space group $P3_1$, $z = 3$. A three-dimensional set of intensities was obtained on the same diffractometer. In the primary treatment of the group of results, weak reflections with $I \leqslant 2\sigma$ were excluded. The final group of structural amplitudes amounted to 1601 independent nonzero reflections.

The structure was determined by the direct method using the Rentgen-75 program [9]. After the standardization of the structural amplitudes for determining the phases of the program, 318 amplitudes with $E \geqslant 1.20$ were selected. An attempt to interpret the structure in the "automatic regime" was unsuccessful. After numerous variations of the coordinate and basis reflections we found a solution in which the basis group consisted of the following reflections:

	h	*k*	*l*	*E*
Coordinate reflections	−6	7	7	3,51
Basis reflections	4	9	1	3,01
	−3	2	1	3.00
	−8	13	0	2.81
	−7	8	7	2,74
	1	10	3	2,64

With this basis group, 512 variant were calculated. In the E-synthesis best with respect to the R factor (0.26), 28 nonhydrogen atoms out of 32 were revealed. To find the lacking atoms and to localize those that had been found more accurately, several ρ(xyz) syntheses were calculated. Then the structure was refined by the method of least squares (MLS) in the isotropic approximation to R = 0.13. In the following stage, the position parameters of all the atoms were refined in the full-matrix anisotropic approximation to R = 0.099. Attempts to determine the positions of the H atoms from an electron density difference synthesis were unsuccessful. The coordinates of the atoms and the isotropic temperature factors are given in Table 3.

CONCLUSION

The spatial structure of the carotane ester lapidolin has been determined by the method of x-ray structural analysis. The relative orientations of the substituents in position 1, 2, 4, 6, 8, and 10 have been revealed.

LITERATURE CITED

1. L. A. Golovina, A. I. Saidkhodzhaev, V. M. Malikov, and S. Melibaev, Khim. Prir. Soedin., 787 (1982).
2. L. A. Golovina and A. I. Saidkhodzhaev, Khim. Prir. Soedin., 318 (1981).
3. L. A. Golovina, A. I. Saidkhodzhaev, N. D. Abdullaev, V. M. Malikov, and M. R. Yagudaev, Khim. Prir. Soedin., 301 (1983).
4. A. I. Saidkhodzhaev and V. M. Malikov, Khim. Prir. Soedin., 854 (1978).
5. A. I. Saidkhodjaev [Saidkhodzhaev], L. A. Golovina, and V. M. Malicov [Malikov], 9th Conference on Isoprenoids. Abstracts of Papers, Prague (1981).
6. A. Linek, C. Novak, L. Vesela, V. Kurčik, Collect. Czech. Chem. Commun., 32, 3437 (1967).
7. Z. Karimov, Sh. Z. Kasimov, M. R. Yugudaev, and G. P. Sidyakin, Khim. Prir. Soedin., 446 (1981).
8. V. A. Raldugin, N. I. Andrianov, Z. Sh. Safina, and Yu. V. Gatilov, Khim. Prir. Soedin., 174 (1981).
9. V. I. Andrianov, Z. Sh. Safina, and B. L. Tarnopol'skii, Zh. Strukt. Khim., 15, 911 (1974).