It has been shown that the bound and strongly-bound lipids differ from the free lipids by a higher level of unsaturated acids. The acid numbers of the bound lipids were 5-6 times higher than those of the free lipids.

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

V. STRUCTURE AND STEREOCHEMISTRY OF FERTICIN

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An x-ray structural investigation has been made of the sesquiterpene ester ferticin: diffractometer, CuK_α radiation, 1037 reflections, direct method, R factor 0.105. The spatial structure of the molecule has been determined.

The chromatographic separation on silica gel of the total neutral components of the roots of <u>Ferula tenuisecta</u> Korov. has yielded a compound $C_{20}H_{32}O_4$, mp 109-110°C (decomp.) which has been called ferticin (I).

An analysis of spectral characteristics permitted the conclusion that ferticin was an ester of angelic acid and a carotane alcohol containing a carbonyl group in a six-membered ring and two tertiary hydroxy groups (one of them being esterified).

The dehydration of ferticin with thionyl chloride led to a compound $C_{20}H_{30}O_3$ (II) in the PMR spectrum of which there were only slight changes in the chemical shift of the signals present in the spectrum of the initial compound, while in the IR spectrum the absorption band of the hydroxy group had disappeared. The absence from the PMR spectrum of (II) of the signals of olefinic protons showed that the double bond formed was fully substituted. This was possible only if the hydroxy group were located at C_5 or C_4 of the carotane skeleton. The latter position was excluded on the basis of the mass spectrum of ferticin which lacked the peak of an ion with m/z $(M - 43)^+$ [1, 2]. Consequently, the second hydroxy group in ferticin, esterified with angelic acid, may be located at C_8.

The value of the chemical shift of the angular methyl group and also the absence of conjugation with the carbonyl group in the dehydro derivative of ferticin showed the possibility of only two positions in the six-membered ring for the keto group — C_7 or C_9. The choice of the alternative position for the carbonyl group and the establishment of the stereochemistry was made with the aid of x-ray structural analysis. The results of the investigation performed showed that ferticin has the following structure and stereochemistry (I) (see scheme on following page).

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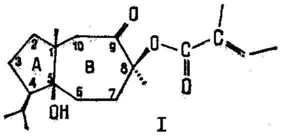

I

Figure 1 shows the spatial structure of the (I) molecule (in a projection on the 010 plane). In ferticin, rings A and B are cis linked with the following orientations of their substituents: The angelic acid residue in position 8, the methyl group in position 1, the hydroxy group in position 5, and the isopropyl group in position 4 have the β-orientation, and the methyl group in position 8 is α-oriented. On the whole, the linkage of the two rings and the orientation of the substituents in ferticin coincide with those observed in vaginatin and rel-(3R, 3aR, 8S, 8aR)-3α-hydroxy-1-oxo-6-daucene-8-yl p-anisate [3-5].

In the refinement of the structure by successive electron density (ED) approximations, it was found that the C_{13} and C_{14} atoms of the isopropyl group each occupied two alternative positions (see Fig. 1). Judging from the ED values the disordered isopropyl group was present in the two positions with equal probability. A disorderedness of hydrocarbon substituents is a fairly common phenomenon in crystal structures and has been reported, for example, in [6], where a phenyl group was unordered.

Table 1 gives the values of the endocyclic torsion angles of the five-membered ring A and the seven-membered ring (B) in comparison with the theoretically calculated torsion angles for unsubstituted cyclopentanes [7]. Ring A in ferticin has a C_4-α-envelope conformation, the departure of the C_4 atom from the plane of the other four atoms amounting to 0.63 Å, with retention by the ring of the intrinsic C_s symmetry [7]. Such a conformation of a five-membered ring is observed in lapidolin, but in it the five-membered ring has a β-envelope conformation [8].

The seven-membered ring has a twist-chair conformation (an approximate twofold axis of symmetry passes through the C_1 atom and the center of the C_7–C_8 bond).

On the whole, no anomalies are observed in the valence distances and angles (see Fig. 1 and Table 2), apart from the isopropyl group because of the disorderedness that has been mentioned. The mean square errors of the determination of the bond lengths and valence angles do not exceed 0.02 Å and 1°, respectively. The standard deviations in the determination of the lengths in the isopropyl group amount to 0.04 Å and the angles at C_{12} were determined with an error of 3°. The values of the valence angles and distances found for the (I) molecule are, in general, close to those observed in related compounds (see, for example, [3-6, 8]).

The packing of the ferticin molecules is shown in Fig. 2 in a projection on the *a*,b plane. The molecules derived from one another by 2_1 [x, 1/4, 0] screw axes are linked by hydrogen bonds of the O–H...O type (the $O_1...O_2$ distance is 2.93 Å) into infinite chains parallel to the crystallographic axis *a*.

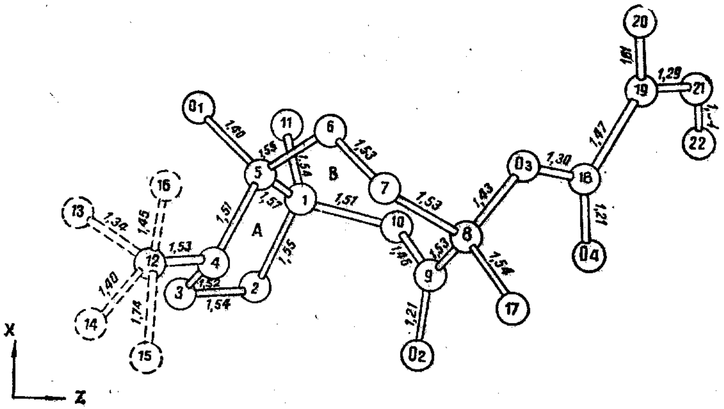

Fig. 1. Geometry of the ferticin molecule.

TABLE 1. Intracyclic Torsion Angles (ω, degrees) of the Ferticin Molecule

Angle	ω	ω_{theor}	Angle	ω	ω_{theor}
1—2—3—4	44,3	—44,4	5—6—7—8	72,6	75,8
2—3—4—5	—32,4	36,7	6—7—8—9	—52,6	—52,8
3—4—5—1	8,4	15,0	7—8—9—10	76,7	75,8
4—5—1—2	18,7	12,6	8—9—10—1	—83,6	—97,0
5—1—2—3	—38,8	—35,3	9—10—1—5	27,3	41,2
1—5—6—7	—95,9	—97,0	10—1—5—6	46,6	41,2

TABLE 2. Valence Angles (φ, degrees) of the Ferticin Molecule

Angle	φ	Angle	φ	Angle	φ
2—1—5	106,1	4—5—6	116,0	9—10—1	115,4
2—1—10	108,2	4—5—O1	107,8	8—O3—18	116,7
2—1—11	110,5	6—5—O1	105,1	O3—18—O4	122,2
5—1—10	113,8	5—6—7	116,9	O3—18—19	108,3
5—1—11	112,5	6—7—8	115,0	O4—18—19	129,5
10—1—11	105,7	7—8—9	109,3	18—19—20	119,2
1—2—3	103,8	7—8—37	108,6	18—19—21	120,3
2—3—4	103,8	7—8—O3	104,4	20—19—21	120,5
3—4—5	102,5	9—8—17	111,9	19—21—22	126,8
3—4—12	116,6	9—8—O3	111,6	4—12—13	117,8
5—4—12	117,8	17—8—O3	110,6	4—12—15	105,2
1—5—4	104,1	8—9—10	117,6	4—12—14	118,7
1—5—6	114,4	8—9—O2	119,7	4—12—16	126,0
1—5—O1	109,2	10—9—O2	122,7	13—12—15	111,8
				14—12—16	114,4

TABLE 3. Coordinates of the Basis Atoms (×10^4) of the Ferticin Molecule

Atom	x	y	z
C1	3410 (6)	2120 (5)	—215 (8)
C2	2330 (4)	1830 (6)	—860 (9)
C3	2158 (7)	2531 (6)	—1912 (9)
C4	2655 (6)	3396 (6)	—1369 (9)
C5	3710 (6)	3061 (4)	—790 (7)
C6	4280 (7)	3712 (6)	125 (8)
C7	3574 (7)	4257 (5)	1028 (7)
C8	3125 (6)	3735 (5)	2207 (8)
C9	2556 (5)	2871 (5)	1715 (7)
C10	3247 (6)	2137 (5)	1231 (7)
C11	4300 (9)	1411 (6)	—492 (11)
C12	2682 (11)	4203 (9)	—2268 (11)
C13	3109 (26)	4101 (13)	—3448 (20)
C14	1382 (17)	4609 (18)	—2312 (19)
C15*	1772 (24)	4410 (17)	—3042 (34)
C16*	3483 (37)	4918 (20)	—2158 (37)
C17	2353 (8)	4335 (7)	2953 (10)
C18	3933 (7)	2926 (7)	3872 (8)
C19	4928 (9)	2864 (8)	4638 (8)
C20	5799 (9)	3695 (7)	4555 (12)
C21	5128 (10)	2174 (9)	5368 (10)
C22	4431(11)	1339 (8)	5480 (12)
O1	4431 (4)	2933 (4)	—1844 (5)
O2	1584 (4)	2862 (4)	1670 (6)
O3	4055 (4)	3532 (4)	2942 (5)
O4	3091 (5)	2518 (5)	3995 (6)

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*Second positions of the C13 and C14 atoms of the unordered isopropyl group.

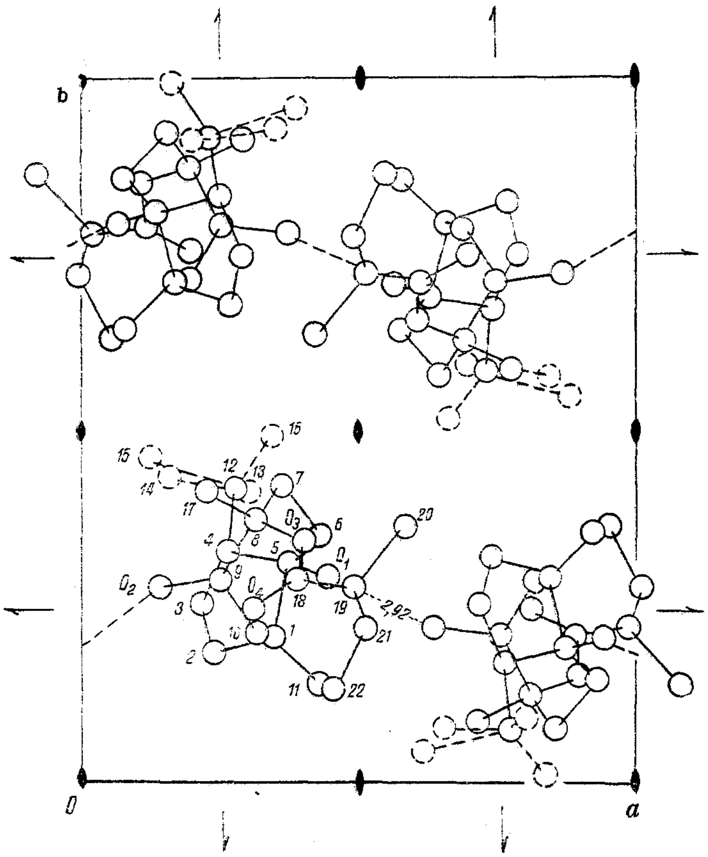

Fig. 2. Packing of the ferticin molecules.

EXPERIMENTAL

The sum of initial compounds (20 g) from the finely cut giant fennel roots were deposited on a column (4 × 80 cm) of silica gel, and the substances were eluted with chloroform–hexane with rising concentrations of the latter. Fractions 27-41 yielded ferticin with the composition $C_{20}H_{32}O_4$, mp 109-110°C (decomp.).

IR spectrum ν_{max} (cm^{-1}) 1250, 1710 (ester group); 1650 (double bond) 3320-3400 (hydroxy group).

PMR spectrum (ppm): 0.85, 0.90 (d, J = 6 Hz, 3H): 0.90 (s, 3H); 1.44 (s, 3H); 1.82 (s, 3H); 1.97 (d, J = 7 Hz, 3H): 6.06 (q, J = 7 and 1.5 Hz).

X-Ray Structural Analysis. Colorless crystals of ferticin of acicular form were grown from solution in hexane–ether and were first investigated by the photographic method. The space group and parameters of the elementary cell were determined from precession x-ray diagrams. These parameters were subsequently refined on a Syntex $P2_1$ diffractometer using CuK_α radiation: a = 12.368(2), b = 14.894(5), c = 10.663(2) Å; ρ_{calc} = 1.18(2) g/cm^3; space group $P2_12_12$; Z = 4. The intensities of the reflections were measured on the same diffractometer. In the primary treatment of the results, weak reflections with $I \leq 2\sigma$ were excluded.

The final group of structural amplitudes amounted to 1037 independent nonzero reflections. The search for a model of the structure was made by the direct method by a program of the "Rentgen-75" group [9]. The calculation was begun in the automatic regime, but the structure could not be interpreted. Then the search was carried out by using the Σ_1 criterion and it was established that the reflections with the indices 640.0, 14.0, 10.80 had the phases φ = 180° with w_1 = 0.691, w_2 = 0.555, and w_3 = 0.579, respectively, and they were included in a new starting set of reference reflections as known. From them, in the light of the known reflections, 1024 variants of the phases were calculated, and then the variant E_2 with R(E) 0.293 stood out sharply. Analysis of the E synthesis revealed 19 nonhydrogen atoms out of 24. In the following electron-density synthesis constructed from the whole group of reflections we found the missing basis atoms. The structure was refined first by successive electron-density approximations (R = 0.232) and by the method of least squares (MLS) in the isotropic approximation (R = 0.208). Subsequently, in the full-matrix MLS with allowance for the anisotropy of the thermal vibrations of the nonhydrogen atoms it was refined to R = 0.105.

Attempts to determine the positions of the H atoms from the electron-density difference synthesis were unsuccessful. The coordinates of the atoms are given in Table 3.

SUMMARY

The stereochemistry of the new carotane ester ferticin has been established unambiguously as 8β-angeloyloxy-5β-hydroxy-9-oxo-cis-carotane.

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CARDIAC GLYCOSIDES OF Cheiranthus allioni.

XIII. GLUCOERYCORDIN

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From plains erysimum (Cheiranthus allioni) Hort., (Erysimum asperum) a new cardiac glycoside has been isolated which has been called glucoerycordin. Its chemical structure has been established mainly by stepwise hydrolysis and the identification of the hydrolysis products. Glucoerycordin $C_{41}H_{64}O_{19}$, mp 131-135°C, $[\alpha]_D^{20}$ −22.2 ± 3° (c 0.65; methanol) is 3β-[O-β-D-glucopyranosyl-(1 → 4)-O-β-D-glycopyranosyl-(1 → 4)-gulomethylopyranosyloxy]-14,19-dihydroxy-5β,14β-card-20(22)-enolide.

Continuing a study of plains erysimum Cheiranthus allioni Hort. (Erysimum asperum) (family Cruciferae), we have isolated from the highly polar fraction a new cardiac glycoside and, after determining its structure, have called it glucoerycordin. The substances were separated with the aid of absorption chromatography in silica gel columns.

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