temperature of 198°C. The determination of the quantitative composition of the sum of the PLs and the saponification of the PLs, NLs and other components were carried out as described in [5, 6].

The pancreactic lipolysis of the TAGs was done as in [2], and the enzymatic hydrolysis of the PE with the aid of phospholipase A_2 in Tris buffer (pH 8.0). The hydrolysis products were separated preparatively in system 5.

The fatty acids from the sn-2 positions were desorbed from the silica gel, methylated, and analyzed by GLC; the lyso products were subjected to saponification, and the sn-1 fatty acids were analyzed as described above.

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CRYSTAL AND MOLECULAR STRUCTURES OF TWO POLYMORPHS OF A FURANOCOUMARIN — SMYRINDIOL FROM Smyrniopsis aucheri

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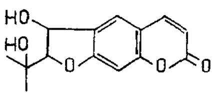
The structures of two polymorphic modifications (I) and (II), of a furocoumarin — smyrindiol from Smyrniopsis aucheri — have been determined by the x-ray structural method. Polymorph I, isolated from the earlier fraction, differed from polymorph II by the presence of a solvate acetone molecule in the crystal. The conformations of the smyrindiol molecule in the two polymorphs differed slightly in the furan ring.

The isolation of a coumarin compound, smyrindiol, from an alcoholic extract of the roots of Smyrniopsis aucheri has been reported previously [1, 2]. A study of spectral characteristics, especially PMR spectra, in comparison with literature information led to two alternative structures [2].



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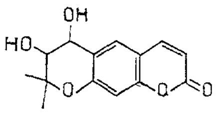

which made it necessary to perform an x-ray structural investigation (XSI). Moreover, on the chromatographic separation of the coumarins of S. aucheri on a column of silica gel with elution by chloroform and a mixture of chloroform and ethyl acetate, together with smyrindiol (fractions 198-212) another coumarin compound, (I), was isolated (from fractions 143-152). On crystallization, compound (I) and smyrindiol (II) gave crystals with different forms and different melting points (ΔT = 15°C), and a mixture gave a depression of the melting point,

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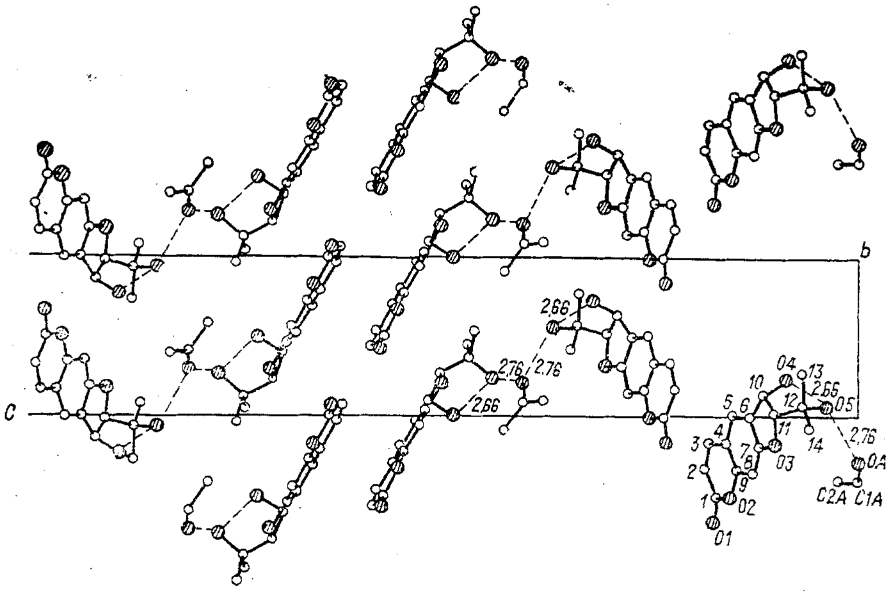

Fig. 1. Projection on bc of the structure of (I).

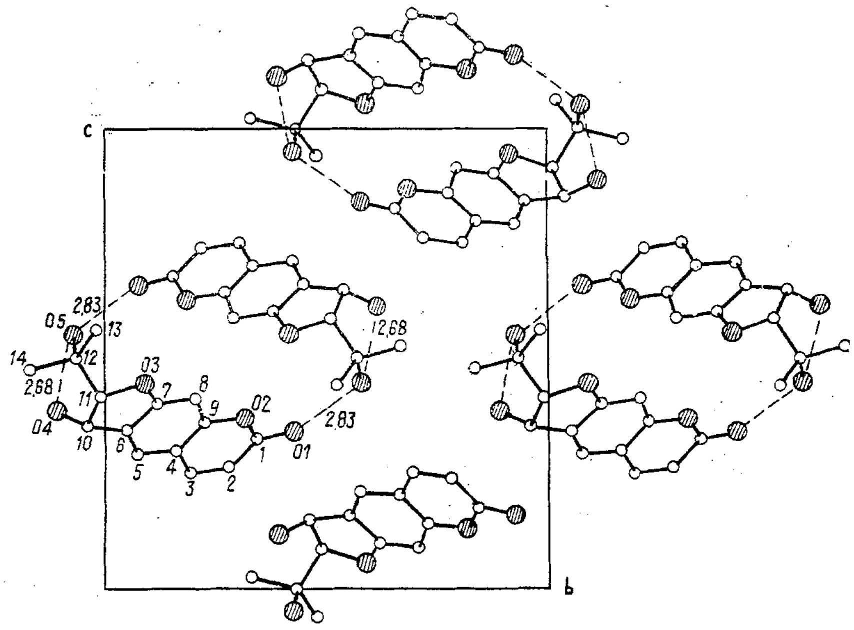

Fig. 2. Projection on bc of the structure of (II).

TABLE 1. Torsional angles of the Furan Rings in Molecules (I) and (II) According to the Results of XSI and MM

Angle	XSI		mm	
	I	II	I	II
O3—C7—C6—C10	4,2	6,0	1,6	1,5
C7—C6—C10 C11	—15,3	−9,5	−12.9	−10,7
C6—C10—C11—O3	20,2	9,6	19,9	16,6
C10—C11—O3—C7	−19,1	−6,8	−20,1	16 4
C11—O3—C7—C6	9,9	0,8	11,9	9,7

although the PMR, IR, and UV spectra of compounds (I) and (II) were very close and both compounds readily formed acetonides. In order to establish the structures of the molecules of (I) and (II) unambiguously, we have carried out a XSI.

TABLE 2. Bond Lengths (r, Å) and Valence Angles (ω, degrees) in Structures I and II

Bond	r_I	r_{II}	Angle	ω_I	ω_{II}	Angle	ω_I	ω_{II}
C1—C2	1,44	1,435	O1—C1—C1	127,8	127,4	C4—C9—C8	122,7	125,3
C1—O1	1,21	1,197	O1—C1—O2	115,4	114,9	O2—C9—C8	116,8	114,3
C1—O2	1,39	1,374	O2—C1—C2	116,7	117,7	O2—C9—C4	120,4	120,4
C2—C3	1,36	1,339	C3 C2 C1	121,5	120,4	C11—C10—C6	101,7	101,5
C3 C4	1,44	1,437	C4—C3—C2	121,8	121,2	O4—C10—C6	110,6	111,6
C4—C5	1,41	1,399	C5—C4—C3	124,4	121,1	C11—C10—O4	114,3	116,4
C4—C9	1,40	1,403	C9—C4—C3	116,9	118,1	C12—C11—C10	119,2	117,6
C5—C6	1,36	1,379	C9—C4—C5	118,7	117,7	C10—C11—O3	105,4	106,6
C6—C7	1,40	1,394	C4—C5—C6	119,4	119,5	C12—C11—O3	108,6	106,4
C6 C10	1,51	1,475	C7—C6—C5	119,2	120,2	C11—C12—C13	110,0	110,2
C7—C8	1,39	1,360	C10—C6—C5	131,7	130,5	C11—C12—C14	110,7	110,3
C7—O3	1,35	1,364	C10—C6—C7	108,7	109,1	C13—C12—C14	110,5	110,9
C8—C9	1,39	1,388	C8—C7—C6	123,8	123,5	O5—C12—C11	109,0	108,5
C9—O2	1,38	1,378	O3—C7—C6	112,9	113,6	O5—C12 C13	106,8	106,3
C10—C11	1,57	1,551	O3—C7—C8	123,1	123,0	O5—C12—C14	109,7	110,6
C10—O4	1,42	1,436	C9—C8—C7	116,1	113,8	O(A) C1(A)—C2(A)		122,2
C11—C12	1,53	1,512						
C11—O3	1,48	1,473						
C12—C13	1,54	1,523						
C12—C14	1,54	1,527						
C12—O5	1,44	1,436						
O(A)—C1(A)		1,202						
C1(A)—C2(A)		1,501						

TABLE 3. Coordinates ($\times 10^4$) of the Nonhydrogen Atoms in Structures (I) and (II)

Atom	I			II		
	x	*y*	*z*	*x*	*y*	*z*
C1	-4763(17)	3459(6)	3237(5)	0002(11)	4904(11)	1051(1)
C2	—5805(17)	2820(6)	2614(5)	—0675(10)	6695(11)	1137(1)
C3	—4971(17)	1950(6)	2496(6)	0216(10)	8318(11)	1104(1)
C4	—3040(16)	1645(5)	2986(5)	2054(9)	8356(9)	0979(1)
C5	-2133(15)	0747(5)	2918(5)	3069(10)	10020(9)	0927(1)
C6	—0307(15)	0526(5)	3416(4)	4734(9)	9886(9)	0804(1)
C7	0645(15)	1184(5)	4107(5)	5394(10)	8093(9)	0733(1)
C8	—0189(16)	2076(5)	4126(5)	4424(11)	6439(10)	0777(1)
C9	—2045(16)	2266(5)	3594(5)	2749(10)	6600(9)	0901(1)
C10	0911(16)	—0389(5)	3517(6)	5075(10)	11359(9)	0704(1)
C11	2899(15)	—0100(5)	4146(5)	7722(10)	10157(10)	0628(1)
C12	3292(14)	—0673(5)	5011(5)	8717(10)	10652(10)	041 (1)
C13	3945(20)	—1674(6)	4759(7)	9506(15)	12685(14)	0422(2)
C14	5087(19)	-0213(7)	5605(8)	0318(13)	9231(14)	0361(1)
O1	—5314(12)	4252(4)	3401(4)	—0729(7)	3366(7)	1069(1)
O2	—2876(10)	3157(3)	3697(3)	1752(7)	4923(6)	0943(1)
O3	2449(10)	0866(3)	4453(3)	7021(6)	8177(6)	0614(1)
O4	—0502(14)	—1101(4)	3855(5)	5004(7)	12323(7)	0524(1)
O5	1230(12)	—0738(5)	5507(4)	7346(8)	10621(8)	0231(1)
O(A)*				7092(8)	7092(8)	0
C1A*				5877(13)	5877(13)	0
C2A*				4139(19)	5998(25)	0147(2)

*Atoms of the acetone solvate molecule.

The XSI of single crystals of (I) and (II) showed that they were polymorphs of a furocoumarin — smyrindiol. In the crystal, compound (I) formed with acetone a 2:1 solvate, while (II) did not. The packing of the molecules in the two crystalline modifications is shown in Figs. 1 and 2. As can be seen from the figures, the orientations of the substituents in the furan moiety of each of the molecules are as follows: the OH group at C10 is β-axial and the isopropanol group at C11 is β-equatorial. Such orientations of the substituents favor the formation of an O4—H···O5 intramolecular hydrogen bond (the O4···O5 and O5—H···5 distances are 2.66 and 1.87 Å, respectively, and the O4—H···O5 angle 114° for molecule (I), the corresponding values for molecule (II) being 2.68 and 2.15 Å and 137°.

The coumarin moieties (the C1-C9, O1, and O2 atoms) in the (I) and (II) molecules are actually planar with accuracies of ±0.05 and ±0.02 Å respectively. A detailed comparative analysis of the torsional angles in (I) and (II) revealed some differences in the conformations of the furan ring (Table 1). In molecule (I), this ring has an 11α-envelope conformation with a deviation of the C11 atom from the plane of the other four atoms by 0.33 Å. In molecule (II), the furan ring is highly planar (±0.05 Å), but its form is closer to a 10β-envelope, the deviation of the C10 atom amounting to 0.14 Å. On the basis of these conformational, differences in (I) and (II), it is possible to explain their separation on a chromatographic column as that of two conformers if one molecule. However, calculation of the free states of molecules (I) and (II) by the method of molecular mechanics (MM) with optimization of the geometry [3] led to a single conformation of the furan ring (with an accuracy of ±3°) — a flattened envelope, as can be seen from the values of torsional angles in Table 1. Consequently, the difference between the torsional angles in the furan rings of (I) and (II) does not show a conformerism of the molecules but is the result of the influence of the crystal field (packing factor).

Analysis of the crystal structure suggests a different hypothesis. It is possible that before separation on a chromatographic column smyrindiol exists in a dynamic equilibrium between two states: in one state (A) it forms with solvent (ethyl acetate) molecules a solvate through H-bonds in a 2:1 ratio, and in the other (B) these H-bonds form an associate between two molecules of smyrindiol. As a result, on chromatography, A and B are separated. When A and B are recrystallized from acetone, instead of from the eluent (ethyl acetate) a molecule of acetone participates in the solvation of A (forming crystals (I)). This hypothesis requires additional experimental confirmation connected with a change in the conditions for the isolation of smyrindiol. It was impossible to eliminate the acetone from the composition of (I) even in recrystallization from ethyl acetate.

The bond lengths and valence angles (Table 2) in the molecules (I) and (II) are the usual ones and are close to the corresponding standard values [4]. The mean square deviations for the bond lengths and valence angles in (I) are not more than 0.009 Å and 0.6°, and in (II) 0.012 Å and 0.8°.

EXPERIMENTAL

For general remarks and the separation of the coumarins, see [2].

Smyrindiol I. On evaporation, fraction 143-152 deposited 1.96 g (0.02% on the weight of the dry plant) of colorless flat tabular crystals with the composition $C_{14}H_{14}O_5$, M^+ 262, mp 153-155°C (from a mixture of ethyl acetate and acetone), $[\alpha]_D + 30°$ (c 1.0, ethanol).

X-Ray Structural Investigation. The parameters of the unit cell and intensities were measured on a Synex $P2_1$ diffrctometer (Cu-K_α radiation, $\theta/2\theta$ scanning, $\theta < 58°$):

Crystals of (I)	Crystals of (II)
a=6,029	a=7,001
в=14,370	в=7,001
c=14,631 Å	c=59,51 Å
d calc=1,374 g/cm^3	d =1,327 g/cm^3
Space group $P2_12_12_1$, Z=4	Space group $P4_12_12$, Z=8
The number F in MLS 1135	The number F in MLS 1078

The structures of (I) and (II) were interpreted by the direct method using the SHELXS-86 program [5]. Refinement was carried out by the full-matrix method of least squares in the isotropic-anisotropic approximation. The acetone molecule of crystallization, where the O(A) and C1A atoms are present in partial positions, was refined anisotropically. The hydrogen atoms were allocated geometrically, or, in the hydroxy groups, were found from a difference electron-density synthesis. The structure was refined by the SHELX-76 program [6] (both programs in the IBM PC versions) to R(I) = 0.079 and R(II) = 0.056. The coordinates of the non-hydrogen atoms are given in Table 3.

The calculations by the method of molecular mechanics were performed on an IBM PC computer by the PCMODEL program, which contains a modified MM2 program [3], with full optimization of the geometry of the molecule.

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