reagent were evaporated off at 40°C in a rotary evaporator. The TMS ethers were extracted with diethyl ether, and the completeness of the reaction was evaluated by TLC in system 1.

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COUMARINS OF *Smyrniopsis aucheri*

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UDC 947.918

Chemical transformations and spectral characteristics have enabled us to establish the structure and configurations of three coumarins: (+)-2',2'-dimethyl-3'β-hydroxy-3',4'-dihydropyrano(5',6':6,7)coumarin (I); (+)-4'β-hydroxy-5'β-(1-hydroxy-1-methylethyl)-4',5'-dihydrofuro(2',3':6,7)coumarin (II); and (+)-4'β-hydroxy-5'-(1-glucopyranosyloxy-1-methylethyl)-4',5'-dihydrofuro(2',3':6,7)-coumarin (III) isolated from the roots of *Smyrnopsis aucheri* Karjag. This is the first time that these compounds, which have been called smyrinol, smyrindiol, and smyrindioloside, have been detected in nature.

Continuing investigations of smyrniopsis roots collected in the flowering and fruit-bearing phase of the plant we have studied the physicochemical and spectral parameters of the substances isolated previously [1] and have established structures of another three coumarin compounds: (I-III).

The presence in the UV spectrum of smyrinol (I) of absorption maxima at 210, 225, 250, 260, 300, and 325 nm showed that the substance was a 6,7-substituted coumarin [2]. Its IR

Institute of Chemistry of Plant Substances, Uzbekistan Republic Academy of Sciences, Tashkent. Azerbaidzhan State University, Baku. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 36-40, January-February, 1992. Original article submitted December 24, 1990; revision submitted August 16, 1991.

TABLE 1. Parameters of the PMR Spectra of the Pyran Rings of Compounds (I) and (IV-VI) (δ, ppm, J, Hz, $CDCl_3$)

Compound	Proton			
	H^a-3′	H^e-3′	H^a-4′	H^e-4′
I. (3′-βOH) [α] +16,8’	3,55; q ^3J=10,5 ^3J=2,0		2,46; q, ^2J=13,8; ^3J=10,5	3,14; q, ^2J=13,8; ^3J=2,0
IV. (3′-βOH) [α] +18°		3.89; q., ^3J=6,5; ^3J=5,0	2.78; q, ^2J=17,0; ^3J=6,5	3,16; q, ^2J=17,0; ^3J=5,0
V. (3′-αOH) [α] −12°	3,94; m, —		2,95; q, ^3J=9,0	3,04; d, ^3J=2,5
VI. (3′-αOH) [α]−10°		5.08; t, ^3J=4,9; ^3J=4,8	2.86; m., ^2J=17,2	3 20; m., ^2J=17,2

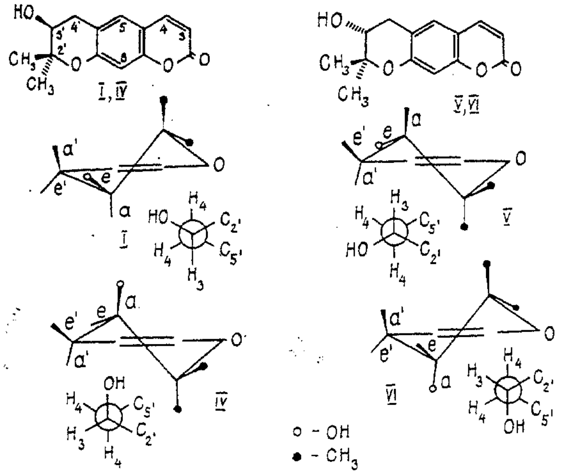
spectrum showed absorption bands at (cm^{-1}) 3500 (OH), 1730 (C=O), 1620, 1585, and 1455 (aromatic ring), which are characteristic for dihydropyranocoumarin derivatives. The mass spectrum of the substance contained the peaks of ions with m/z 246 (M^+), 230 (M^+ − OH), 216 (M^+ − $2CH_3$), 185 (M^+ − 61), 162 (M^+ − 85).

The acetylation of smyrniol with acetic anhydride in pyridine gave a monoacetate with the composition $C_{16}H_{16}O_5$, M^+ 288, which was confirmed by its IR and PMR spectra. In the mass spectrum of the acetyl derivatives peaks of ions with m/z 288 (M^+) and 246 (M^+ − 42) were observed.

The PMR spectrum of smyrinol showed the signals of gem dimethyl groups at 1.19 ppm (6H, s, $2CH_3$-2′), of the protons of a methylene group at 2.46 ppm (1H, q, H-4′, ^2J = 13.8 Hz, ^3J = 10.5 Hz), and at 3.14 ppm (1H, q, H-4′, ^2J = 13.8 Hz, ^3J = 2.0 Hz), of a gem-hydroxylic proton at 3.55 ppm (1H, q, H-3′, ^3J = 10.5 Hz, ^3J = 2.0 Hz), and the signals of the aromatic protons of a coumarin nucleus at 6.08 ppm (1H, d, H-3, ^3J = 9.5 Hz), 6.64 ppm (1H, s, H-8), 7.30 ppm (1H, s, H-5), and 7.73 ppm (1H, d, H-4, ^3J = 9.5 Hz).

The spin—spin coupling constant (SSCC) of the proton at C-3′ (^3J = 10.5 Hz) showed its axial orientation, and, consequently, the hydroxy group was oriented equatorially.

On the basis of the facts given above it may be concluded that smyrinol has the structure and configuration of (I).



The characteristics of three pyranocoumarins close in structure to smyrinol are given in the literature: decurennol (IV), aegelinol (V), and an "aegelinol conformer" (VI) [2-5]. By comparing their physicochemical constants and the corresponding constants of smyrinol (Table 1) it was established that they were pairs of enantiomers (I:IV) and (V:VI) and of diastereoisomers (I:V) and (IV:VI). A study of the SSCCs of the signals of the protons at C-3′ and C-4′, and also thermodynamic modeling* showed that the pyran ring in these coumarins has the most energetically favorable conformation — a distorted half-chair.

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*Materials on the thermodynamic modeling of the compounds will be published later.

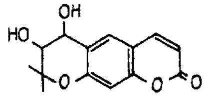
TABLE 2. PMR Spectra of (II) and (III) (in $CDCl_3$ and C_5D_5N, 0 – HMDS)

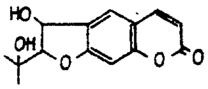
Proton	Smyrindiol (II)		Smyrindioloside (III)	
	δ, ppm	Hz	δ, ppm	Hz
H-3	6,03 d	$^3J=10{,}0$	6,13 s	$^3J=10{,}0$
H-4	7,45 d	$^3J=10{,}0$	7,47 s	$^3J=10{,}0$
H-5	7,34 s		7,42 s	
H-8	6,51 s		6,71 s	
H-4′	5,28 dd	$^3J=6{,}6$ $^3J=6{,}6$	5,47 dd	$^3J=6{,}8$ $^3J=6{,}8$
H-5′	4,23 d	$^3J=6{,}6$	4,58 d	${}_3J=6{,}8$
$-(CH_3)_2$	1,45 s 1,50 s		1,73 s	
HO-4′	5,08 d	$^3J=6{,}6$		
HO-6′	3 90 s			
H-1″			5,19 d	$^3J=8{,}0$
H-2″–5″			4,04–4,13m	
2H-6″			3,76 m	

In the PMR spectrum of smyrindiol (II) a signal was observed from a gem-hydroxylic proton at 5.28 ppm in the form of a triplet. Such a nature of the splitting is connected with spin–spin coupling not only with the vicinal methine protons at C-5' ($J_{4',5'}$ = 6.6 Hz), but also with the hydroxy group $J_{4',4'\text{-OH}}$ = 6.6 Hz. On the addition of trifluoroacetic acid, the doublet signal of the C-4'-OH hydroxy group shifted downfield, while the triplet signal from the proton at C-4' was transformed into a doublet. The downfield shift of the triplet signal (Δδ 1.01 ppm) and its transformation into a doublet was also observed when smyrindiol was acetylated. In the PMR spectrum of the smyrindiol diacetate a downfield shift was also observed of the doublet signal at 4.32 ppm by Δδ 0.23 ppm with a spin–spin coupling constant equal to the SSCC of the vicinal gem-hydroxylic proton at 5.28 ppm (J = 6.6 Hz).

Smyrindiol gave an acetonide with acetone under mild conditions. Consequently, the (II) molecule contains two close hydroxy groups which are readily cyclized. The shifts of the signal from two interacting vicinal protons in the diacetate and the formation of the acetonide are evidence in favor of a cis-diol. At the same time, the assignment of the doublet signal at 4.23 ppm to the gem-hydroxylic proton is questionable since the shift Δδ by only 0.23 ppm in the spectrum of the diacetate is insufficient for a gem-acetyl proton.

The facts given above may correspond to two alternative structures of smyrindiol:





Correlations between the PMR spectra and structures of dihydrofuro- and dihydropyranocoumarins have been described in the literature and interpreted [2, 6, 7]. A study and comparison of our results and those given in the literature did not lead to an ambiguous conclusion (see scheme on top of following page).

The x-ray structural analysis performed* showed that smyrindiol was a dihydrofurocoumarin. The substituents in the dihydrofuran ring have the cis orientation and therefore the secondary and tertiary hydroxy groups are close to one another and there is a strong hydrogen bond between them.

The spectral (IR, PMR, and mass spectra) characteristics showed that compound (III), having the composition $C_{20}H_{24}O_{10}$, M^+ 424, was a glycosylated furocoumarin. In actual fact, the acid hydrolysis of the substance yielded D-glucose and an aglycon the physicochemical properties of which were identical with those of smyrindiol (II) (Table 2).

The position of the glucose residue was established by the formation of a pentaacetate, $C_{30}H_{34}O_{15}$, M^+ 634. In the PMR spectrum of the acetyl derivative of smyrindioloside the signal relating to the C-4 proton had undergone a paramagnetic shift by 0.73 ppm and appeared at 6.20 ppm (1H, d, ^3J = 6.8 Hz). This unambiguously showed that the glucose was present in the C-6' position.

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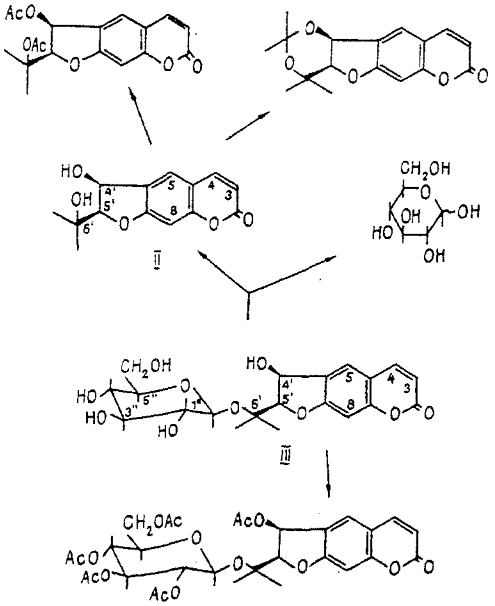
*The results of the x-ray structural analysis will be published later.



The spin–spin coupling constant of the anomeric proton (5.19 ppm, 1H, d, ^3J = 8.0 Hz) showed its axial orientation and, consequently, the glucose was attached to the aglycon by a β-bond.

Thus, smyrindioloside is smyrindiol glucosylated at C-6'.

EXPERIMENTAL

General Remarks. Melting points were determined on a Boëtius stage. Specific optical rotations were measured on a Jasco J-20 spectropolarimeter. UV spectra were recorded in alcoholic solution on a Hitachi EPS-3T instrument. The IR spectra of the compounds under investigation were recorded on a UR-20 spectrometer in the 3700-750 cm^{-1} region by the method of molding the compounds into tablets with potassium bromide. The mass spectra of the coumarins and their derivatives were obtained on a MKh 1310 mass spectrometer with double focusing and a system for the direct introduction of the sample into the ion source at an ionizing voltage of 40-50 eV and a temperature of 170-190°C. PMR spectra were taken on a Tesla BS 567A/100 Mz instrument. The concentrations of the substances ranged between 3 and 4%.

The monitoring of the course of the reactions and the purity of the compounds was effected with the aid of TLC on Silufol plates (Czechoslovakia). Revelation was by means of a Mig UV lamp, a 1% solution of vanillin in 5% H_2SO_4 in alcohol, and diazotized sufanilamide. The solvent systems used were chloroform–ethyl acetate (4:1, 2:1, and 1:1), and chloroform–methanol (8:1 and 4:1). Column chromatography was conducted on the sorbent Silicagel L (Chemapol) with a particle size of 100-160 μm.

Extraction of the Raw Material. The air-dry comminuted roots of smyrniopsis (10 kg) were extracted with ethanol (6 × 50 liters). The alcoholic extracts were combined, and the alcohol was distilled off. The viscous extract (1.2 kg) was diluted with water (1:3) and was treated successively with hexane (6 × 1 liter) and ethyl acetate (6 × 1.5 liters). The ethyl acetate extracts were combined, and the solvent was distilled off. This gave 105 g of ethyl acetate extract, which amounted to 1.05% on the weight of the raw material taken.

Isolation of the Coumarins. The ethyl acetate extract (100 g) was mixed with silica gel (100 g) and deposited on a column of silica gel (6 × 140 cm). The substances were eluted successively with hexane (fractions 1-30), with hexane–chloroform (initially 4:1, with increasing concentrations of chloroform) (fractions 31-195), and then with chloroform–ethyl acetate (initially 4:1, with increasing concentrations of ethyl acetate) (fractions 196-360). The volume of each fraction was 50-100 ml.

Smyrinol (I). Elimination of the solvent from fractions 101-131 yielded 6.67 g (0.07% on the weight of the dry plant) of colorless crystals, $C_{14}H_{14}O_4$, M^+ 246, mp 179-180°C, $[\alpha]_D^{24}$ +16.8° (c 1.0; $CHCl_3$); +50° (c 1.0; ethanol).

Smyrindiol (II). After evaporation of the solvent, fractions 198-221 yielded 2.76 g (0.03%) of colorless acicular crystals with the composition $C_{14}H_{14}O_5$, M^+ 262, mp 168-170°C, $[\alpha]_D^{24}$ +30° (c 1.0; ethanol).

Smyrindioloside (III). On evaporation, fractions 332-351 yielded 2.11 g (0.02%) of a colorless crystalline powder with the composition $C_{20}H_{24}O_{10}$, M^+ 424, mp 253-254°C, $[\alpha]_D^{24}$ +40° (c 1.0; DMFA).

Smyrinol Monoacetate. Smyrinol (20 mg) was acetylated with 2 ml of acetic anhydride in 1 ml of pyridine at room temperature for 24 h. After working up by the usual method and recrystallization of the product from methanol, 11 mg of the monoacetate $C_{16}H_{16}O_5$, M^+ 288 was obtained.

Smyrindiol Diacetate. A solution of 30 mg of the substance in 2 ml of acetic anhydride–pyridine (1:1) was heated in the water bath for 1 h. Then the reaction mixture was worked up by the usual method, giving 26 mg of the diacetate $C_{18}H_{18}O_7$. M^+ 346.

Smyrindiol Acetonide. A solution of 25 mg of the substance in 3 ml of anhydrous acetone was treated with 5 mg of molybdophosphoric acid, and the mixture was well stirred. After 10 min it was evaporated in vacuum to the minimum volume, and this was then diluted with water and the precipitate that deposited was extracted with chloroform. The extract was washed with water to neutrality, the solvent was distilled off, and the residue was chromatographed on a column of silica gel. Elution was conducted with hexane–chloroform (1:4), giving 14 mg of an amorphous substance with the composition $C_{17}H_{18}O_5$, M^+ 302.

Acetylation of Smyrindioloside. A solution of 40 mg of glycoside (III) in 2 ml of pyridine was treated with 2 ml of acetic anhydride, and the reaction mixture was heated in the water bath for 3 h. After the usual working up procedure, the reaction mixture yielded 33 mg of the pentaacetate, $C_{30}H_{34}O_{15}$, M^+ 634. PMR: 1.40, 1.47 (3H, s, $2CH_3$-2'); 4.41 (1H, d, ^3J = 6.6 Hz); 6.20 (1H, d, ^3J = 6.6); 6.74 (1H, s, H-8); 7.49 (1H, s, H-5); 7.53 (1H, d, H-4, ^3J = 10.0); 6.18 (1H, d, H-3, ^3J = 10.0); 5.16 (1H, d, H-1"); 4.84-5.13 (4H, m, H-2"-5").

Acid Hydrolysis of Smyrindioloside. A solution of 50 mg of the substance in 10 ml of methanol was treated with 10 ml of 5% HCl solution and the mixture was boiled in the water bath for 4 h. Then the methanol was distilled off in vacuum and the precipitate that had deposited was extracted with ethyl acetate. The extract was dried over anhydrous Na_2SO_4, the solvent was distilled off, and the residue was recrystallized from acetone. This gave 18 mg of a crystalline substance with the composition $C_{14}H_{14}O_5$, M^+ 262, mp 168-170°C, the IR and PMR spectra of which were identical with those of smyrindiol. The aqueous residue was neutralized on an anion-exchange resin and was concentrated to small volume. D-Glucose was detected in the residue by TLC on Silufol [in the n-butanol–methanol–water (5:3:1) system].

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