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A NEW QUINOID PIGMENT FROM Lithospermum erythrorhizon

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In a study of the composition of the pigments from the roots of the plant Lithospermum erythrorhizon Sieb. et Zucc., family Boraginaceae (Maritime Territory) a new quinone of unknown structure was detected. This substance was first isolated by repeated chromatography on silica gel with subsequent purification on Sephadex LH-20 [1].

Subsequently, a different method of isolation was used: the total hexane extract from 500 g of air-dry roots was evaporated, and the residue was dissolved in chloroform and chromatographed on neutral alumina (activity grade III). The naphthoquinoid pigments were retained completely by the alumina, and the substance under investigation was eluted from the column in the form of an orange zone. After further purification on KSK silica gel in the hexane–ether (6 : 1) system, 90 mg of orange yellow needles of (I) were obtained with mp 72-74°C (hexane), $[\alpha]_D^{20} - 81°$.

On the basis of the results of elementary analysis and the mass spectrum (M^+ 354), the composition $C_{21}H_{22}O_5$ was proposed for (I). When it was subjected to TLC on Silufol plates in the petroleum ether–diethyl ether (10 : 3.5) system it had R_f 0.42.

The pigment was unstable in acid and alkaline media. Under the action of the Ehrlich reagent [2], a change in color from orange to dark green was observed. Alkaline hydrolysis gave β,β-dimethylacrylic acid, which was identified with the aid of GLC. Absorption spectrum: $\lambda_{max}^{C_2H_5OH}$ 222, 244, 287, 444 nm (log ε 4.41; 4.38; 4.25; 3.67).

The IR spectrum had the absorption bands of quinoid carbonyls (1657 and 1670 cm^{-1}), of an ester carbonyl (1720 cm^{-1}), of methyl and methylene groups (2840-3020 cm^{-1}) and of the CH vibrations of an aromatic ring (3060 cm^{-1}), and also the characteristic absorption band of the vibrations of CH groups of an α-substituted furan ring (3160 cm^{-1}). The NMR spectra were taken on a Bruker HX-90E instrument with a working frequency of 22.63 MHz for ^{13}C nuclei and 90 MHz for ^1H in $CDCl_3$ (δ scale) with TMS as internal standard.

^1H NMR spectrum (s, singlet; d, doublet; t, triplet; m, multiplet): 1.61 (s, 3H, $3H_{15}$); 1.68 (s, 3H, $3H_{16}$); 1.89 (d, 3H, $3H'_4$, J = 0.9 Hz); 2.16 (d, 3H, $3H'_5$, J = 1.2 Hz); 2.56 (t, 2H, $2H_{12}$); 5.07 (t, 1H, $1H_{13}$); 5.76 (t, 1H, $1H_{11}$, J = 6.7 Hz); 5.68 (m, 1H, $1H'_2$); 6.74 (d, 2H, $1H_3$ and $1H_4$, degenerate AB spectrum); 7.03 (s, 1H, $1H_1$); 7.46 (s, 1H, $1H_9$), and 7.52 (s, 1H, $1H_8$).

In the ^{13}C NMR spectrum the signals of 21 carbon atoms were detected, five of which were quaternary and three of which belonged to carbonyl groups. The assignment of the signals of the carbon atoms was performed by the method of selective decoupling from the protons.

On comparing the ^{13}C and ^1H NMR spectra for (I) with the analogous spectra of esters of shikonin [1], it was found that the signals corresponding to the isopentenyl part of the chain coincided completely. The chemical shifts of H_{11}, and also of C_{11}, confirmed the position of the ester substituent at this carbon atom [1]. The C_2 and the C_5 chemical shifts (187.0 and 185.1 ppm, respectively) are characteristic for a monosubstituted

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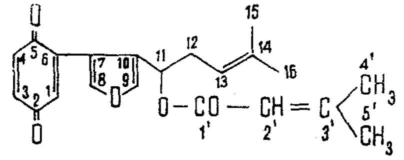
benzoquinone [3].

The two aromatic protons (7.46 and 7.52 ppm) can belong only to a symmetrically disubstituted furan ring. Thus, on the basis of the spectral characteristics and results of alkaline hydrolysis the pigment isolated may be assigned the structure (I)



However, additional information is necessary to confirm the positions of the substituents in the furan ring.

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COUMARINS AND ESTERS OF *Ferula foliosa* AND *F. ferganensis*

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We have shown the presence of four substances revealed by the diazo reagent, with R_f 0.1, 0.21, 0.42, and 0.5 (chloroform system) in the roots of *Ferula foliosa* Lipsky collected in the Fergana range in the valley of the river Arslanbob by chromatography on Silufol. By column chromatography on KSK silica gel with elution by hexane–ethyl acetate we isolated two substances of coumarin nature. Substance (I) $C_{24}H_{30}O_4$ (M^+ 380), mp 191-192°C, R_f 0.42. IR spectrum: ν_{max} 1710 (C=O), 1725 (C=O of an α-pyrone), 1615, 1560, 1515 cm^{-1} (aromatic nucleus). Substance (II), $C_{24}H_{32}O_4$ (M^+ 382), mp 141-142°C R_f 0.21. IR spectrum, ν_{max}, cm^{-1}: 3400-3600 (hydroxy group), 1715 (C=O of an α-pyrone), 1615, 1565, 1515 (aromatic nucleus).

The PMR spectrum of (I) had signals at 0.75 and 1.07 ppm (s, 3H, $2{-}\overset{|}{\underset{|}{C}}{-}CH_3$), 0.90 and 1.02 ppm (d, 3H each, J = 7.5 Hz, $2{-}\overset{H}{\underset{|}{C}}{-}CH_3$), and 3.75 ppm (s, 2H, $Ar{-}O{-}CH_2$). The signals of five protons of a 7-hydroxy-substituted coumarin nucleus were observed in the 6.20-7.57 ppm region.

The PMR spectrum of (II) differed from that of (I) by the fact that it contained the signal of a hemihydroxylic proton with its center at 3.40 ppm (br. m, 1H) and the signals of the methyl groups were shifted. A comparison of the physicochemical constants and spectral (IR, NMR) characteristics showed that substance (I) was kamolone and (II) was kamolol [1, 2].

In the roots of *F. ferganensis* Lipsky collected in the flowering period in the same locations as *F. foliosa* we found three substances with R_f 0.35, 0.45, and 0.5 [petroleum ether–ethyl acetate (3 : 1) system], revealed by vanillin in sulfiric acid. Separation on a column of KSK silica gel yielded two esters: substance (I), $C_{23}H_{32}O_5$ (M^+ 388), 141-142°C, $[\alpha]_D^{20}$ −97.0° (c 1.2; chloroform), R_f 0.45; and substance (II) $C_{22}H_{30}O_4$ (M^+ 385), mp 190-191°C, $[\alpha]_D^{20}$ −91.7° (c 1.2; chloroform), R_f 0.5. Hydrolysis by heating with a 5% aqueous solution of caustic potash led to the saponification of both substances with the formation of the same sesquiterpene diol

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