rapid in use. To isolate homogeneous fractions of X_1 - and X_2 -PLs after the separation requires merely rechromatography in a thin layer of silica gel.

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THE STRUCTURES OF FEROPOLIN, FEROPOLOL,

FEROPOLONE, AND FEROPOLIDIN

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Continuing a study of the coumarins of the roots of Ferula polyantha (Eug. Kor.) [1], collected in the Fergana oblast, we have isolated four new coumarins which we have called feropolin (I), feropolol (II), feropolone (III), and feropolidin (IV). Substance (I) has the composition $C_{26}H_{36}O_7$, mp 63-65°C, $[\alpha]_{12}^{20}$ +85.0° (c 1.33; chloroform) M^+ 460; (II) - $C_{24}H_{34}O_6$, mp 96-98°C, $[\alpha]_{12}^{20}$ +38.2° (c 1.1; chloroform), M^+ 418; (III) - $C_{24}H_{32}O_6$, mp 225-226°C, $[\alpha]_{12}^{20}$ -7.5° (c 1.0; chloroform), M^+ 416; and (IV) - $C_{24}H_{30}O_4$, mp 154-156°C, $[\alpha]_{12}^{20}$ +154° (c 1.0; chloroform), M^+ 382. All the substances have a neutral character and are readily soluble in organic solvents and insoluble in water.

On acid hydrolysis with a mixture of sulfuric and acetic acids, (I-IV) formed umbelliferone. The dehydrogenation of (IV) with selenium gave only 1,2,5,6-tetramethylnaphthalene (V), while (I-III) gave (V) and also 1,2,3,4-tetramethylbenzene (VI).

The UV spectra of (I-IV) have the absorption bands characteristic for 7-hydroxycoumarin derivatives at λ_{max} 220, 244, 328 nm. The hydrolysis of (I) by heating it with a 5% solution of caustic potash yielded (II), and the oxidation of (II) with chromium trioxide in acetone gave (III). Thus, it has been established that (I) and (III) are the natural acetate of (II) and the ketone corresponding to it, respectively. Of the six oxygen atoms in the molecule of (II), three are present in the coumarin and the remainder in the terpenoid moieties. The absence of absorption bands of carbonyl and epoxy groups in the IR spectrum shows that in (II) the oxygen atoms are present in the form of hydroxy groups. The formation of a monoketone and a monoacetate shows that (II) contains one secondary and two tertiary hydroxy groups. The NMR spectrum of (II) show signals at (ppm): 0.84, 0.95, 1.24, and 1.28 (s, 3H each), 3.34 (t, $W_{1/2} = 7$ Hz), 4.09 (m, 2H), 6.15 (1H, d, J = 10 Hz), 6.73 (d, 1H, 2H), 6.73 (d, 1H, 2H), 6.73 (d, 1H), 1H, 1H2 Hz), 6.80 (q, 1H, J = 9.0; 2.0 Hz), 7.30 (d, 1H, J = 9 Hz), and 7.55 (d, 1H, J = 10 Hz). The dehydration of (II) with phosphorus pentoxide in abs. benzene and also with sulfuric acid in ethanol gave two anhydro derivatives with the composition $C_{24}H_{30}O_4$ (VII), mp 177-178°C (yield 20%) and $C_{24}H_{30}O_4$, mp 155-156°C (VIII) (yield 80%). From its IR and NMR spectra and a mixed melting point, substance (VII) was identified as gummosin [2], which we have also isolated from <u>F</u>. samarcandica. The second dehydration product (VIII) was identified by its IR and NMR spectra as feropolidin (IV). When (IV) was oxidized, a ketone C24H28O4 the IR spectrum of which had an absorption band at 1710 cm⁻¹ and lacked the absorption of a hydroxy group was obtained. The NMR spectrum of (IV) shows signals at (ppm): 0.85 (s, 3H), 0.90 (s, 6H), 1.68 (br. s., 3H), 3.79 (q, 1H, J₁ = 10, J₂ = 2.5 Hz), 4.11 (q, 1H, $J_1 = 10$, $J_2 = 5.5$ Hz), 3.35 (br. s., 1H, $\Sigma_{1/2} = 7$ Hz), 5.45 ppm (br. s., $\Sigma_{1/2} = 6.0$ Hz). In addition, in the 6.12-7.56 ppm region there are the signals from the five protons of a 7-hydroxy-substituted coumarin.

The mass spectrum of (IV) shows the peaks of ions with m/e 382 (M^+), 364 ($M-H_2O$)⁺, 220 (M-ArOH)⁺, 203 ($M-ArO-H_2O$)⁺, 162 (ArOH)⁺, which are characteristic for the spectra of iresane coumarins [3].

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On the basis of the facts presented, for (IV) we propose the empirical structure shown below, which explains the position of the tertiary hydroxy groups in (II), these being split out with the formation of a cyclic product of dehydration.



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NEW METHODS OF IDENTIFYING NATURAL HYDROXYCOUMARINS

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At the present time, hydroxycoumarins are identified by characteristic physical, physicochemical, and chemical properties [1-3]. As compared with alkylated coumarins, they have a stronger fluorescence in UV light [1-3], a reduced sublimability, diffuse absorption bands of the lactone ring in the UV spectra [1], a low value of the integral intensity of the absorption of the carbonyl group of the lactone ring in the IR spectra [1], a characteristic formation of intermolecular hydrogen bonds, ease of acetylation and esterification [2], and other chemical properties.

In an investigation of complex-formation with metal salts and of electrochemical reduction at a dropping mercury electrode (DME), we found a series of new chemical and physicochemical properties of the natural hydroxy coumarins. On electrochemical reduction at a DME of the natural hydroxy coumarins, diffuse polar-graphic waves are formed because of the appearance of intermolecular hydrogen bonds. Alkylation and complex formation with metal salts eliminates the diffuseness of the waves and permits the energy of the intermolecular hydrogen bond to be estimated from the shift in the polarographic half-wave potential.

On electrolysis at a DME, solutions of fraxinol are colored the intense lemon yellow that is characteristic for quinoid compounds [4]. There is a linear relationship between the optical density of this coloration and the concentration of the depolarizer (fraxinol), as we showed on an SF-4 instrument. Esculetin gives a similar coloration in the presence of Al_2O_3 . The remaining alkyl- and hydroxycoumarins of the 40 compounds that we investigated do not give such a coloration, which can be used for their specific identification.

The inhibiting action of hydroxycoumarins revealed in a reduction of the rate of oxidation of sulfites by molecular oxygen is two to three times greater than for alkylated coumarins. With an increase in the number of phenol groups and of the molecular weight, the inhibiting action rises symbatically. The detection of the reaction was performed by a polarographic method at a DME until the complete disappearance of the maximum of the first oxygen wave [5].

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