THE ELIMINATION OF PIGMENTS FROM MINOR PHOSPHOLIPIDS

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It is known that the seeds of the cotton plant contain a considerable amount of gossypol and compounds related to it [1]. In spite of the repeated extraction of the seed kernels with acetone [2] it is impossible to eliminate the pigments from them completely, and these pass partially into the total phospholipids when the kernels are extracted with chloroform–methanol (2:1).

The pigments were not retained on Molselekt G-25 when the combined phospholipids was freed from the bulk of the carbohydrates. When the phospholipids were fractionated on a column of silica gel, the accompanying pigments were eluted with chloroform–methanol (95:5 and 90:10) together with the feebly polar minor X_1 and X_2 phospholipids (PLs) and a small amount of phosphatidylethanolamine (PE). In the UV spectra the eluates showed a weak absorption band characteristic for gossypol (356-366 nm) [1]. Attempts to isolate homogeneous fractions of the X_1- and X_2-PLs free from pigments by repeated TLC on silica gel in various solvent systems and in a column of silica gel did not give satisfactory results and led to high losses of the phospholipid fractions.

As is well known, gossypol is strongly retained on Al_2O_3 [3]. We made use of these properties of alumina to free the minor phospholipids from pigments by column chromatography. A 1 × 5 cm column was filled with 1.5 g of Al_2O_3 in the form of a suspension in chloroform. The combined substances under investigation (containing 1.42% of lipid phosphorus) (78 mg) in 5 ml of chloroform were deposited on the column and eluted; the best results with respect to the qualitative and quantitative yield of substance were given by chloroform and by $CHCl_3$–CH_3OH–NH_4OH (65:5:5) (see Table 1).

Of the 78 mg of substances, 65 mg (84%) was eluted and 16% consisted of retained pigments. The recovery of lipid phosphorus amounted to 96%, which shows the fairly good desorption of the phospholipids applied. The proposed method of purifying the minor phospholipids from pigments of the gossypol group is simple and

TABLE 1

Fraction	Eluent	Amount of eluent, ml	Yield of the fraction, mg	Lipid P, %		Qualitative composition of the fraction
				in the fraction	recovered	
1	Chloroform	25	5	—	—	Non-phosphorus-containing
2	$CHCl_3$–CH_3OH–NH_4OH (65:35:5)	50	30	2,5	66,4	X_1-PL + PE
3	The same	50	30	1,4	29,6	X_2-PL + PE
		125	65	—	96	

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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, $[\alpha]_D^{20}$ +85.0° (c 1.33; chloroform) M^+ 460; (II) – $C_{24}H_{34}O_6$, mp 96-98°C, $[\alpha]_D^{20}$ +38.2° (c 1.1; chloroform), M^+ 418; (III) – $C_{24}H_{32}O_6$, mp 225-226°C, $[\alpha]_D^{20}$ −7.5° (c 1.0; chloroform), M^+ 416; and (IV) – $C_{24}H_{30}O_4$, mp 154-156°C, $[\alpha]_D^{20}$ +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, J = 2 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 F. samarcandica. The second dehydration product (VIII) was identified by its IR and NMR spectra as feropolidin (IV). When (IV) was oxidized, a ketone $C_{24}H_{28}O_4$ 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, J_1 = 10, J_2 = 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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