

New ethers of chrysophanol and frangula-emodin have been obtained: the dipropyl ether of chrysophanol (1,8-di-propoxy-3-methylantraquinone),  $C_{21}H_{22}O_4$ , mp 106° C, yield 87.1%; the diisobutyl ether of chrysophanol (1,8-di-isobutoxy-3-methylantraquinone),  $C_{23}H_{26}O_4$ , mp 126° C, yield 89.3%; the tripropyl ether of frangula-emodin (1,6,8-tripropoxy-3-methylantraquinone),  $C_{24}H_{28}O_5$ , mp 125° C, yield 86.7%; and the triisobutyl ether of frangula-emodin (1,6,8-triisobutoxy-3-methylantraquinone),  $C_{27}H_{34}O_5$ , mp 142° C, yield 85.9%.

The alkylation was carried out with an alkyl iodide in the presence of dry silver oxide, the mixture being boiled for 30 min [3]; the products were purified by chromatography from benzene on magnesium carbonate and by crystallization from petroleum ether (bp 80° C).

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#### THE DYNAMICS OF THE ACCUMULATION OF PSORALEN IN PSORALEA DRUPACEA

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Psoralen has been studied previously and introduced into medical practice [1, 2].

We have investigated the dynamics of the accumulation of psoralen in *P. drupacea* [3] (according to the phases of development) collected in the territory of the Chimkent Oblast in 1966 (table).

Date of collection of the seeds	Phenophase of <i>P. drupacea</i>	Height of the plant, cm	Content of psoralen in absolutely dry plant, %				
			roots	stem	leaves	seeds	
						ripe	unripe
13. III	Before the beginning of the vegetation of the epigeal part	—	0.52	—	—	—	—
28. III	Early period of vegetation of the epigeal part	2-3	0.48	—	—	—	—
26. IV	Bud formation	20-25	0.46	0.13	—	—	—
28. V	Flowering	75-80	0.44	0.22	trace	—	—
13. VI	Beginning of fruit-bearing and flowering	80-100	0.39	0.11	0.06	—	0.63*
13. VII	Abundant fruit-bearing and end of flowering	80-100	0.32	0.10	trace	1.1*	—
20. VIII	End of fruit-bearing, flowering of second-order branches	80-100	0.38	0.10	"	1.0*	—
IX	End of vegetation of the epigeal part	80-100	0.57	0.10	"	—	0.70**
16. XI	" " "	—	0.57	—	—	—	—

\*Seeds of first-order branches; \*\*of second-order branches.

According to our observations, the beginning of the vegetation of the plant is at the end of March, flowering in the first days of May, continuing into July, and the seeds are ripe 30-40 days from the moment of flowering. The formation of second-order branches was found in the second half of August; flowering and fruit-bearing on these branches continued until the first autumn frosts.

The psoralen was extracted from the *P. drupacea* with 40% aqueous acetone with the subsequent removal of the organic component by evaporation. The precipitate that deposited was separated off and technical psoralen was ex-

tracted from it with benzene. The mother liquors, containing a small amount of psoralen, were extracted with chloroform. The concentrated extract was passed through activated alumina (Brockmann activity II-III) and the psoralen was eluted with benzene. The content of psoralen in the technical product was determined by the polarographic method [4].

It can be seen from the table that the most desirable raw material for the industrial production of psoralen is formed by the roots and seeds. However, the seeds are preferable since they contain a larger amount of psoralen and, in addition, the natural thickets of the plants are preserved. The best period for collecting the seeds is from the second half of July to the end of August.

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#### A STUDY OF THE ANTHOCYANINS OF THE COTTON PLANT

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We have extracted flowers of cotton plants of variety 315-F (*Gossypium hirsutum*) with methanol in 1% hydrochloric acid. The anthocyanins were precipitated from the extract with ether; they were freed from contaminating flavonols, catechins, and waxes by chromatography on a column of cellulose powder. As eluant we used system 1:1-butanol-acetic acid-water (4:1:5).

On paper chromatography in system 2 [water-acetic acid-concentrated hydrochloric acid (82:15:3)], two anthocyaninins were detected with  $R_f$  0.25 (I) and 0.36 (II). The anthocyanins were separated by chromatography on a column of cellulose powder with the same solvent (II). The clearly separated zones were cut out and eluted with methanol containing 0.01% of hydrochloric acid. After recrystallization from ethanol 2 N with respect to hydrochloric acid, anthocyanin (I) was isolated with mp 215-217° C (decomp) and composition  $C_{24}H_{21}O_{11}Cl \cdot 2H_2O$ . The paper chromatography of anthocyanin (I) in the presence of chrysanthemin (from the aster) in system 2 showed that they were identical.

The hydrolysis of the anthocyanin with 2 N hydrochloric acid led to the decomposition of the substance into the aglycone and glucose. The glucose was identified by paper chromatography in two systems: ethyl acetate-pyridine-water (2:1:2) and 1-butanol-acetic acid-water (4:1:5). The position of the OH group in the anthocyanin was shown by its absorption spectra. The UV spectrum of the glycoside had its maximum absorption at 525 m $\mu$  or, in the presence of aluminum chloride, at 568 m $\mu$  [1, 2]. The anthocyanidin cyanidin was identified by comparing it with the cyanidin obtained from red rose petals (on chromatograms) and by absorption spectra (maxima at 535 m $\mu$ ).

When the anthocyanidin was heated in 15% barium hydroxide for 30 min at 100° C, phloroglucinol and protocatechuic acid were formed, these being identified by paper chromatography in various systems in the presence of authentic samples of phloroglucinol and protocatechuic acid.

The results obtained show that the anthocyanin (I) from the cotton plant is chrysanthemin (cyanidin 3- $\beta$ -glucoside).

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