

It has been found that the relative amounts of free gossypol contained in the products of the extraction of defatted high-gossypol cottonseed flour by chloroform, diethyl ether, and acetone falls with an increase in the polarity of the solvents. It has been shown that, in addition to gossypol, gossypurpurin is extracted. Its highest amount (4.82%) was found in an acetone extract, and its lowest amount (2.68%) in an ethereal extract.

In the separation of cottonseed flour by the hydrocyclone method [1], two fractions are obtained: a gossypol-free fraction which can be used to isolate protein or for direct employment in the food industry, and a gossypol-rich fraction. The latter is a source for the isolation of gossypol and pigments related to it.

We have studied the gossypol-rich fraction with the aim of the maximum extraction of the gossypol from it by various solvents, as which we used chloroform, diethyl ether, and acetone.

Depending on the extractants, products were obtained which differed in color and melting points. Chloroform solutions were colored bright red and on evaporation gave brown-bordeaux crystals with mp 177°C (product I). Ethereal extracts had a red color and the crystals obtained from them were yellowish-brown, mp 147°C (product II). The first portion of an acetone extract was also colored red, and the subsequent portions were yellow. The crystals isolated from them had a greenish-yellow color with mp 145°C (product III).

All three products gave a positive qualitative reaction for gossypol with concentrated sulfuric acid (red coloration), and their R_f values when they were chromatographed on Silufol thin-layer chromatographic plates coincided with that of gossypol. Like gossypol, they did not dissolve in petroleum ether but were readily soluble in acetone, diethyl ether, ethanol, methanol, benzene, and chloroform. The red color of solutions of the products isolated in benzene, chloroform, and diethyl ether were stable for a long time; in more polar solvents such as acetone, ethanol, and methanol, the red color lasted for only a few minutes, changing to yellow.

A comparative study of the UV spectra of pure gossypol and the products isolated from the defatted gossypol-rich fraction showed that in the ultraviolet region the spectra of their chloroform solutions were similar and had characteristic absorption maxima at 236, 288, and 366 nm. In the visible region of the spectrum, a chloroform solution of pure gossypol contained no absorption bands, while in the spectra of products (I), (II), and (III) slight absorption was observed at 535 and 570 nm. This absorption is specific for a gossypol-like pigment - gossypurpurin - which consists of dark purple crystals with mp 200-204°C [2, 3]. Its presence was shown both by the red color of the solutions of the products isolated and by its instability in polar solvents. The similarity of (I), (II), and (III) to gossypol was due to the considerable amount of gossypol in it, and the differences due to the gossypurpurin impurity. The amounts of gossypurpurin in the products obtained were determined from the UV spectra of their water-saturated chloroform solutions in the interval of 450-650 nm. Calculation was made from the values of the optical density D at 565 nm [4]. The spectra of (I-III), which are shown in Fig. 1, are characterized by the presence of two distinct absorption bands at 535 and 570 nm.

The total yields and pigment compositions of the products extracted from 25 g of the defatted gossypol-rich fraction of cottonseed flour by the solvents used are given below:

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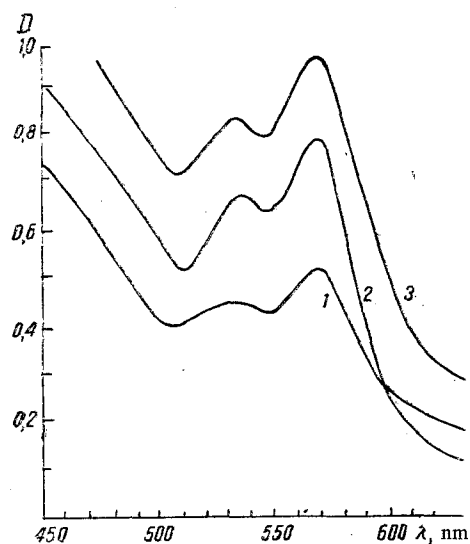


Fig. 1. Spectra of chloroform solutions of products obtained on extraction: 1) with diethyl ether (0.0371 g); 2) with chloroform (0.0393 g); 3) with acetone (0.0490 g).

Product	Yield of product, g	Free gossypol		Gossypurpurin	
		%	g	%	g
I	0.5930	74.30	0.4405	3.95	0.0224
II	0.6534	69.35	0.4531	2.68	0.0175
III	0.8480	52.32	0.4436	4.82	0.0409

With a rise in the polarity of the solvent, the yield of products rose and, correspondingly, the relative amount of free gossypol in them fell while its absolute amount was almost constant in all three products.

The largest amount of gossypurpurin (4.82%) was found in the product extracted with acetone, and the smallest amount (2.68%) in the product (II) from the ethereal extract. This agrees with literature information on the better solubility of gossypurpurin in acetone than in diethyl ether and chloroform [3].

EXPERIMENTAL

UV spectra were taken on a Hitachi spectrophotometer – in chloroform in the case of gossypol and in water-saturated chloroform in the case of gossypurpurin.

The gossypol-rich fraction was isolated by fractionating cottonseed flour with the aid of a liquid cyclone. The kernels were obtained from cotton seeds stored in the Tashkent Oils and Fats Combine.

The amount of free gossypol was determined by the p-anisidine method [5]. Pure gossypol was obtained from the technical product by repeated recrystallization from a mixture of chloroform and hexane.

Products (I), (II), and (III) were isolated by the repeated steeping with the appropriate solvent at room temperature of 25 g of the defatted hexane fraction of cottonseed flour containing 3.6% of free gossypol. The extracts collected were evaporated in a rotary evaporator at 35–50°C and the products were crystallized by the addition of hexane to the residue in the flask. TLC was performed on Silufol in the petroleum ether–formic acid (7:3:1)* solvent system. The chromatograms were made visible with a 1% ethanolic solution of phloroglucinol in 2 N HCl [6].

*As in Russian original – Publisher.

To determine the amounts of gossypurpurin in (I), (II), and (III), we used a method described for cotton seed kernels [4]. The amount of gossypurpurin was calculated as a percentage of the weight of the sample taken, which did not exceed 30-40 mg of substance.

SUMMARY

It has been established that on the extraction of the defatted gossypol-rich fraction of cottonseed flour by chloroform, diethyl ether and acetone, with a rise in the polarity of the solvent the total yield of products rises and, correspondingly, the relative amount of free gossypol in them falls.

It has been shown that, in addition to gossypol, gossypurpurin is extracted, its amount depending on the nature of the solvent used. The highest proportion of gossypurpurin (4.82%) was detected in acetone extract and the lowest (2.68%) in an ethereal extract.

LITERATURE CITED

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