CHANGES IN LIPIDS AND PIGEMENTS OF COTTON SEEDS DURING THEIR PROCESSING

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The lipid and pigment compositions of crude and refined bleached cottonseed oil have been studied and the influence of the technological treatment on the composition and structure of the components is discussed. It has been found that the color and the difficult refinability of the crude oil are due partially to the presence in it of stable radical dications of gossypol photoinduced in the presence of O_2.

At the present time, an intensive search is being carried on for methods of increasing the efficiency of the processing of cotton seeds from modern selection varieties. The oil obtained in such seeds has inferior technological properties [1] and, in particular, it is more difficult to refine. Some user and chemical indices of industrial samples of cottonseed oil are known [2], but a detailed analysis of the composition of the crude oil has not been made and it has not been determined which components are responsible for the change in its technological properties.

The existing technology of the processing of cotton seeds provides for the two-stage extraction of the oil first by prepressing and then by extraction with hydrocarbon solvents. The mixture of prepressed and extraction oil (crude oil) is purified by alkali refining followed by treatment with bleaching clays.

This paper gives the results of an investigation of the compositions of prepressing, extraction, crude, and refined bleached cottonseed oils. The characteristics of the samples are given in Table 1. The total fatty acid compositions of the samples were practically identical; they included (% GLC): 0.5 of the 14:0 acid; 20.3 of the 16:0; 0.9 of the 16:1; traces of the 17:0; 1.6 of the 18:0; 18.0 of the 18:1; and 58.7 of the 18:2 acid (crude oil). As was to be expected [3], the extraction oil was darker in color but its total gossypol content was lower than that of the prepressed oils. The level of free fatty acids (FFAs) in the unrefined samples was high and did not depend greatly on the method of extracting the oil. The bulk of the tocopherols remained in the oil after refining and only a small amount of them was entrained in the residue (soapstock).

To determine their acid and pigment compositions, the oils were separated by column chromatography (CC) and by thin-layer chromatography (TLC). In view of the irreversible sorption of part of the gossypol pigments on silica gel, the separation of the neutral lipids

TABLE 1. Characteristics of the Samples of Cottonseed Oil

Index	Prepressed	Extraction	Crude	Refined
Color in a 13.5 cm layer, red units*	Not considered			10,5
Color in a 1 cm layer, red units	61,5	Not considered	64,0	2,9
Acid No., mg KOH	3,9	4,5	4,3	0,4
Content, %, of:				
free gossypol	0,23	0,06	0,14	—
total gossypol	0,70	0,12	0,38	—
tocopherol, mg-%	83,3	86,6	85,0	74,0

*Red units at 35 yellow units.

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TABLE 2. Yields of the Fractions of Unrefined Oil from Polyamide

Fraction	Eluent	Yield, % of weight of the oil sample		
		prepressed	extraction	crude
I	Hexane-ether (1:1)	93,1	95,3	94,8
II	Ether	3 0	2,3	2,2
III	Acetone	2.6	0,8	1,4
IV	Methanol	1,3	1.6	1,6

TABLE 3. Compositions of the Neutral Lipids of the Crude and Refined Cottonseed Oils

Class	Amount, % of weight of the neutral lipids of the oil	
	crude	refined
Hydrocarbons (paraffins, aromatics)	3,20	0,04
Fatty acid esters	—	0,02
Triacylglycerols	88,10	93,50
Tocopherols	0,08	0,07
Epoxyacyldiacyglycerols	0,50	1,30
Oxoacyldiacylglycerols	0,30	0,20
Free fatty acids	1,40	0,05
Fatty alcohols	0,10	Trace
Diacylglycerols	1 90	1,80
Hydroxyacyldiacylglycerols	1,60	0,60
Triterpenols	0,07	0,04
4-Monomethyl sterols	0,06	0,04
Sterols	1 30	1,20
Dihydroxyacyldiacylglycerols	0,50	0,60
Monoacylglycerols	0,80	0,30
Chlorophylls	0,06	—
Glycolipids	0,03	0,24
Gossypol pigments.	—	

TABLE 4. Composition of the Lipids of Cottonseed Husks

Class	Amount, % of weight of extract	Class	Amount, % of weight of extract
Polyamide		Epoxyacylglycerols	3,1
Phenolic pigments	6,1	Free fatty acids	19,5
Silica gel		Fatty alcohols	5,3
Paraffins	5,1	Mono- and polyhydroxyacyldiglycerols, Phytosterols, Diacylglycerols	10,6
Aromatic hydrocarbons	0,8	Monoacylglycerols, Unidentified	3,6
Phytosterol esters	2,3	Brown unidentified compounds	16,7
Wax esters	1,8		
Triacylglycerols	25,1		

of the unrefined samples from the polar lipids and gossypol pigments was performed on polyamide. Four fractions were obtained, the yields of which are given in Table 2. The compositions of the fractions were confirmed by TLC in the systems used for the separation of the neutral substances (system 1), the glyco- and phospholipids (system 2), and the gossypol pigments. The systems proposed for the separation of gossypol pigments in [4] were tested, and the best results were obtained in system 3.

According to the results of TLC, fraction I consisted of neutral lipids and the other, brown-colored fractions of neutral lipids and glycolipids (II), of glycolipids (III), and of phospholipids in admixture with pigments (IV).

The acetone eluate was enriched with the darkest-colored forms of the pigments.

In the prepressing oil, six dark brown spots were revealed with R_f 0.98, 0.92, 0.63, 0.47, 0.44, and 0.41; and in the extraction oil another not less than nine bright yellow spots (R_f 0.38-0.1), presumably of flavonoid nature.

The detection in cottonseed oils of quercetin and its derivatives has been reported [5]. In system 3, authentic quercetin revealed a yellow spot with R_f 0.37, and native gossypol one with R_f 0.64. Not one of the pigments of the samples gave the coloration characteristic for native gossypol with the well-known reagents ($SbCl_3$, H_2SO_4, phloroglucinol) [3, 6]. The pigments of fraction (IV) migrated as one band.

The subsequent analyses were performed with the crude and the refined oils.

Neutral Lipids (NLs). The combined fractions I and II of the crude oil and the refined sample were chromatographed by CC on silica gel. The yield of the NLs of the crude oil from the silica gel amounted to 99.95% and those of the refined oil to 99.76%. Homogeneous classes were obtained when the eluates were rechromatographed by TLC in systems 4-6.

The compositions of the NLs of the samples are given in Table 3.

From the high amounts of lipophilic substances and nonpolar acylglycerols and the low level of triacylglycerols (TAGs), the neutral lipids of the crude oil approximated to the lipids of unripe cotton seeds [7]. It must be mentioned that the samples of oil were taken during the processing of freshly gathered seeds that had not undergone post-harvest ripening. Furthermore, the crude oil contained an appreciable amount of the products of the autooxidation of the TAGs.

The lipid components with free hydroxy groups possessed pronounced emulsifying properties. The high amount of such lipids in the crude oil is apparently one of the reasons for its poor refinability.

The aromatic hydrocarbons among the paraffins were identified from the results of UV and mass spectroscopy (see the experimental section). In an investigation of the reason for the high amount and complexity of the composition of this class in the crude oil, we investigated the composition of the extraction gasoline and of the gasoline extract of cottonseed husks.

The UV spectrum of a dilute solution of the gasoline in pentane had λ_{max} 227 nm. When a batch of type A gasoline (bp 70-90°C) was fractionated at 70-90°C, a nonvolatile residue (yield 0.7%) was obtained in which (by TLC in systems 6 and 8) several components were detected, including hydrocarbons. When the residue was separated by CC on silica gel, about 70% (on the weight of the residue) of hydrocarbons with TLC, GLC, and UV- and mass-spectroscopic characteristics close to those of the crude oil were obtained. Thus, the gasoline contained aromatic and paraffinic hydrocarbons which passed into the crude oil on the extraction of the material.

The set of lipids of cottonseed husks extracted by cold petroleum ether is known [8]. We used as the extractant hot redistilled type A gasoline and obtained 1.6 times more extractive substances of more complex composition. A composition of the husk extracts similar to that of the crude oil was established by chromatography (Table 4).

It was found that hot gasoline extracted more carbohydrates and waxy and pigmentary substances from the husks. Thus, the husks of cotton seeds are also a source of the lipophilic compounds and the pigments passing into the crude oil.

On comparing the NLs of the crude and refined oils (see Table 3), we see that refining and the subsequent operations of washing, drying, and bleaching the oil did not lower the amounts of the products of hydrolysis and oxidation of the TAGs (apart from the FFAs). Furthermore, in the refined oil the level of epoxides had risen more than 2.5-fold (as compared with the crude oil).

Attention is attracted by the appearance in the refined oil of fatty acid esters with lower alcohols. In their behavior on TLC and GLC they corresponded to methyl or ethyl esters. The alcohol moiety was not investigated.

The acyl-containing lipids were hydrolyzed with alkali in order to study their fatty-acid compositions, the unsubstituted and oxidized fatty acids being analyzed separately. GLC and the mass spectrometry of the trimethylsilyl (TMS) derivatives at the hydroxy groups were used for analysis. The results of the analysis of the unsubstituted acids are given in Table 5.

In the refined oil, the FFAs, oxidized forms of TAGs, and diacylglycerols were more, while the TAGs, the monoacylglycerols, and the glycolipids were less unsaturated than the

TABLE 5. Composition of the Unsubstituted Fatty Acids of the Crude and Refined Oils

Class of lipids	Acid (GLC, % of weight of the acids)*						
	x	14:0	16:0	16:1	18:0	18:1	18:2
Crude oil							
Triacylglycerols	Tr.	Tr.	16,5	0,9	2,0	18.5	61,1
Epoxyacylglycerols	—	1,1	26,4	Tr.	3.7	17.3	51,5
Oxoacylglycerols	—	0,6	26,8	Tr.	5,3	27.1	40,2
Free fatty acids	—	0,4	26,7	1.7	3,2	39.7	28.3
Hydroxyacylglycerols	—	0,3	18,5	1,3	1,4	36,9	41,6
Diacylglycerols	—	0,8	25,2	1,4	3,9	20,2	48,5
Dihydroxyacylglycerols	—	0.4	22,2	1,1	1,7	28,1	46,5
Monoacylglycerols	1,3	0,5	22,0	1,0	2,3	32,1	40,8
Glycolipids							
Refined oil							
Fatty acid esters	11,6	Tr.	11,1	Tr.	3,1	55,1	19,1
Triacylglycerols	—	0,2	22.3	1,2	0,6	16,9	58,7
Epoxyacylglycerols	—	—	23,3	Tr.	0,5	17,4	58,8
Oxoacylglycerols	2.8	0,5	21,4	Tr.	0,7	17.2	57,4
Free fatty acids	—	—	13,5	0.9	0,5	33,4	51,7
Hydroxyacyllglycerols	—	Tr.	26,3	Tr.	0,5	22,8	55,4
Diacylglycerols	—	1,0	28.1	Tr.	3,3	22,6	43,0
Dihydroxyacylglycerols	—	1,3	48,0	Tr.	5,8	27,4	15,7
Monoacylglycerols							
Glycolipids							

*In all the classes of lipids of the crude oil and in the PAGs and FFAs of the refined oil there were trace amounts of the 17:0 acid, and the 18:3 acid was present in the glycolipids (1.8% in the refined oil and trace amounts in the crude oil).

TABLE 6. Compositions of the Acylglycerols of the Crude and the Refined Cottonseed Oils

Index	Crude oil	Refined oil	Index	Crude oil	Refined oil
2-Monoacylglycerols:			Species composition:		
16:0	3 7	1,6	POP**	1.2	2.0
16:1	0.6	0,3	PLP	5,2	8,5
18:0	0,7	—	POO	1,7	1.8
18:1	17,8	18,0	POL	4.8	5,7
18:2	77,2	80,1	PLO	7,4	7,5
Type composition:			PLL	21,0	25,6
SSS	0.3	0,2	OOL	3,4	1,3
SSU, USS	1.8	0,8	OLO	2,6	1,7
SUS	7.8	12.2	SLL	2,0	2,0
SUU,UUS	39,1	44,9	LOL	4,8	4,5
USU	2,2	0,7	OLL	14.8	11,6
UUU	48,8	41.2	LLL	20,9	19.5

*S, sum of the saturated 16:0 and 18:0 acids; U, sum of the unsaturated 16:1, 18:1, and 18:2 acids.
**P, 16:0 + 18.0; O, 18:1 + 16:1; L, 18:2.

analogous classes of the crude oil. Furthermore, in the refined sample the compositions of the FFAs and the TAGs were close, which was not characteristic for the crude oil. It follows from this that the FFAs may be liberated in the hydrolysis of the PAGs during the technological processing of the crude oil.

The oxidized fatty acids of the samples under discussion consisted of complex mixtures of isomers of natural and secondary origin.

Of the epoxy acids in the crude oil the cis-12,13-epoxy-9-18:1, the cis-9:10-epoxy-12-18:1, and the cis-9,10-epoxy-18:0 acids, which are known for ripe cotton seeds, were identified [9], while in the refined oil the isomeric trans-epoxides were also detected (IRS, 890 cm^{-1}).

No natural oxo acids were detected in the cotton seeds. In two samples of oil, according to UV (λ_{max}^{hexane} 228, 270 nm) and mass spectrometry, there were the oxo-18:0 (M^+ 312), oxo-18:1 (M^+ 310), and oxo-18:2 (M^+ 308) acids with the most probable position of the keto group in the 18:0 chain at C-9 (m/z 185, 200, 168, 170) and in the 18:1 and 18:2 chains at C-9 and C-13 (m/z 239, 254, 222, 151, 237).

In the mixtures of hydroxy acids of the two samples, the natural monohydroxy-17:1, -18:0, -18:1, and -18:2 acids were detected [10]. In addition, medium-strong peaks of ions with m/z 241 and 285 in the mass spectrum of the TMS derivatives suggested the presence of allyl isomers of hydroxyoleic acids, the 8-hydroxy-9-18:1 and 11-hydroxy-9-18:1 acids, which have been found previously in the products of the autooxidation of the 18:1 methyl ester [11].

The dihydroxy acids in cottonseed oil, just like the oxo derivatives, are secondary products. The main components of this mixture were the dihydroxy-18:0 and dihydroxy-18:1 acids in which the two hydroxy groups are located mainly in vicinal positions at C-9 and C-10 (the dihydroxy-18:0 and -18:1 acids) and at C-12 and C-13 (the dihydroxy-18:1 acid). It is clear from a comparison of structures that the dihydroxy acids are the products of the oxidative decomposition of epoxy acids.

As mentioned above, in the process of isolating and purifying the oil, part of the unsaturated TAGs are oxidized and hydrolyzed. In order to determine what forms of acylglycerols undergo transformation, we performed the lipolysis of the TAGs of the two samples and from its results were determined the structure and set of species. It was found that the crude and refined oils each consisted of 33 species.

Table 6 gives the fatty acid compositions of the 2-monoacyl-sn-glycerols isolated after lipolysis, the position-type composition, and the main species of the TAGs. Alkali refining and bleaching lead to a loss of the most unsaturated species OLO, OOL, OLL, and LLL. At the same time, the changes in the fatty acid composition of the 2-monoacylglycerols were very slight, which shows the greater hydrolyzability of the acyl radicals in the extreme positions of the TAGs. Since it is known that oxidized acyl radicals are more readily hydrolyzed by alkali than unoxidized ones [12], it is easy to understand that the unsaturated TAGs are oxidized first, and are then hydrolyzed, the rate of oxidation also determining the rate of hydrolytic breakdown.

Gossypol Pigments and Polar Lipids. Preliminary results on the pigment compositions of the oils were obtained by a chemical method. It was found that in the prepressing oil, the extraction oil, and the crude oils the total amounts of gossypol were, respectively, 0.7, 0.12, and 0.39%, and the amounts of free gossypol 0.23, 0.06, and 0.14% (on the weights of the oils). The presence of free gossypol in the crude and prepressed oils was also confirmed by their characteristic UV spectra ($\lambda_{max}^{CHCl_3}$ 274, 285, 376 nm).

Separation on polyamide enabled the gossypol pigments to be concentrated into the two fractions containing the glycolipids (fraction III) and the phospholipids (fraction IV).

The sets of polar lipids of fractions III and IV were the usual ones for the seeds of higher plants, including the cotton plant [13]. Of them were identified (by TLC in system 2): mono- and digalactosylglycerols (MGDGs, R_f 0.78; DGDGs, R_f 0.58), steryl glycosides (SGs, R_f 0.67), and their esters (ESGs, R_f 0.86), phosphatidylcholines (R_f 0.44) and their lyso analogs (R_f 0.14), phosphatidylethanolamines (R_f 0.6) and their N-acyl derivatives (R_f 0.8), phosphatidylinositols (R_f 0.28), and phosphatidic acids (R_f 0.11). The spots of the lipids were revealed with specific reagents against a background of a diffuse brown band of the gossypol pigments.

In system 3, the pigments of these fractions were separated into the same components as were present in the prepressing and extraction oils, the spot of native gossypol (R_f 0.64) being masked by the dark brown spot of a derivative of it.

The coloration and complexity of the composition of the gossypol and flavonoid substances of the fractions are undoubtedly explained by the circumstance that in crude oil the pigments were present as a complex of oxidized forms.

An attempt to separate the gossypol pigments from the polar lipids by their extraction as phenolic compounds with 2% $NaHCO_3$ [14] proved to be unsuccessful. The compositions of the lipid-pigment complex isolated from the organic and aqueous phases differed little from one another.

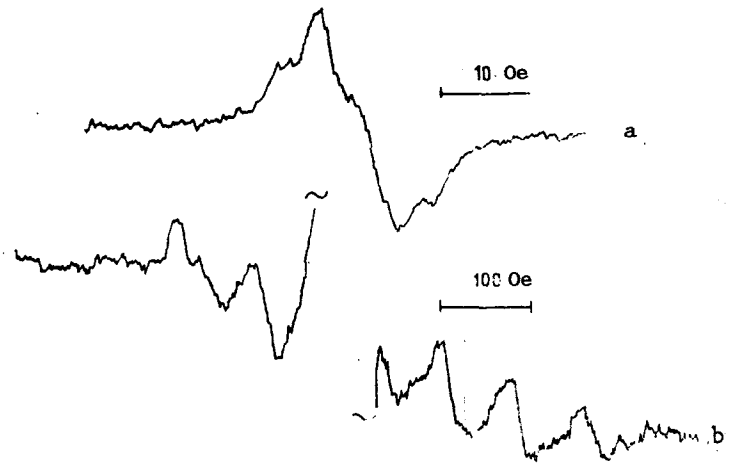

Fig. 1. ESR spectra: a) crude cottonseed oil; b) fraction III.

No satisfactory results were obtained either when fraction III was chromatographed in order to separate the main gossypol pigments (R_f 0.98, 0.92, and 0.59) from the MGDGs, the ESGs, and the SGs. The glycolipids and pigments were not separated in systems 2 and 3.

The UV spectra of the isolated glycolipid-pigment fractions were uninformative because of the absence of sharp absorption bands of the binaphthyl series and of the aldehydonaphthyl group.

Having investigated in parallel the properties of the native gossypol, we established that gossypol, when dissolved in the TAGs in the presence of atmospheric O_2 (particularly at the boundary of separation of the TAG–air phases), readily forms a complex with O_2 under the action of brief illumination. There is then a one-electron oxidation of the gossypol with the formation first of radical monocations (G^+) and then of radical dications (G^{2+}) [15]. More prolonged illumination of the TAG–gossypol system is accompanied by its darkening.

The results presented above permitted the assumption that among the gossypol and flavonoid pigments of the crude oils it is possible to find the products of their photochemical reaction that have taken place in the individual stages of the technological processing of the cotton seeds. In actual fact, in the high-resolution ESR spectrum of the crude oil and of the extract of cottonseed husks a weak stable signal of the radical ions of pigments were observed (Fig. 1a). The spectrum of fractions (III) and (IV) contained a stronger signal of the radical ions of gossypol pigments with the presence (in the case of fraction III) of an additional signal from the cation of bivalent manganese (Fig. 1b). When the samples under discussion were illuminated with light, the intensity of the isolated signal increased, which is characteristic for the signal of the radical dications of gossypol, G^{2+} [15].

The stability of the radical ions is due not only to the chemical structure of the compounds forming them, but also to the properties of the medium in which they are present [16]. In pure TAGs, the radical dications of gossypol appear on brief illumination of the system and disappear after its cessation. In the crude oil, where the presence of the radical ions was recorded without preliminary illumination, one must assume the existence of a number of factors favoring the stabilization of these forms. Such factors may include lipid components capable of forming aggregates with G^{2+}, such as fatty acids and their hydroperoxides, certain glycolipids [17], and phospholipids, and also the presence in the crude oil of traces of moisture and metals and the action of high temperatures upon it.

Thus, the contact of the crude oil in individual technological stages with atmospheric O_2 and light is accompanied by the accumulation of oxidized forms of the pigments, including stable radical dications of gossypol and, possibly, radical ions of the flavonoids. The photochemical reactions of the gossypol pigments may apparently also take place in comminuted cotton seeds during their hot moist treatment preceding the extraction of the oil.

The radical cations of gossypol, G^{2+}, like those of other organic compounds [16], are more highly colored than gossypol and have a reactivity different from that of neutral gossypol, which can explain the difficulty of eliminating them from the crude oil by alkali refining.

EXPERIMENTAL

ESR spectra were recorded as in [15]. The conditions for the recording of the UV, IR, and mass spectra for GLC analysis, and for performing CC on polyamide have been described in [13]; those for CC on silica gel and the identification of the lipid classes in [7]; and those for the analysis of the oxidized forms of the lipid in [10]. For TLC we used Silufol (Czechoslovakia) and silica gel L, 5/40 (Chemapol) with 6.5% of $CaSO_4$ and the following solvent systems: 1) heptane–methyl ethyl ketone–acetic acid (43:7:0.1); 2) chloroform–methanol–25% NH_4OH (65:25:4); 3) benzene–methanol (20:5); 4) hexane–diethyl ether (95:5); 5) (7:10); and 6) (10:7); 7) hexane–diethyl ether–acetic acid (7:3:0.1); 8) hexane–benzene (2:1); and 9) dichloroethane.

The samples of oil and husks for analysis were taken from the production line during the preparation of high-quality cotton seeds, and the extraction gasoline was factory material.

A sample of quercetin was kindly provided by workers of the coumarin and flavonoid laboratory of the Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR.

Hydrocarbons. R_f 0.95, 0.90 (system 8); on treatment with 50% H_2SO_4 and brief heating, the color of the spots was greyish. On GLC chromatograms, 14 peaks were obtained, the C_{sp} values of which differed from those of paraffins. The quantitative evaluation of the chromatograms was difficult because of the absence of a stable zero line during the analysis of this mixture. IR spectrum, ν_{max}^{film}, cm^{-1} 2980, 2870, 1470, 1380, 1310, 980, 730. UVS, $\lambda_{max}^{pentane}$, nm: 227.5. Mass spectrum, m/z: 358, 330, 306, 304, 302, 300, 266, 264, 262, 260, 252, 250, 248, 236, 222, 119 (di- and trisubstituted aryls), 105 (disubstituted aryls), and 91 (monosubstituted aryls) [18].

Cotton Husks. The husks freed from weeds and kernel residues (100 g) were ground in a hammer mill and were extracted three times with boiling type A gasoline (1 liter each time). Yield 0.94%. The concentrated extract was separated by CC on polyamide, giving 93.9% of lipids (with chloroform as eluent) and 6.1% of a dark brown residue (with ethanol as the eluent) which was not investigated. The lipids were separated by CC on silica gel.

The triterphenols (R_f 0.40), 4-monomethylsterols (R_f 0.36), and sterols (R_f 0.32, system 7) appeared when TLC chromatograms were sprayed with 50% H_2SO_4 followed by heating, in the form of orange, pink, and red spots, respectively. Mass spectrum (70-80°C, 50 eV, 0.5 mA), m/z: 426, 414, 412, 400 [19].

Tocopherols. Their amount was determined by a standard method [20]; on TLC in system 9, α-, γ-, and δ-tocopherols (R_f 0.85, 0.74, and 0.60, respectively) were detected [21].

CONCLUSIONS

1. The amounts and sets of lipophilic components of crude cottonseed oil, including brown pigments, depend on the degree of ripeness of the seed, the proportion of husk in the raw material processes, and the degree of purity of the extractant.

2. In the purification of the crude oil, part of the tetra-, penta-, and hexaenic species of triacylglycerols are lost as the result, first, of the oxidation of the unsaturated acyls of the extreme positions to epoxy, oxo, hydroxy, and dihydroxy derivatives, and then because of their easier hydrolyzability.

3. The presence in crude cottonseed oil of incomplete acyl glycerols, hydroxylipids, and oxidized forms of gossypol pigments, including stable radical dications of gossypol, impairs its technological properties.

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CRYSTAL AND MOLECULAR STRUCTURES OF THE SESQUITERPENE LACTONE PYRETHROIDININ

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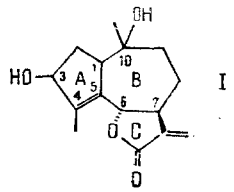
The crystal structure of the sesquiterpene lactone pyrethroidinin, in the independent part of the elementary cell of which there are two molecules, has been determined by x-ray structural analysis. A stereochemical analysis is given of the results, and the structure 3α,10α-dihydroxy-1α,6β,7α(H)-guaia-4(5),11(13)-dien-6,12-olide is proposed for pyrethroidinin.

The sesquiterpene lactone pyrethroidinin $C_{15}H_{20}O_4$ (I), isolated from Pyrethrum pyrethroides was subjected to a preliminary study by spectral methods and for it was proposed a guaianolide structure with the translinkage of rings B/C [1]:



I

In order to ascertain the other stereochemical aspects of the structure of pyrethroidin – the configuration of the three asymmetric centers C1, C3, and C10, and the conformations of the rings – we have performed an x-ray structural investigation.

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