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TRIACYLGLYCEROLS OF OITICICA OIL

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UDC 665.35:547.426.21/.23.001.5

The composition of the triacylglycerols (TAGs) of oiticica oil has been studied by enzymatic hydrolysis with pancreatic lipase. It has been established that the majority of TAGs of the 96 types present have a mixed character. The four main types make up 60% of the total TAGs and the remainder consist of minor components. A high content of TAGs with octadeca-9,11,13-trienoic acids (including licanic) in the extreme positions has been detected.

A source of oiticica oil is formed by the seeds of the tree *Licania rigida* (family Rosaceae) growing in Brazil, Mexico, and Central America [1]. The oil belongs to the group of tung-like drying oils [2, 3]. Because of its high film-forming capacity, this oil is widely used for modifying alkyd resins [4].

The physicochemical indices [5] and fatty-acid composition [6] of oiticica oil have been studied. In view of the presence of licanic acid in oiticica oil in an amount of 74-82%, it is considered that it consists mainly of glycerides of licanic acid, which are responsible for its high film-forming properties [3]. In the present work we consider the composition of the triacylglycerols of oiticica oil studied by the method of enzymatic hydrolysis with pancreatic lipase. The results of a determination of the fatty-acid compositions of the initial triacylglycerols (TAGs), of the 2-monoacylglycerol fraction of the oil (MGs), and also of the enrichment and selectivity factors (EF and SF) [7] are given in Table 1.

As can be seen from Table 1, α-eleostearic, β-eleostearic, and licanic acids, which are highly unsaturated, have low values of the selectivity factor and mainly esterify the primary hydroxy groups of the glycerol.

TABLE 1. Fatty-Acid Compositions of the Triacylglycerols and 2-Monoacylglycerols of Oiticica Oil

Acid	Amounts of the acid in the fractions		Enrichment factor	Selectivity factor
	TAGs	MGs		
Palmitic	3,2	4,7	1,47	0,70
Stearic	4,2	3,5	0,83	0,39
Oleic	9,4	18,9	2,01	0,96
Linoleic	3,6	10,6	2,94	1,40
α-Eleostearic	5,3	0,0	0,00	0,00
β-Eleostearic	2,8	0,0	0,00	0,00
Licanic	71,5	62,3	0,87	0,41

*Deceased.

Kalinin Polytechnic Institute. Moscow Branch of the All-Union Scientific-Research Institute of Fats. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 316-319, May-June, 1980. Original article submitted February 1, 1980.

On the basis of the fatty-acid compositions of the TAGs and MGs we have calculated position-species composition (PSC) of the TAGs by Coleman's method as modified by Markman [8] using a M-222 computer with a program drawn up in the algorithmic language "ALGOL-60" [9]. The calculated figures for the PSC of the triacylglycerols of oiticica oil are given below (the following abbreviations for the acids are used: P, palmitic; S, stearic; O, oleic; L, linoleic; α-El, α-eleostearic; β-El, β-eleostearic; Lc, licanic):

Tag	Amount	Tag	Amount	Tag	Amount
PPS	0.01	SSαEl	0.03	SOβEl	0.07
PPO	0.01	SSβEl	0.01	SOLc	1.31
PPαEl	0.02	SSLc	0.24	OOO	0.04
PPLc	0.18	OSαEl	0.03	OOαEl	0.14
SPO	0.02	OSβEl	0.01	OOβEl	0.07
SPαEl	0.03	OSLc	0.25	OOLc	1.34
SPβEl	0.02	αElSαEl	0.02	LOLc	0.03
SPLc	0.33	αElSβEl	0.02	αElOαEl	0.12
OPO	0.01	αElSLc	0.42	αElOβEl	0.13
OPαEl	0.03	βElSLc	0.22	αElOLc	2.29
OPβEl	0.02	LcSLc	2.03	βElOβEl	0.03
OPLc	0.33	POP	0.01	βElOLc	1.21
αElPαEl	0.03	POS	0.04	LcOLc	10.95
αElPβEl	0.03	POO	0.04	PLS	0.02
αElPLc	0.57	POαEl	0.07	PLO	0.02
βElPLc	0.30	POβEl	0.04	PLαEl	0.04
LcPLc	2.72	POLc	0.70	PLβEl	0.02
PSαEl	0.01	SOS	0.04	PLLc	0.40
PSLc	0.13	SOO	0.08	SLS	0.02
SSO	0.01	SOαEl	0.14	SLO	0.04
SLαEl	0.08	ElLLc	0.68	SLcLc	4.31
SLβEl	0.04	LcLLc	6.14	OLcO	0.13
SLLc	0.73	PLcP	0.04	OLcαEl	0.46
OLO	0.02	PLcS	0.14	OLcβEl	0.24
OLαEl	0.08	PLcO	0.14	OLcLc	4.41
OLβEl	0.04	PLcαEl	0.24	LLcLc	0.09
OLLc	0.75	PLcβEl	0.13	αElLcαEl	0.39
LLLc	0.02	PLcLc	2.32	αElLcβEl	0.42
αElLαEl	0.07	SLcS	0.13	αElLcLc	7.54
αElLβEl	0.07	SLcO	0.26	βElLcβEl	0.11
αElLLc	1.28	SLcαEl	0.45	βElLcLc	3.98
βElLβEl	0.02	SLcβEl	0.24	LcLcLc	36.08

Thus out of the 196 TAGs theoretically possible (taking position isomerization into account) [10], 96 are actually present in the oil. The majority of the TAGs have a mixed nature (the trilicanate amounts to only 36.08%). The main TAGs — LcOLc, LcLLc, ElLcLc, and LcLcLc — make up more than 60%, and the others form minor components.

Summarizing the information given with respect to the characteristic of saturatedness (S) and unsaturatedness (U) of the fatty acid radicals, we obtain the following type composition of the TAGs of oiticia oil:

S_3	S_2U	SU_2	U_3
0.01	1.48	18.95	79.37

The type composition shows the practically complete absence of trisaturated TAGs and a high content of triunsaturated TAGs.

Taking position isomerism into account, we obtain the following position-type composition of TGs:

SSS	SSU	SUS	SUU	USU	UUU
0.01	1.04	0.44	11.91	7.04	79.37

The position-type composition shows that among the monounsaturated TAGs those with saturated fatty acids in the secondary hydroxy group of the glycerol predominate, while among the diunsaturated TAGs those with unsaturated fatty acids in this position predominate.

On summarizing the TAGs containing conjugated trienoic acids (including licanic) in various positions, we obtain the following pattern of the position specificity of these acids in oiticica oil:

in 1 or 3	in 1,3	in 2,3 or 2,1	in 1,2,3	in 2	total
7.78	29.35	12.89	48.52	0.84	99.38

The facts given show a high content of TAGs with octadeca-9,11,13-trienoic acids (including licanic) in the extreme positions.

A comparison of the structures of the TAGs of oiticica, tung, catalpa [11], and pomegranate [12] oils shows that high content of TAGs with conjugated octadecatrienoic acids in the extreme positions of glycerol is characteristic for oils possessing the highest film-forming capacity.

EXPERIMENTAL

The conditions of determining the fatty-acid composition by the GLC of the fatty acid methyl esters and the glyceride composition by the method of enzymatic hydrolysis have been described previously [13].

Licanic acid was determined by the spectrophotometric method in the form of the 2,4-dinitrophenylhydrazone [14].

The UV spectra of the 2,4-dinitrophenylhydrazone of the fatty acids of oiticica oil in 96% ethanol were recorded on a Specord UV-Vis spectrophotometer with a thickness of the absorbing layer of 1 cm. The amount of licanic acid was calculated from the optical density at 360 nm.

SUMMARY

It has been established that of the 196 TAGs theoretically possible (taking position isomerism into account) only 96 are actually present in oiticica oil. Trisaturated TAGs are practically absent. The majority of TAGs have a mixed nature. A high content of triunsaturated TAGs has been found. Licanic and α- and β-eleostearic acids, which have low selectivity factors (0.41, 0.00, and 0.00) give a high percentage of TAGs containing these acids at the primary hydroxy groups of glycerol and are responsible for the high film-forming properties of oiticica oil.

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LIPID COMPOSITION OF THE SEEDS OF THE COTTON PLANT INFECTED WITH WILT

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UDC 633.511.581.4:632.4:547.915

The qualitative and quantitative set of lipid components of the seeds of healthy cotton plants of the variety Tashkent-1 and plants infected with verticillium wilt have been studied. It has been established that the compositions of the lipids of the two samples differ considerably. The greatest differences are observed in the amounts of total lipids, gossypol, and low-molecular-weight volatile acids.

On prolonged permanent cultivation, the resistance of various varieties of the cotton plant to attack by the pathogenic fungus *Verticillium dahliae* Kleb. falls and the degree of injury and of the harmfulness of the disease increase [1]. The susceptibility of the plant to the disease leads not only to a reduction in yield and a deterioration of the quality of the fiber but also to a decrease in the germinating capacity and energy of growth of the seeds [2]. Although the opinion is generally accepted that the seeds of the cotton plant are the bearers of the infection, the presence of endogenous infection in them in cases of wilt damage is disputed [3]. It has been established that infected seeds of the medium-resistant variety 108-F possess a smaller weight, an undersized nucleus, and a lower oil content [4]. There is no information in the literature on the lipid composition of the seeds of the wilt-infected plant.

In the present communication we give the results of a comparative study of the neutral lipids of the seeds of a healthy cotton plant of the variety Tashkent-1 and of a plant attacked by verticillium wilt. The analysis of the lipid composition was carried out in duplicate with samples of freshly-gathered seeds of the 1977-1978 harvest. The combined lipids of the seeds of the samples mentioned of the 1978 harvest preserved the same features as in the lipids of samples from the preceding year. We studied the lipids of the seeds of the 1978 harvest.

The yields of neutral lipids from the seeds of the healthy cotton plant (sample I) and of the plants suffering with wilt (sample II) amounted to 22.5% and 15.9%, respectively. The total lipids were separated by column chromatography into individual classes of compounds. In the lipids of sample I we found hydrocarbons, triacylglycerols (TAGs), high-molecular-weight fatty alcohols, free fatty acids (FFAs), epoxyacylglycerols (EAGs), hydroxyacylglycerols (HAGs), free sterols, gossypol, and polar lipids. In the lipids of sample II, in addition to the nine classes mentioned, there were also diacylglycerols (DAGs) and monoacylglycerols (MAGs). The assignment of each fraction to a definite class of compounds was carried out on the basis of chromatographic and spectral characteristics. The compositions of the oils from the healthy and infected cotton plant according to classes were as follows (%):

	Sample I	Sample II
Hydrocarbons	0.1	0.1
TAGs	92.5	90.3
High-molecular-weight fatty alcohols	tr.	tr.
FAAs	0.8	1.1
EAGs	0.5	1.1

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 319-325, May-June, 1980. Original article submitted February 8, 1980.

 0009-3130/80/1603-0232$07.50