

LIPIDS OF COTTONSEED AND PALM OILS AND COMPOSITIONS BASED ON THEM*

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UDC 665.335.9.094.1

The physicochemical indices and the fatty-acid and triacylglycerol compositions of cottonseed and palm oils, of cottonseed oil hydrogenate, and of compositions based on them have been determined with the aid of IR and UV spectroscopies, GLC analysis, and chemical transformations. The compositions and amounts of the main classes of lipids in the initial oils and the hydrogenate have been studied. It has been found that in the process of hydrogenation the amount of oxygenated components falls.

Recently, a tendency has appeared to the use not only of plant oils but of compositions based on them.

We have studied the lipids of refined palm oil (obtained from Malaysia), cottonseed oil, and cottonseed oil hydrogenate (from the Tashkent Oils and Fats Combine) that we have used for making two compositions of fatty bases for the preparation of new products. Composition 1 included 52% of cottonseed oil hydrogenate, 12% of cottonseed oil, and 36% of palm oil, and composition 2 contained 77% of the hydrogenate and 23% of cottonseed oil. The characteristics of the materials investigated are given in Table 1.

The initial oils were characterized by identical acid numbers and levels of conjugated dienic acid and also by the absence of *trans*-acids. The higher hardness and melting point of the palm oil as compared with the cottonseed oil were determined by the difference in their compositions. The high acid number and considerable proportion of *trans*-acids in the hydrogenate affected these indices in the compositions produced. However, the addition of palm oil to composition 1 somewhat lowered their indices in comparison with composition 2.

To establish their lipid compositions, the initial oils and the hydrogenate were separated into individual components by column chromatography and PTLC on silica gel. The lipids were identified by qualitative reactions, mobilities in a thin layer of silica gel in comparison with markers, and chemical transformations. The amounts of lipids were determined gravimetrically (Table 2).

TABLE 1. Physicochemical Indices of the Oils, the Hydrogenate, and the Compositions

Index	Palm oil	Cotton-seed oil	Hydrogenate	Composition 1	Composition 2
Melting point, °C	33.5	—	38	35	36
Hardness, g/cm	110	—	260	200	210
Acid No., mg KOH/g	0.52	0.51	1.30	0.83	1.09
Content, %, of:					
<i>trans</i> -acids	Abs.	Abs.	49.8	30.2	44.5
conjugated dienic acids.	3.7	3.6	2.0	2.2	2.9

*The work was conducted with the financial support of the Uzbek Fund for Fundamental Investigations.

TABLE 2. Compositions of the Lipids of Cottonseed Oil (1), Palm Oil (2), and the Hydrogenate (3)

Lipid	Content, % on the oils		
	1	2	3
Hydrocarbons	Tr.	Tr.	Tr.
Triacylglycerols (TAGs)	92.2	92.8	94.0
Epoxyacyldiacylglycerols (EDAGs)	1.1	—	—
Free fatty acids (FFAs)	0.2	0.2	0.6
Hydroxyacyldiacylglycerols (hDAGs)	1.8	0.6	0.7
Diacylglycerols (DAGs)	4.3	4.6	2.3
Sterols	0.4	0.5	0.3
Monoacylglycerols (MAGs)	Tr.	1.1	0.4
Unidentified.	—	0.1	1.7

TABLE 3. Compositions of the Fatty Acids of the Triacylglycerols, GLC, % by Weight

Material	14:0	16:0	16:1	18:0	18:1	18:2	Total sat.	Total unsat.
Cottonseed oil	0.3	21.3	1.0	1.1	17.8	58.5	22.7	77.3
TAGs	0.2	22.7	0.6	0.4	18.0	58.1	23.3	76.7
2-MAGs	—	2.5	—	—	44.6	52.9	2.5	97.5
Palm oil	0.3	45.5	—	2.0	44.2	8.0	47.8	52.2
TAGs	—	40.4	—	2.8	46.3	10.5	43.2	56.8
2-MAGs	—	3.8	—	1.5	74.6	20.1	5.3	94.7
Cottonseed oil hydrogenate	0.2	24.4	0.5	5.4	55.8	13.7	30.0	70.0
TAGs	0.4	25.9	0.9	9.0	54.2	9.6	35.3	64.7
2-MAGs	—	4.8	—	5.4	79.0	10.8	10.2	89.8
Composition 1	0.2	32.9	—	5.0	49.8	12.1	38.1	61.9
TAGs	—	33.9	—	6.1	50.6	9.4	40.0	60.0
2-MAGs	—	4.6	—	3.8	73.6	18.0	8.4	91.6
Composition 2	0.7	25.1	—	8.4	51.8	14.0	34.2	65.8
TAGs	—	25.4	—	6.1	54.5	14.0	31.5	68.5
2-MAGs	—	4.2	—	5.4	71.0	19.4	9.6	90.4

Apart from the main component of the lipids — triacylglycerols — seven other classes were identified. Oxygenated lipids were identified in all the materials with a fairly high content in the sample of cottonseed oil investigated (~3%) and were represented by acylglycerols including in one of the acyl groups either an epoxy or a hydroxy group. The palm oil, like the cottonseed oil hydrogenate, was characterized by a lower level of these lipids (less than 1%).

Oxygenated lipids are undesirable components of edible oils, since they are toxic for the animal cell [1]. The addition of palm oil in composition 1 lowered their level.

The lipophilic components in the oils were represented mainly by sterols.

In order to determine the disposition of the acyl radicals in the TAGs of the materials investigated, we carried out enzymatic hydrolysis. The 2-MAGs were isolated from their hydrolysis products by PTLC in the solvent system hexane—ether (1:4). The compositions and amounts of fatty acids in the initial oils and their TAGs and 2-MAGs were determined by the GLC of the methyl esters of the fatty acids obtained by alkaline hydrolysis (Table 3).

The set of the main fatty acids of the cottonseed and palm oils were identical, the differences being of quantitative nature. Thus, cottonseed oil and the TAGs contained more than 70% of unsaturated acids, among which the 18:2 acid predominated. The total unsaturation of the palm oil was 25% lower than that of the cottonseed oil, while its main acids were the 16:0 and 18:1 species. The cottonseed oil hydrogenate and, correspondingly, the fatty bases were enriched with the 18:1 acid. The addition of palm oil to the fatty base 1 somewhat raised the proportion of the 16:0 acid in comparison with fatty base 2. The central position in the TAGs of all the materials was enriched by more than 90% with unsaturated acids.

From the composition of the fatty acids of the TAGs and 2-MAGs we calculated the position-species compositions of the TAGs by Coleman's method [2] (Table 4). It was found that of the two extreme positions, palmitic and oleic acids enriched the sn-1 position and linoleic acid the sn-3 position [3].

TABLE 4. Position-Species Composition of the Triacylglycerols, % by Weight

TAG	Cottonseed oil	Palm oil	Hydrogenate	Composition 1	Composition 2
SSS	0.3	2.0	2.3	2.5	2.3
SSO	0.1	2.2	4.2	3.6	5.6
SSL	1.0	0.4	0.9	0.6	1.5
SLS	6.0	7.7	2.5	5.6	3.0
SOS	5.0	28.7	18.0	22.9	10.6
SLO	2.0	8.0	4.4	7.8	7.7
SLL	21.7	1.5	1.0	1.0	1.5
SOO	1.7	29.7	32.6	32.1	25.6
SOL	18.3	5.4	6.8	4.3	5.9
OSL	0.2	0.2	0.8	0.4	1.7
OSO	—	0.5	1.9	1.3	3.5
LSL	0.9	—	0.1	—	0.2
OOO	0.1	7.7	14.7	11.2	15.7
OLO	0.2	2.1	2.0	2.7	4.6
OOL	3.0	2.8	6.2	2.9	7.2
LOL	16.5	0.3	0.7	0.2	0.9
OLL	3.5	0.7	0.8	0.8	2.2
LIL	19.5	0.1	0.1	0.1	0.3

S — saturated acyl radicals; O — oleoyl radical; L — linoleoyl radical.

TABLE 5. Position-type Compositions of the Triacylglycerol, % by Weight

Material	SSS	SSU	SUS	SUU	USU	UUU
Cottonseed oil	0.3	1.1	11.0	43.7	1.1	42.8
Palm oil	2.0	2.6	36.4	44.6	0.7	13.7
Hydrogenate	2.3	5.1	20.5	44.8	2.8	24.5
Composition 1	2.5	4.2	28.5	45.2	1.7	17.9
Composition 2	2.3	7.1	13.6	40.7	5.4	30.9

U — unsaturated acyl radicals.

Table 5 gives the position-type compositions of the fats investigated. The cottonseed oil contained a high percentage of triunsaturated and monosaturated—diunsaturated TAGs. Among the latter the TAG types with saturated acyls in the extreme positions dominated. These types of TAGs also predominated in the palm oil, the cottonseed oil hydrogenate, and the fatty bases composed of more than 40% by weight of TAGs. In addition, the palm oil included more than 75% of disaturated monounsaturated TAGs with the unsaturated acyls in the sn-2 positions. The latter types of TAGs, together with the triunsaturated types amounted from 34 to 44% of the weight of the TAGs of the hydrogenate and of the fatty bases.

EXPERIMENTAL

The UV spectra of the fats were taken on a Hitachi spectrometer in hexane, the content of dienes being determined from the absorption band at λ 234 nm with calculation by the formula given in [4]. The IR spectra of the methyl esters were recorded on a UR-10 instrument in carbon tetrachloride. The levels of *trans*- acids were calculated by measuring the intensities of the absorption bands at ν 970 cm^{-1} and comparing them with that of the absorption band of methyl elaidate [5].

The GLC of the fatty acid MEs was conducted on a Chrom-41 instrument with a flame-ionization detector. A 4 \times 2000 mm column filled with 15% of PEGS on Chrom W, 60–80 mesh, was used at a temperature of 200°C with helium as the carrier gas.

with the addition of 4% of gypsum. The alkaline hydrolysis of the fats and the enzymatic hydrolysis of the TAGs were performed as described in [6]. The hardness of the fats was determined by Kaminskii's method [7].

REFERENCES

1. V. Mahadevan, J. Am. Oil Chem. Soc., **42**, 582A (1965).
2. M. H. Coleman, J. Am. Oil Chem. Soc., **38**, 685 (1961); **40**, 568 (1963).
3. O. V. Ozerinina, N. S. Geiko, and K. Kh. Mazhidov, Maslo-Khir. Prom-st, 31 (1982).
4. V. R. Sterlin and A. N. Mironova, Trudy VNIIZh, Leningrad, No. 27, 276 (1967)
5. A. N. Mironova, Trudy VNIIZh, Leningrad, No. 17, 63 (1957).
6. G. U. Tillaeva, N. T. Ul'chenko, I. P. Nazarova, and Kh. N. Isaev, Khim. Prir. Soedin., 509 (1987).
7. Handbook on Methods of Investigation, Technical and Chemical Control, and the Accounting of Production in the Oils and Fats Industry [in Russian], Leningrad, Vol. 3 (1969), p. 243.