CHROMATOGRAPHIC SEPARATION OF THE ISOMERS FORMED IN THE LOW-TEMPERATURE HYDROGENATION OF COTTONSEED OIL IN SOLVENTS

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In the hydrogenation of vegetable oils, a large number of position isomers and geometric isomers are formed. Their analysis and identification is difficult because they possess very similar physical and chemical properties.

The use of various methods of chromatography, including chromatography in the presence of silver ions, has made it possible to separate and identify the isomers formed in the hydrogenation of these oils. In the present paper we give the results of an investigation of two samples of cottonseed oil partially hydrogenated with a disperse palladium catalyst (sample I) and with an Al–Ni–Cu (50 : 40 : 1) catalyst (sample II) (Table 1). The composition of the acids isolated from their hydrogenizates by the lead–alcohol method [5] is given in Table 2. It can be seen from Table 2 that hydrogenation on the Ni–Al–Cu catalyst takes place more selectively, i.e., the linolenic acid is first hydrogenated to oleic, and then the oleic to stearic.

The liquid fraction in the form of methoxymercury derivatives was separated on a column of silica gel on the basis of the degree of unsaturation. According to GLC, the dienic fraction was obtained with a purity of 100%; the monoenic fraction contained 0.7% of $C_{16:0}$, 97.4% of $C_{18:1}$, and 1.9% of $C_{18:2}$; the amount of trans acids in the monoenoic fraction was 2.6% and in the dienoic fraction 20.8%, and the amount of acids with conjugated double bonds was 12.8%. Both the dienoic acid and the monoenoic fractions were separated into isomers. Five zones were marked out on a chromatogram of the octadecadienoic fraction. Each zone was isolated preparatively. The results of GLC confirmed that all five zones contained only dienoic acids. According to UV spectroscopy, conjugated dienes were present only in zone 4 (14.3%). The positions of the double bonds in the dienoic acids of each zone were determined by studying the products of their permanganate–periodate oxidation.

It can be seen from Table 3 that the bulk of the dienoic acids remain in the native state (zone 3 is the most intense). The double bonds migrate only by one methylene group from the initial Δ^9 or Δ^{12} position to the left or to the right. The presence of the $\Delta^{8,12}$ acid in several zones shows that it is present in them in different geometrical configurations (cis, cis; cis, trans; trans, cis; and trans, trans).

The separation of the monoenoic fraction into isomers gave seven spots well separated from one another. The preparative isolation of each zone and its investigation by GLC showed that pure octadecenoic

TABLE 1. Properties and Fatty Acid Compositions of the Hydrogenated Oils

Sample No.	Fatty acid comp.						trans-Acid, %	Iodine No., %
	$C_{14:0}$	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{13:2}$		
I	1,60	26,00	—	7,30	43,10	22,0	24,61	76,35
II	0,60	26,20	1,60	4,50	49,60	17,50	32,41	75,60

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TABLE 2. Fatty Acid Composition of the Fractions

Acid	Sample I		Sample II	
	fractions			
	liquid	solid	liquid	solid
$C_{14:0}$	0,9	1,5	0,8	0,9
$C_{16:0}$	3,3	51,5	4,0	36,3
$C_{16:1}$	1,7	0,9	1,6	0,4
$C_{18:0}$	–	17,6	–	8,0
$C_{18:1}$	52,8	26,8	79,8	50,5
$C_{18:2}$	41,3	1,7	13,8	3,9

acids were present in the third to fifth spots. The first spot was not identified and the second consisted of the small amount (1.9%) of the dienoic fraction present among the monoenes.

The structures of the isomeric monoenoic and octadecadienoic acids were determined after oxidation with permanganate–periodate (Table 4). In the monoenes from both samples of the hydrogenated oil, the fourth spot – that of the native oleic acid – was the most intense. In sample (II), the seventh spot appeared very feebly. The degradation of the monoenes gave mainly Δ^8-, Δ^9-, and Δ^{10}-acids, which shows the predominant hydrogenation of the Δ^{12} double bond – the one the more remote from the carboxy group. This corresponds to literature information explaining this phenomenon from the point of view of the electronic theory [6]. A residual Δ^9 bond migrates one place to the left or to the right, forming the Δ^8 and Δ^{10} isomers. The Δ^{11} isomer can be obtained by the hydrogenation of the conjugated dienes usually formed from linoleic acid in the first stages.

The primary hydrogenation of the Δ^{12} bond is also shown by the results of the oxidation of the monoenoic fraction of sample (II) by the permanganate method [7]. The compositions and amounts of the mono- and dicarboxylic acids formed on oxidation are given below:

Monocarboxylic acids, %		Dicarboxylic acids, %	
C_6	6,14	C_7	2.8
C_7	7,37	C_8	16,6
C_8	21.29	C_9	52.8
C_9	53.89	C_{10}	11,0
C_{10}	11.31	C_{11}	8.5
		C_{12}	8.3

TABLE 3. Results of the Destructive Oxidation of the Octadecadienoic Acids

Zone No.	Rf of the zone	Dicarboxylic acids		Monocarboxylic acids	Structure of the octadecadienoic acids	Positions of the double bonds
		low-molecular-weight	high-molecular-weight			
1	0,1	C_3, C_4	C_8, C_{10}	C_6, C_5	$CH_3(CH_2)_4CH{=}CH\,CH_2CH_2CH{=}CH(CH_2)_6COOH$ $CH_3(CH_2)_3\cdot CH{=}CH\,CH_2CH{=}CH(CH_2)_8\cdot COOH$	8,12 10,13
2	0,27	C_3, C_4	C_8	C_6, C_7	$CH_3(CH_2)_4\cdot CH{=}CH\,CH_2CH_2CH{=}CH(CH_2)_6\cdot COOH$ $CH_3(CH_2)_5\cdot CH{=}CH\,CH_2CH{=}CH(CH_2)_6\cdot COOH$	8,12 8,11
3	0,45	C_3	C_9	C_6	$CH_3(CH_2)_4\cdot CH{=}CH\,CH_2CH{=}CH(CH_2)_7\cdot COOH$	9,12
4	0,55	C_2*, C_3	C_9, C_{10}	C_6, C_7	$CH_3(CH_2)_4\cdot CH{=}CH\cdot CH_2CH{=}CH(CH_2)_7\cdot COOH$ $CH_3(CH_2)_5\cdot CH{=}CH\cdot CH{=}CH(CH_2)_7\cdot COOH$ $CH_3(CH_2)_4\cdot CH{=}CH\cdot CH{=}CH\cdot(CH_2)_8\cdot COOH$	9,12 9,11 10,12
5	0,68	C_4	C_8, C_9	C_6, C_5	$CH_3(CH_2)_3\cdot CH{=}CH\cdot CH_2CH_2CH{=}CH(CH_2)_7COOH$ $CH_3(CH_2)_4\cdot CH{=}CH\cdot CH_2CH_2CH{=}CH(CH_2)_6COOH$	9,13 8,12

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* We did not detect oxalic acid because of its oxidation to CO_2.

TABLE 4. Results of the Destructive Oxidation of the Octadecenoic Acids

Zone No.	Rf of the zone	Dicarboxylic acids	Monocarboxylic acids	Structure of the monoenoic acids	Position of the double bond
3	0,57	C_8	C_{10}	$CH_3(CH_2)_8\cdot CH{=}CH\cdot(CH_2)_6\cdot COOH$	8–9
4	0.61	C_9	C_9	$CH_3(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_7COOH$	9–10
5	0,73	C_{10}	C_8	$CH_3(CH_2)_6\cdot CH{=}CH\cdot(CH_2)_8\cdot COOH$	10–11
6	0.79	C_{11}	C_7	$CH_3(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_9\cdot COOH$	11–12
7	0,84	C_{12}	C_6	$CH_3(CH_2)_4\cdot CH{=}CH\cdot(CH_2)_{10}\cdot COOH$	12–13

TABLE 5. Composition of the Dicarboxylic Acids of the Oxidized Fractions of the Monoenes

Dicarboxylic acids	Amount in monoenes, %	
	liquid fraction	solid fraction
C_7	2,8	—
C_8	16,6	13,4
C_9	52,8	33,8
C_{10}	11,0	27,7
C_{11}	8,5	17,0
C_{12}	8,3	8,1

The saturation of the Δ^{12} double bond forms the following amounts of acids (% of the total mono- and dicarboxylic acids):

$$\begin{array}{ll} \text{Monocarboxylic} & C_8+C_9+C_{10}=21.29+53.89+11.31=86.49, \\ \text{Dicarboxylic} & C_8+C_9+C_{10}=16.6+52.8+\underline{11.0=80.40} \\ & \qquad\qquad\qquad\qquad\quad 166.89 \end{array}.$$

The saturation of the Δ^9 bond:

$$\begin{array}{ll} \text{Monocarboxylic} & C_5+C_6+C_7=6,14+7,37=13.51, \\ \text{Dicarboxylic} & C_{11}+C_{12}+C_{13}=8.5+\underline{8.3=16.8} \\ & \qquad\qquad\qquad\qquad 30.31 \end{array}.$$

Thus, the value of 166.89 shows the primary saturation of the Δ^{12} double bond, and the saturation of the Δ^9 bond corresponds to a figure of only 30.31.

The results of an investigation of the products of the oxidation of the trans-unsaturated acids isolated from the solid fraction of sample (II) in comparison with the monoenic liquid fraction, which is present mainly in the cis form, are given in Table 5. It can be seen from this table that in the trans monoenes the amount of the Δ^{10} and Δ^{11} isomers increases as compared with the cis acids. This shows that the hydrogenation process takes place through a stage of semihydrogenation.

EXPERIMENTAL

The saturation of the oil with hydrogen was performed in an apparatus for liquid-phase hydrogenation [8]. Each experiment was performed with 5 g of cottonseed oil (iodine No. 107.4) in 40 ml of solvent at 50°C.

Sample I – c 0.02% of Pd (on the weight of the oil) on aluminum in hexane; sample II – c 1% of leached and washed Ni–Al–Cu catalyst in ethanol–hexane (1 : 1).

The methoxymercury derivatives of the methyl esters of the fatty acids were obtained by Stahl's method [9]. The separation of the acids according to their degree of unsaturation was performed by the method of Jantzen and Andreas [10].

The separation of the acids into isomers was performed on silica gel impregnated with 6% of $AgNO_3$ as described previously [11]. The dienes were run twice and the monoenes once in the benzene–chloroform (3 : 25) system. The spots were revealed by heating the edges of the plates to 200°C. The layers of silica gel corresponding to particular spots were removed from the plate and extracted repeatedly with diethyl ether. After distillation of the ether, the individual groups of acids were obtained.

The oxidation of the methyl esters of the fatty acids was performed by the permangante–periodate method [12].

The oxidized fragments were identified in a thin layer on cellulose plates [12] in the form of the monocarboxylic acids and the monomethyl esters of the dicarboxylic acids. The monocarboxylic acids were identified by comparison with reference samples. Because of the absence of reference samples of the monomethyl esters of the dicarboxylic acids, we based their identification on literature information [12] according to which in the hexane–diethyl ether–dimethylformamide (40 : 20 : 1) solvent system the R_f value of the monomethyl ester of suberic acid coincides with that of propionic acid, that of the monomethyl ester of azelaic with that of butyric acid, and that of the monomethyl ester of sebacic acid with that of valeric acid. To confirm the assumption made, the monomethyl esters of the dicarboxylic acids of the oxidized products of each zone of the monoenoic fraction were converted into the dicarboxylic acids by saponification with ethanolic alkali for 0.5 h and subsequent decomposition by acid. The dicarboxylic acids formed were identified with reference samples on cellulose in the propanol–ammonia–water (9 : 1 : 2) system.

The low-molecular-weight dicarboxylic acids formed in the degradation of the medium part of the dienoic acids were detected in the form of the ammonium salts on a thin layer of cellulose in the ethanol–ammonia–water (20 : 3 : 2) system in comparison with reference samples of the ammonium salts of malonic, succinic, and glutaric acids [13].

SUMMARY

The separation of the isomers formed in the low-temperature hydrogenation of cottonseed oil in solvents has been performed by thin-layer chromatography.

The primary hydrogenation of the Δ^{12} double bond in linoleic acid radicals has been shown.

The migration of a double bond takes place mainly by one methylene group to the left or to the right of the original position.

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