THE STRUCTURE OF THE OCTADECADIENOIC ACIDS FORMED IN THE HYDROGENATION OF SUNFLOWERSEED OIL

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The position isomerization and geometrical isomerization of unsaturated fatty acids taking place during the hydrogenation of oils [1-4] permit the expectation of the appearance in the hydrogenizates of a series of unsaturated acids besides the native oleic and linoleic acids. We have studied this phenomenon widely in the case of the hydrogenation of sunflowerseed oil.

We hydrogenated refined sunflowerseed oil with an iodine number (I. No.) of 107.67 in a continuous column (h = 45 cm) on a stationary fused nickel–copper catalyst with the addition of titanium at 180°C. The rate of feed of hydrogen was 1 liter/min. The time of contact of the oil with the catalyst was 55 min. Some properties of the hydrogenizate were determined: I. No. 77.37, mp 33-34°C. The fatty-acid composition, according to gas-liquid chromatography (GLC) was as follows (%):

$C_{12:0}$ – traces	$C_{18:0}$ – 5.9
$C_{14:0}$ – 0.7	$C_{18:1}$ – 51.4
$C_{16:0}$ – 26.2	$C_{18:2}$ – 15.8.

The content of trans acids (IR spectroscopy) was 44%, and that of dienic acids with conjugated double bonds (UV spectroscopy) 2.8%.

The bulk of the saturated acids were separated from the acids obtained by cold saponification [5] by the precipitation of the lead salts. The unsaturated acid fraction, which still contained a very small amount of saturated acids, was methylated and was then converted into the acetoxymercuri-methoxy derivatives [5, p. 402]. The latter were separated according to their degrees of unsaturation in a thin layer of silica gel. Two fractions were obtained, consisting of derivatives of monoenoic acids (R_f 0.91) and of dienoic acids (R_f 0.46); after the saponification of the methoxy and the acetoxymercuri groups, fractions of monoenoic and dienoic acids were obtained. The dienoic fraction, according to GLC, consisted of octadecadienoic acids (88.7%), octadecenoic acids (6.8%), and saturated acids (4.5%).

Then the combined octadecadienoic acids were separated into subgroups by the method that we have developed of thin-layer chromatography (TLC) on silica gel impregnated with silver nitrate. Seven zones were formed. On the preparative isolation of each of zone and its investigation by GLC, it was found that zones I-V contained only dienoic acids, zone VI monoenoic acids, and VII a mixture of monoenoic and saturated acids. We studied the acids of the first five zones.

It was found by UV spectroscopy that only zones I and II contained acids with conjugated double bonds (3-4%). This was confirmed by destructive oxidation. In all the zones, the presence of acids with the trans configuration was found by IR spectroscopy (peaks at 970 or 990 cm^{-1}).

The structure of the octadecadienoic acids of each zone was determined by permanganate-periodate oxidation with subsequent identification of the degradation products in a thin layer of cellulose [6] (Table 1).

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TABLE 1. Results of the Destructive Oxidation of the Octadecadienoic Acids

Zone No.	R_f	Dicarboxylic acids: low-molecular-wt	Dicarboxylic acids: high-molecular-wt	Monocarboxylic acids	Structure of the octadecadienoic acids	Positions of the double bonds
I	0,09	C_4	C_9, C_{10}	C_5, C_6, C_7	$CH_3(CH_2)_4CH=CH-CH_2-CH_2-CH=CH(CH_2)_6COOH$	8,12
					$CH_3(CH_2)_3CH=CH-CH_2-CH_2-CH=CH(CH_2)_7COOH$	9,13
					$CH_3(CH_2)_5CH=CH-CH=CH(CH_2)_7COOH$	9,11
					$CH_3(CH_2)_4CH=CH-CH=CH(CH_2)_6COOH$	10,12
II	0,24	C_3	C_{11}, C_{10}	C_6, C_7	$CH_3(CH_2)_5CH=CH-CH=CH(CH_2)_7COOH$	9,11
					$CH_3(CH_2)_4CH=CH-CH=CH(CH_2)_6COOH$	10,12
					$CH_3(CH_2)_4CH=CH-CH_2CH=CH(CH_2)_7COOH$	9,12
III	0,42	C_1, C_2	C_8, C_9	C_5, C_6	$CH_3(CH_2)_4CH=CH-CH_2-CH_2-CH=CH(CH_2)_6COOH$	8,12
					$CH_3(CH_2)_3CH=CH-CH_2-CH_2-CH=CH(CH_2)_7COOH$	9,13
					$CH_3(CH_2)_5CH=CH-CH_2-CH_2-CH_2-CH=CH(CH_2)_7COOH$	8,13
IV	0,57	C_3	C_9	C_4	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH(CH_2)_7COOH$	9,12
V	0,73	C_2	C_8	C_7	$CH_3(CH_2)_5CH=CH-CH_2-CH=CH(CH_2)_7COOH$	8,11

The table shows, in the first place, that the double bonds of the acids were shifted by only one methylene group in one direction or the other (a Δ^9 bond to position 8 or position 10; a Δ^{12} bond to position 11 or 13); in the second place, that conjugated systems of bonds – 9,11 and 10,12 – were found only among the acids of zones I and II; and, in the third place, that acids with similar positions of the double bonds were found in different zones (for example, the 8,12- and 9,13-dienoic acids in zones I and II and the 9,12-dienoic acid in zones II and IV). The latter circumstances can be explained by their different spatial configurations: it is known that in a thin layer of silica gel impregnated with silver nitrate the trans isomers migrate faster than the cis isomers.

EXPERIMENTAL

The fatty acids were methylated in methanol with catalytic amounts of H_2SO_4 [7].

Preparation of the Acetoxymercuri-methoxy Derivatives of the Methyl Esters of the Fatty Acids [5, p. 403]. A solution of 14 g of mercury acetate in 250 ml of methanol containing 2.5 ml of water and 1 ml of CH_3COOH was prepared. For each gram of fatty acid methyl esters, 40 ml of this solution was taken. The mixture was left in the dark for two days. (This time is sufficient to bind all the trans acids.) Then the methanolic solution was evaporated in an atmosphere of nitrogen at 40°C. The residue was dissolved in chloroform. The chloroform solution was washed with water to eliminate the excess of mercury acetate and was then dried over anhydrous sodium sulfate and evaporated in vacuum in a current of nitrogen at 40-50°C.

Preparative Separation of the Acetoxymercuri-methoxy Derivatives of the Fatty Acids according to Their Degree of Unsaturation. Plates (18 × 24 cm) were covered with a paste consisting of 14 g of KSK silica gel (particle dimensions 0.1 mm), 10% of gypsum, and 38 ml of water. The plates were dried in the air for 18 h, after which a 20% solution of the acetoxymercuri-methoxy derivatives of the fatty acids in chloroform was deposited on them in an amount of 25 mg per plate. For the fractionation, n-propanol–glacial acetic acid (100 : 1) was used as the solvent. After 7 h, the front had moved 12-13 cm. The acids were detected by spraying the edge of the plate with a 0.1% solution of diphenylcarbazone in 96% ethanol (violet spots on a white background). The adducts of the monoenoic acids (R_f 0.91) were sharply separated from those of the dienoic acids (double spot with R_f 0.69 and 0.46).

The zones of the silica gel corresponding to the dienoic fraction were scraped from the plates and were then shaken in a flask with 70 ml of CH_3OH and 35 ml of concentrated HCl. The solution was decanted. The precipitate was treated with the same mixture again. The combined solutions were diluted with 150 ml of H_2O, filtered, and extracted with diethyl ether (1 × 50 ml and 4 × 20 ml). The ethereal extracts were washed with water and dried over Na_2SO_4. The ether was distilled off to give the octadecadienoic acid fraction.

Separation of the Octadecadienoic Acids into Subgroups. A mixture of 14 g of KSK silica gel and 10% of gypsum was mixed with 37 ml of 6% silver nitrate solution and deposited on plates (18 × 24 cm). The plates were dried in the air for 18 h. Then a solution of the octadecadienoic acids in benzene was deposited on them at the rate of 15 mg per plate at a distance of 1.5 cm from one edge. The acids were separated with benzene–chloroform (3 : 25). The spots were revealed by spraying the edge of a plate with 50% H_2SO_4 and heating it at 200°C (yellow-brown spots on a gray background). The layers of silica gel corresponding to each spot were scraped off the plates and extracted with diethyl ether (4 × 50 ml). The ether was distilled off to give individual fractions, which were studied by GLC and by IR and UV spectroscopy.

Permanganate-Periodate Oxidation of the Fatty Acid Methyl Esters [6]. A solution of 0.001 mole of K_2CO_3 and 0.001 mole of $KMnO_4$ in 10 ml of H_2O was mixed with a solution of 0.001 mole of KIO_4 in 10 ml of H_2O in a ratio of 1 : 2. This oxidizing mixture was added dropwise to a small flask containing 5-10 mg of fatty acid methyl esters. Each successive drop of oxidizing mixture was added after the disappearance of the color of the solution from the preceding drop. When the solution ceased to change color, the dropwise addition of a 2 N solution of HCl was begun, and then this was followed by a solution of sodium bisulfite until decoloration had been achieved. The contents of the flask were shaken with a small amount of diethyl ether for the fullest possible extraction of the oxidation products. However, the lower dicarboxylic acids (malonic, succinic, glutaric) remained in the aqueous layer. The oxalic acid was oxidized to CO_2, so that we did not detect it.

Identification of the Oxidation Products in a Thin Layer of Cellulose [6]. Cellulose mixed with water to a creamy consistency was deposited in a thin layer on plates (18 × 6 cm) which were left in the air overnight and were then dried at 105°C for 1 h. After cooling, the plates were impregnated with a 40% solution of dimethylformamide in benzene and were dried in the air for 5-10 min. On each plate was deposited by means of a capillary a diethyl ether solution of the oxidation products, among which was to be expected the presence of monomethyl esters of dicarboxylic acids, together with monocarboxylic acids; as markers the corresponding monocarboxylic acids and monomethyl esters of dicarboxylic acids were deposited on the same plates. The fragments were separated with hexane–diethyl ether–dimethylformamide (40 : 20 : 1). The chromatograms were run for 20 min. Then the plates were placed in a chamber saturated with ammonia for 10 min, after which they were sprayed with Duncan's indicator [8]. Bright yellow spots appeared on a green background.

To establish the mutual positions of the double bonds in the dienoic acids, the low-molecular-weight dicarboxylic acids (the products of the oxidation of the segments of the initial acids lying between the two double bonds in each case) that had remained in the aqueous solution were also chromatographed in a thin layer of cellulose. The plates with the cellulose were prepared as described above. The acid aqueous solution was deposited on them by 10 applications of a capillary, and malonic, succinic, and glutaric acids were deposited on the same plate as markers. Thw low-molecular-weight dicarboxylic acids were separated by means of n-propanol–water–ammonia (6 : 2 : 1), the running time being 1 h. The plates were dried in the air for 30 min, until the small of ammonia had disappeared. The acids were revealed by spraying the plates with Bromphenol Blue. Blue spots appeared on a yellow background.

CONCLUSIONS

A method for the partial separation of the combined octadecadienoic acids isolated from the hydrogenation of sunflowerseed oil has been developed. This method is considered as the first stage of the separation of the octadecdienoic acids into the individual isomers.

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