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 (%):

- C12:0 -- trace
- C14:0 -- 0.7
- C16:0 -- 26.2
- C18:0 -- 5.9
- C18:1 -- 51.4
- C18:2 -- 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 (Rf 0.91) and of dienoic acids (Rf 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

<table>
<thead>
<tr>
<th>Zone No</th>
<th>k&lt;sub&gt;f&lt;/sub&gt;</th>
<th>Dicarboxylic acids (low-molecular wt)</th>
<th>Mono-&lt;br&gt;carboxylic acids (high-molecular wt)</th>
<th>Structure of the octadecadienoic acids</th>
<th>Position of the double bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.09</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;, C&lt;sub&gt;5&lt;/sub&gt;, C&lt;sub&gt;6&lt;/sub&gt;, C&lt;sub&gt;9&lt;/sub&gt;, C&lt;sub&gt;10&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH=CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt; &lt;br&gt;CH&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH=CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt; &lt;br&gt;CH&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>8,12, 9,13</td>
</tr>
<tr>
<td>II</td>
<td>0.24</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;, C&lt;sub&gt;6&lt;/sub&gt;, C&lt;sub&gt;10&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH=CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt; &lt;br&gt;CH&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH=CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt; &lt;br&gt;CH&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>9,11, 10,12</td>
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<tr>
<td>III</td>
<td>0.42</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;, C&lt;sub&gt;4&lt;/sub&gt;, C&lt;sub&gt;6&lt;/sub&gt;, C&lt;sub&gt;7&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH=CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt; &lt;br&gt;CH&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH=CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt; &lt;br&gt;CH&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>8,12, 9,13</td>
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<tr>
<td>IV</td>
<td>0.57</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;, C&lt;sub&gt;7&lt;/sub&gt;, C&lt;sub&gt;8&lt;/sub&gt;</td>
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<tr>
<td>V</td>
<td>0.73</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;, C&lt;sub&gt;9&lt;/sub&gt;, C&lt;sub&gt;10&lt;/sub&gt;</td>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;(CH=CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt; &lt;br&gt;CH&lt;sub&gt;3&lt;/sub&gt;COOH</td>
<td>8,11</td>
</tr>
</tbody>
</table>

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<sup>8</sup> bond to position 8 or position 10; a Δ<sup>12</sup> 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<sub>2</sub>SO<sub>4</sub> [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<sub>3</sub>COOH 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 x 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<sub>f</sub> 0.91) were sharply separated from those of the dienoic acids (double spot with R<sub>f</sub> 0.69 and 0.46).