DETERMINATION OF THE POSITION OF THE DOUBLE BONDS IN THE RADICALS OF THE FATTY ACIDS FROM HYDROGENIZATES OF COTTONSEED OIL

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It is known that the hydrogenation of fats is accompanied by the isomerization both of the glycerides and of the fatty acid radicals present in them.

The present paper gives the results of a study of the question of the possibility of determining the position of the double bonds in the radicals of the fatty acids of hydrogenated cottonseed oil, which is a mixture of a large number of reduction products.

From a scheme of the probable migrations of the double bonds in the hydrogenation of linoleic acid it can be seen that in this process five position-isomeric octadecadienoic acids ($\Delta^{9,12}$-, $\Delta^{10,12}$-, $\Delta^{8,12}$-, $\Delta^{9,13}$- and $\Delta^{9,11}$-) and six isomeric octadecenoic acids (Δ^{9}-, Δ^{10}-, Δ^{8}-, Δ^{12}-, Δ^{11}- and Δ^{13}-), differing in the position of the double bonds may be obtained. The following symbols are used in the scheme $R = CH_3(CH_2)_3$-, $R_1 = -(CH_2)_6COOH$. According to the scheme given, the migration of a double bond by only one methylene group is assumed, since, as our experiments have shown, a double shift takes place rarely and to a very small degree (furthermore, its result may be the regeneration of the initial acid). See scheme on following page.

To confirm the presence of all the isomeric octadecenoic and octadecadienoic acids shown in the scheme in the hydrogenation products, from the total fatty acids of the hydrogenizate we isolated the unsaturated acids by the mercury adduct method [1]. After the separation of the unsaturated acids according to their degree of unsaturation by the TLC method [2], the fractions of the octadecenoic and octadecadienoic acids obtained were methylated and were then oxidized [3], and the degradation fragments were identified on an impregnated layer of cellulose [2].

To identify the oxidation products, markers were used (Fig. 1A) in the form of the monocarboxylic acids (1-8) – propionic, butyric, valeric, caproic, enanthic, caprylic, pelargonic, and capric. For the octadecenoic acids (Fig. 1B) we found the following monocarboxylic acids: valeric, caproic, enanthic, caprylic, pelargonic, and capric, corresponding to spots 3-8. The presence of these acids unambiguously shows the presence of all the octadecenoic acids that can be formed in the process of the saturation of oleic and linoleic acids and shown in the scheme. A gas–liquid chromatogram of the methyl esters of the dicarboxylic acids confirmed the presence of double bonds in the octadecenoic acids in the Δ^{8}–Δ^{13} positions.

A chromatogram of the products of the oxidation of the octadecadienoic acids (Fig. 1C) showed the presence of all the monocarboxylic acids (valeric, caproic, and enanthic, spots 3-5) the appearance of which should have been expected in the destructive oxidation of the various octadecadienoic acids shown in the scheme. The same octadecadienoic acids on oxidation should also give methyl esters of dicarboxylic acids: suberic, azelaic, and sebacic acids. Spot 2 does actually show the presence of monomethyl azelate (its R_f value coincides with the R_f of butyric acid [2] which cannot be expected in the oxidation products). On the basis of literature data [2], it was assumed that spot 1, corresponding to propionic acid (which also cannot be expected in the oxidation products) owed its appearance to monomethyl suberate, which was detected on a gas–liquid chromatogram. Spot 3, at the level of valeric acid, had the greatest intensity of coloration, which gives grounds for assuming that monomethyl sebacate was present in it. The intense coloration of

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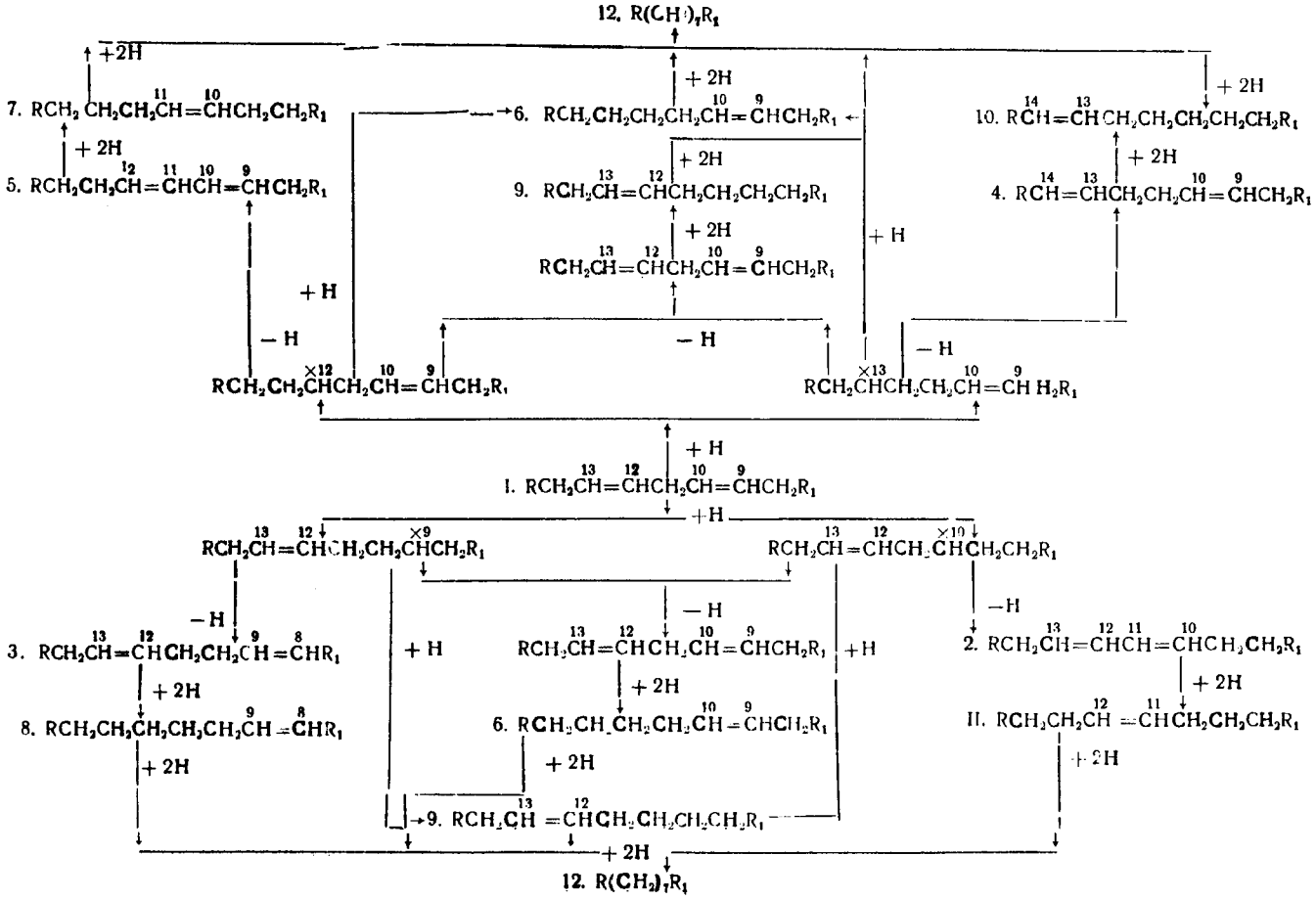
12. R(CH2)7R1
+2H
7. RCH2CH2CH2CH=CHCH2CH2R1
+2H
5. RCH2CH2CH=CHCH=CHCH2R1
+H
−H
RCH2CH2CHCH2CH=CHCH2R1
×12
+2H
6. RCH2CH2CH2CH2CH=CHCH2R1
+2H
9. RCH2CH=CHCH2CH2CH2CH2R1
+2H
RCH2CH=CHCH2CH=CHCH2R1
+H
−H
RCH2CHCH2CH2CH=CHCH2R1
×13
+2H
10. RCH=CHCH2CH2CH2CH2CH2R1
+2H
4. RCH=CHCH2CH2CH=CHCH2R1
−H
I. RCH2CH=CHCH2CH=CHCH2R1
+H
RCH2CH=CHCH2CHCH2CH2R1
×10
−H
2. RCH2CH=CHCH=CHCH2CH2R1
+2H
II. RCH2CH2CH=CHCH2CH2CH2R1
+2H
RCH2CH=CHCH2CHCH2CH2R1
×9
−H
3. RCH2CH=CHCH2CH2CH=CHR1
+2H
8. RCH2CH2CH2CH2CH2CH=CHR1
+2H
+H
RCH2CH=CHCH2CH=CHCH2R1
+2H
6. RCH2CH2CH2CH2CH=CHCH2R1
+2H
9. RCH2CH=CHCH2CH2CH2CH2R1
+H
+2H
12. R(CH2)7R1

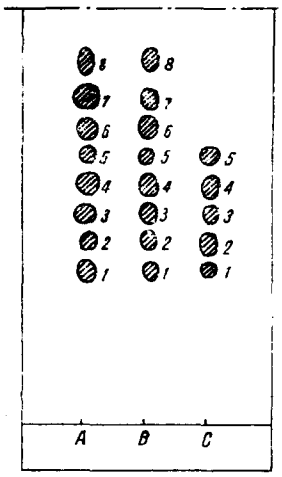

Fig. 1. Chromatogram of the separation of the acids.

the spot cannot be due to valeric acid alone, since the latter is formed in the degradation only of octadeca-9,13-dienoic acid which, with a large proportion of valeric acid, would also give a considerable amount of succinic acid. However, we always found succinic acid in very small amount (this amount also being ascribed to octadeca-8,12-dienoic acid). In our experiment, the gas–liquid chromatography of the methyl esters of the dicarboxylic acids showed that only 4.2% of succinic acid was present, while the amount of sebacic acid was 10.8%.

We detected malonic and succinic acids in a thin layer of cellulose [4]. Oxalic acid, which is formed in the oxidation of conjugated dienic acids, was not found because of its oxidation to CO_2 and H_2O. However, the presence of the conjugated octa-9,11- and -10,12-dienoic acids in the hydrogenizate was confirmed by ultraviolet absorption in the 234 nm region and the presence of the spots corresponding to enanthic and sebacic acids.

The presence of octadeca-9,13- and -8,12-dienoic acids is shown unambiguously by the spots corresponding to valeric acid and to monomethyl suberate.

Hence, on the basis of the qualitative results of the chromatogram it can be stated that all the octadecadienoic acids shown in the scheme are actually present in the hydrogenation products. Since on the chromatogram of the octadecadienoic acids the intensity of the coloration of the spot corresponding to monomethyl suberate is low and the amounts of conjugated dienoic acids (1.39%) and of valeric acid in the hydrogenizate are also low (as stated above), with a total proportion of octadecadienoic acids in the hydrogenizate of 20.64% the bulk of them consist of native linoleic acid.

Thus, in the oxidation of various initial octadecenoic and octadecadienoic acids the monocarboxylic acids valeric, caproic, and enanthic and the dicarboxylic acids suberic, azelaic, and sebacic are always obtained, and as a result of this it is impossible from a combination of the oxidation indices of the mixture of fatty acids of the hydrogenizates (or of the liquid fraction of the acids) unambiguously to establish the presence of individual acids (and, all the more, their amounts) and one can only speak of the direction of migration of the double bonds.

In a study of the influence of the temperature of hydrogenation (120, 140, 160, 180, and 200°C) of cottonseed oil on the migration of the double bonds, we always found all the acids given in the scheme in the hydrogenation products. Thus, in the study of the influence of any factor whatever on the hydrogenation process and the isomerization accompanying it, to establish the presence of individual fatty acids in the hydrogenizates it is sufficient to perform all the operations described above with one of the hydrogenation products.

In those cases where the aim of the investigation is only to establish the preferred direction of migration of the double bonds during the hydrogenation process, it is possible to limit oneself to a quantitative determination of the amount of dicarboxylic acids in the products of destructive oxidation.

EXPERIMENTAL

The hydrogenation of the cottonseed oil was performed on a stationary aluminum–nickel–copper–chromium alloy catalyst at 120°C with a time of contact of the oil and the catalyst of 69.4 min (the iodine number of the hydrogenated oil was 67.22% of I_2, mp 36°C, content of conjugated dienoic acids 1.38%).

The methyl esters of the fatty acids were separated according to their degree of unsaturation on silica gel impregnated with dodecane in the acetone–acetonitrile (1:1) system [2]. The methyl esters of the fatty acids were oxidized with potassium permanganate in dry acetone [3]. After the acidification and decoloration of the potassium permanganate, the combined monocarboxylic acids and monomethyl esters of dicarboxylic acids that had been formed were extracted with diethyl ether. Then the extract was partially evaporated, and a small amount of it was deposited on a thin layer of cellulose impregnated with dimethylformamide (40:20:1) system. The acids were detected by spraying the plates with Duncan's indicator [5] after they had been saturated with ammonia.

To detect the low-molecular-weight dicarboxylic acids formed by the oxidation of the central sections of the octadecadienoic acids located between the two double bonds, a small amount of the aqueous solution remaining after the diethyl ether extraction of the oxidized mixture was deposited on a thin layer of cellulose. The aqueous solution was previously treated with ammonia to a strongly alkaline reaction [4]. The chromatograms were run in the ethanol–ammonia–water (20:3:2) system, after which the plates were dried and sprayed with the indicator Bromphenol Blue. The malonic and succinic acids were detected in the form of blue spots on a yellow background. The markers used for identifying the spots were deposited in the form of the ammonium salts.

SUMMARY

To determine the structures of the products of the isomerization accompanying the hydrogenation of fats it is necessary to determine the amounts of monocarboxylic and dicarboxylic acids in the products of destructive oxidation.

To determine the predominant direction of the migration of the double bonds, however, it is sufficient to determine the composition of the dicarboxylic acids alone.

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