Shifting of the Double Bond in Methyl Oleate During Hydrogenation

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SHIFTING OF THE DOUBLE BOND during hydrogenation of methyl oleate can be demonstrated by the application of partition chromatography. The partly hydrogenated ester is oxidized, and the dicarboxylic acids formed can be separated and identified by means of partition chromatography through a silica gel column.

In 1953 it was demonstrated in this laboratory (1) that, during the catalytic hydrogenation of several fatty acid esters with a nickel on kieselguhr catalyst, migration of double bonds occurs in each direction but with a preference in the direction opposite the carboxyl group. Samples of partially hydrogenated esters were oxidized with $KMnO_4$ in glacial acetic acid (2); the dicarboxylic acids obtained were isolated and separated quantitatively by means of the partition chromatographic method described by Miss Haverkamp Begemann *et al.* (3).

Recent research work by Allen and Kiess (4), in which ozone was selected as the oxidizing agent and in which the analytical procedure of Higuchi (5) was applied for the investigation of the dicarboxylic acids, showed an equal shifting of the double bond of methyl oleate in both directions to and opposite the carboxyl group. They attributed these somewhat deviating results to possible losses of lower molecular dicarboxylic acids in the water phase during the ether extraction that was applied to isolate and purify the dicarboxylic acids after the oxidation with $KMnO_4$. There might also have taken place a certain further break-down of lower dicarboxylic acids during the oxidation process (3).

In this paper the oxidation procedure of methyl oleate and partly hydrogenated samples therefrom was studied more thoroughly. Both methods of oxidation mentioned above, using ozone and $KMnO_4$ in glacial acetic acid, respectively, were applied. Chromatographic separation of the mixtures of dicarboxylic acids allowed a direct comparison of both analytical techniques.

Preparation of Methyl Oleate

Pure methyl oleate was prepared from olive oil fatty acids by crystallizations from acetone at −20°C. and −50°C. (1 g. of acids in 12 ml. of acetone), followed by a three-fold crystallization as urea-complex (6) from methyl alcohol to remove higher unsaturated fatty acids. The product was finally transformed into the methyl esters and fractionated *in vacuo*, by which methyl palmitate was removed in a separate lower boiling fraction. Properties of the product were as follows:

iodine value (Wijs)	85.4	(theor. 85.6)
refractive index n_D^{20}	1.4523	
density d_4^{20}	0.8728	
specific refraction $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	0.3093	
saturated fatty acids (Bertram's method)	1,3%	

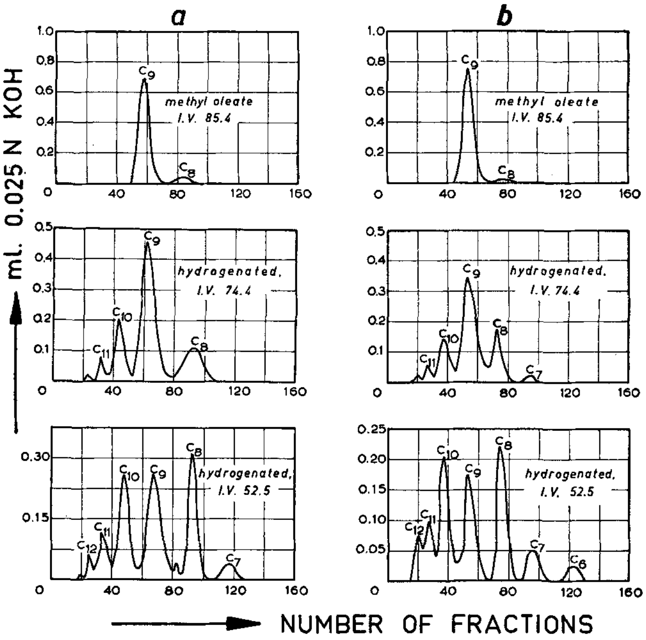

FIG. 1. Chromatographic analysis of dicarboxylic acids obtained from partly hydrogenated methyl oleate: a) by $KMnO_4$ oxidation; b) by ozonization.

Hydrogenation

Hydrogenation was carried out at 180°C. in an open vessel, placed in an oil bath and provided with a clock stirrer; 3% of weight of a 20% nickel on kieselguhr catalyst were used. The hydrogen stream was introduced by means of an inlet tube under the clock. Preheating of the oil was done in a nitrogen stream. Samples were withdrawn after 5, 10, 15, 25, 35, and 55 min. The degree of hydrogenation was controlled by means of the iodine value (Wijs method).

Oxidation of Samples

Samples of partly hydrogenated methyl oleate were oxidized, according to Armstrong and Hilditch, (3, 9) in a glacial acetic acid solution at 50°C.

Other samples were transformed into corresponding fatty acids by saponification, ozonized at room temperature in methyl-acetate solution by introducing ozonized oxygen, and treated with excess of 30% H_2O_2 during 24 hrs., again at room temperature.

Separation and purification of the mixtures of dicarboxylic acids from the oxidation products were carried out as described elsewhere (1, 3). The yield amounted to 80–90% of the theory, calculated on the hydrogenated esters.

Chromatographic Analysis

Chromatographic separation of the dicarboxylic acid mixtures was performed, according to Miss Haverkamp Begemann (3), in a glass column (approx. 50 x 1 cm.).

The water phase (stationary phase) and benzene

TABLE I

Displacement of Double Bonds During Hydrogenation of Methyl Oleate

Ester	Iodine value (Wijs)	Composition of C_6–C_{12} dicarboxylic acids obtained by oxidation with													
		KMnO₄ in acetic acid (mol %)							Ozone (mol %)						
		C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
Methyl oleate	85.4	0	0	4	96	0	0	0	0	0	3	97	0	0	0
id, hydrogenated															
5 min	78.2	0	0	13	72	13	2	0	0	0	14	73	11	2	0
10 min	74.4	0	0	21	58	18	3	0	0	3	18	58	17	4	0
15 min	63.7	0	4	21	43	22	8	2	2	7	23	39	19	7	3
25 min	52.5	0	4	26	35	23	9	3	4	8	24	27	23	9	5
35 min	48.1	0	5	21	31	24	13	6	5	10	20	29	20	10	6
55 min	42.1	0	9	22	24	22	14	9	....	....	....	....	....	....	....

phase (mobile phase) needed for the partition chromatography were prepared by shaking 3 vol. of ethanol, 4 vol. of methanol, and 3 vol. of water with 10 vol. of benzene and separating the layers. Then 8 g. of silicagel (8) were suspended in 150 ml. of the mobile phase, and 28 ml. of water phase were added gradually under shaking. The glass column was filled with the mobile phase, and the gel was added in small portions. During sedimentation the column was kept quivering by means of a vibrator, and a small flow of the mobile phase was maintained through the column.

To start the percolation the column was drained in portions of 2 ml., using gauged siphons. As soon as the liquid surface had disappeared into the silicagel, 20 mg. of dicarboxylic acid mixture, in a weighing flask dissolved in 5 ml. of mobile phase, were brought on the gel, followed by two portions of 2 ml. of the mobile phase to clean the flask. The percolation was continued regularly. The percolated fractions were titrated with 0.025N KOH, the C_8, and lower dicarboxylic acids in 4-ml. fractions. The composition of the mixtures was calculated from percolation chromatograms, as represented in Figure 1. The results are shown in Table I.

Discussion of Results

When comparing the results of the analyses of dicarboxylic acids obtained by oxidation of partially hydrogenated methyl oleate with $KMnO_4$ in acetic acid on the one hand, and with ozone on the other, it can be concluded that:

a) a considerable degradation of lower dicarboxylic acids takes place in the $KMnO_4$-oxidation process, as follows from the poor yields of adipic (C_6) and pimelic (C_7) acids in comparison with the ozonization process;

b) formation of dicarboxylic acids of lower molecular weight caused by the disruption of esters during the oxidation processes, though not absolutely inevitable, is of little importance in view of the presence of only very small amounts of suberic (C_8) acid in addition to the expected azelaic (C_9) acid in the oxidation products of pure methyl oleate;

c) the presence of equivalent molar quantities of dicarboxylic acids with more and less than nine carbon atoms in the ozonization products indicates an equal migration of the double bond of methyl oleate in both directions during hydrogenation with a nickel on kieselguhr catalyst at 180°C. in accordance with the recent work of Allen and Kiess (4).

d) oxidation experiments with $KMnO_4$ in glacial acetic acid are unsuitable for a quantitative analysis of migration phenomena of double bonds in unsaturated fatty acid esters.

Summary

The displacement of the double bond of methyl oleate during hydrogenation with a nickel-kieselguhr catalyst at 180°C. was investigated, particularly with respect to the analysis of dicarboxylic acids, obtained either by oxidation of the reaction products with $KMnO_4$ in acetic acid or by means of ozone.

In the oxidation experiments with $KMnO_4$ a considerable degradation of lower molecular dicarboxylic acids occurs that makes a quantitative analysis of the isomerization phenomena uncertain.

According to the ozonization experiments an equal migration of the double bond in both directions, toward and opposite the ester group, takes place.

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Report of the Referee Board, 1956-1957

In the year ended May 31, 1957, 38 laboratories were granted Referee Certificates among their various members, of which 33 were issued on the Cottonseed, Oil Cake and Meal, and Fatty Oils; 11 the Cottonseed and Oil Cake and Meal; two on Oil Cake and Meal and Fatty Oils; three on Oil Cake and Meal; and two on Fatty Oils.

During the year one of the laboratories, Commercial Testing Laboratories, Fort Worth, Tex., ceased its operation, and the certificate was voided. The trade associations were so notified. In addition, M. L. Hartwig, Law and Company, Montgomery, Ala., announced his retirement. He was replaced by P. C. Whittier, who also held a Referee Certificate with this laboratory.

Changes in the constitution and by-laws of the American Oil Chemists' Society have been approved, and the Referee Board is prepared to present revised operating instructions.

The chairman extends his thanks to all members of the Referee Board, to R. W. Bates, R. T. Doughtie, Jr., and to H. C. Black for the efficient and cooperative manner in which they have responded to all requests.

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