Displacement of the Double Bonds During Hydrogenation of Unsaturated Fatty Acid Methyl Esters

C. BOELHOUWER, J. GERCKENS, ONG TIAN LIE, and H. I. WATERMAN, Laboratorium voor Chemische Technologie der Technische Hogeschool, Delft, Holland

IN the literature several methods are described to investigate the possibility of a migration of double bonds during the hydrogenation of fatty oils and their derivatives. The oxidation experiments of Moore (1) and Hilditch and Vidyarthi (2) with partially hydrogenated derivatives of oleic acid indicated a displacement of the double bond with formation of $\Delta^{8,9}$ and $\Delta^{10,11}$ compounds. Their conclusions were confirmed by Scheffers (3) and Bauer and Krallis (4), but because none of these investigators confirmed their conclusions by comparative oxidation experiments of their starting materials, the question arises as to the purity of those products. Besides, the oxidation of the hydrogenated fatty acid derivatives was attended with considerable losses, and the analysis of the oxidation products had a very preliminary character.

Some years ago a new method for the determination of the place of double bonds in monounsaturated fatty acid esters was described (5), depending on a partition chromatographic analysis (6) of the dicarboxylic acids formed by an oxidation of the esters. In the experiments described below this method was applied for a more exact investigation of the migration phenomena of the double bond during the hydrogenation of methyl esters of oleic, elaidic, petroselinic, and linoleic acid.

Experimental

Starting materials for the hydrogenation experiments were:

a) Methyl oleate, prepared by methanolysis of oleic acid, isolated from tea seed oil by Bertram's method (7).
b) Methyl elaidinate, obtained from tea seed oil fatty acids, which were elaidinized, using selenium as a catalyst (8); the elaidic acid, isolated from the solid reaction products (obtained by a Twitchell separation) by a repeated recrystallization from acetone, was methanolized with methyl alcohol.
c) Methyl petroselinate, the acid being isolated from parsley seed oil (10) by Bertram's method (7).
d) Methyl linoleate, the linoleic acid being prepared by a debromination of tetrabromostearic acid (11).

Hydrogenation. Hydrogenation was executed in a small reaction tube, using approximately 10 g. of ester and 3% of a nickel on guhr catalyst (20% wt. of Ni) in each experiment. Hydrogen was introduced by means of a narrow capillary. The gas bubbles caused an intimate contact between oil, gas, and catalyst. By means of an oil bath the temperature was kept between 170° and 180°C. The course of the hydrogenation was followed by means of the refractive index; samples were withdrawn when the decrease of the refractive index indicated saturation of about 30% and 65%, respectively. The real degree of unsaturation was determined by means of the iodine value.

In other experiments nitrogen was used instead of hydrogen to investigate the influence of the nickel-kieselguhr catalyst and of the kieselguhr alone in the absence of hydrogen.

Oxidation of Reaction Products. The reaction products as well as the starting materials were oxidized by $KMnO_4$ in acetic acid solution (9); this method of oxidation gave rise to only a very small disruption of the fatty acid esters (5). To 1 part of methyl ester, dissolved in 6 to 8 parts of glacial acetic acid, were added 2 to 3 parts of finely powdered $KMnO_4$. The temperature was maintained below 50°C. by external cooling. After a few hours the acetic acid was removed by a low temperature vacuum distillation (20 mm. Hg., temperature <50°C.), the residue treated with dilute sulphuric acid and sodium bisulphite until complete decolorization, and the acids formed extracted with ether.

The ether solution was extracted with a 20% sodium carbonate solution and the extract saponified completely by boiling with a small excess of sodium hydroxide on a steam bath. The mixture of mono- and dicarboxylic acids was isolated by extraction of the acidified solution with ether. The extract was washed two or three times with concentrated brine, dried with sodium sulphate, filtered, and freed from solvent by distillation.

The monocarboxylic acids were withdrawn from the mixture by a repeated extraction with petroleum ether (boiling point 40-60°C.). The remaining mixture of dicarboxylic acids (the yield amounted to 80-90% of the theory, calculated on the hydrogenated esters) was analyzed by means of partition chromatography.

Chromatographic Analysis. Chromatographic analysis of the dicarboxylic acid mixtures was executed according to Miss Haverkamp Begemann, c.s. (5) in a glass column (50 x 1 cm.).

The water phase and benzene 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 two layers in a separating funnel. To treat the silica gel (prepared according to Gordon, Martin, and Synge (6) from pure sodium silicate) with the amount of water phase required, it is advisable to cover the gel with the benzene phase before adding the water phase; in this way evaporation losses due to the heat of adsorption, which are inevitable when treating the dry gel immediately with water phase, are avoided. In our experiments to 10 g. of silica gel, suspended in a glass-stoppered Erlenmeyer flask in 100 ml. of benzene phase, 12-14 g. of water phase were added little by little under continuous shaking. The amount of water phase must be large enough to prevent the possibility of direct adsorption of the dicarboxylic acids on the gel during the percolation process, but not so large that the silica gel loses its crumbly consistency. The wetted silica gel, suspended in the benzene phase, was then brought into the column and its content filled up uniformly by the use of a small glass pestle.

The column of silica gel must be kept covered with benzene phase to avoid evaporation losses of

TABLE I

Displacement of the Double Bonds During Hydrogenation of Fatty Acid Methyl Esters

Ester	Treatment	Reaction time, min.	Temp. °C.	Catalyst	Refractive index n_D^{45}	Iodine value (Wijs)	Composition of dicarboxylic acids obtained by oxidation with $KMnO_4$ in acetic acid (mol. %)								
							C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}[a]
Methyl oleate	....	......	......	....	....	85.0	....	....	....	....	5	95	....	....	....
Methyl oleate	Hydrogenation	20	170-180	3% Ni-guhr	....	55.2	....	....	....	....	20	35	27	11	7
Methyl oleate	Hydrogenation	37	170-180	3% Ni-guhr	....	30.2	....	....	....	....	21	26	21	15	17
Methyl elaidinate	....	......	......	....	1.4418	87.8	....	....	....	....	2	98	....	....	....
Methyl elaidinate	Hydrogenation	15	180	3% Ni-guhr	1.4391	52.0	....	....	....	....	19	50	22	7	2
Methyl elaidinate	Hydrogenation	30	180	3% Ni-guhr	1.4362	25.7	....	....	....	....	17	32	25	13	13
Methyl elaidinate	Heated in N_2-stream	240	180	3% Ni-guhr	1.4420	87.2	....	....	....	....	2	97	1	....	....
Methyl elaidinate	Heated in N_2-stream	240	225	3% Ni-guhr	1.4428	87.0	....	....	....	....	6	90	4	....	....
Methyl elaidinate	Heated in N_2-stream	240	225	3% Guhr	1.4420	87.5	....	....	....	....	2	98	....	....	....
Methyl petroselinate	....	......	......	....	1.4429	87.7	....	....	100	....	....	....	....	....	....
Methyl petroselinate	Hydrogenation	10	180	3% Ni-guhr	1.4370	64.4	....	15.0	63	19.0	3	....	....	....	....
Methyl petroselinate	Hydrogenation	25	180	3% Ni-guhr	1.4350	25.8	....	13.0	54	24.0	9	....	....	....	....
Methyl petroselinate	Heated in N_2-stream	240	225	3% Ni-guhr	1.4434	87.3	....	0.5	99	0.5	....	....	....	....	....
Methyl petroselinate	Heated in N_2-stream	240	225	3% Guhr	1.4431	87.5	....	....	100	....	....	....	....	....	....
Methyl linoleate	....	......	......	....	1.4512	174.0	....	....	....	....	2	98	....	....	....
Methyl linoleate	Hydrogenation	25	180	3% Ni-guhr	1.4459	136.2	0.5	0.5	....	....	8	40	27	9	15
Methyl linoleate	Hydrogenation	55	180	3% Ni-guhr	1.4410	96.0	....	....	....	....	10	9	10	49	22

[a] C_{12} and higher.

the water phase. To start the percolation the column is drained in portions of exactly 1 ml., using small gauged siphons. When the benzene phase has just disappeared into the silica gel, approximately 20 mg. of a mixture of dicarboxylic acids, dissolved in 5 ml. of benzene phase, are brought on the gel. These 5 ml. are followed by portions of 2 and 1 ml. benzene phase. Then the percolation is continued regularly with the benzene phase, after having introduced an overpressure (10-12 cm. Hg.) on the top of the column. The percolated fractions are titrated with 0.025 N alcoholic NaOH and phenolphthalein as an indicator.

The amounts of alkali necessary for the neutralization of the percolated fractions are plotted against the total amount of percolate, thus giving a direct impression of the dicarboxylic acids present (see Figures 1 and 2). By executing blank percolation experiments with dicarboxylic acid mixtures of known composition the nature of the percolated acids was determined. Analyses of the dicarboxylic acids obtained by oxidation of the pure starting materials ascertained the reliability of the analysis.

The composition of the percolated dicarboxylic acid mixtures was calculated from the amounts of NaOH necessary for neutralizing the succeeding acids. The percolation losses were very small and amounted to approximately 1-2% of the intake.

The results of chromatographic analyses of the different products are collected in Table I, and some of the chromatograms are represented in Figures 1 and 2.

Discussion of Results

Chromatographic analysis of mixtures of dicarboxylic acids allows a sharp separation into the composing acids as follows from the distinct peaks in the chromatograms.

The analyses of dicarboxylic acids obtained by oxidation of pure fatty acid methyl esters with $KMnO_4$ in glacial acetic acid show that the formation of acids of a lower molecular weight due to disruption of the esters during the oxidation process, though not absolutely inevitable, is of little importance and does not influence the results of the experiments.

During hydrogenation of monounsaturated fatty acid esters with a nickel on guhr catalyst at 180°C., a considerable migration of the double bond occurs, resulting in a mixture of a large number of position isomers as is shown by the chromatographic analysis of the oxidation products. Migration of the double bonds in the direction of the ester group is restricted to the nearest place and occurs only to a small extent. Migration of the double bonds in the opposite direction results in the formation of larger amounts of several isomeric acids.

When heating the esters with a nickel on guhr catalyst in a nitrogen stream, a small displacement of the double bonds takes place only at higher temperatures (225°C.). In the absence of nickel however no formation of position isomers could be detected.

Hydrogenation of linoleic acid methyl ester shows the same migration phenomena of the double bonds: migration is strongly pronounced in a direction opposite the ester group. This confirms the well known fact of the applicability of Bertram's method for the

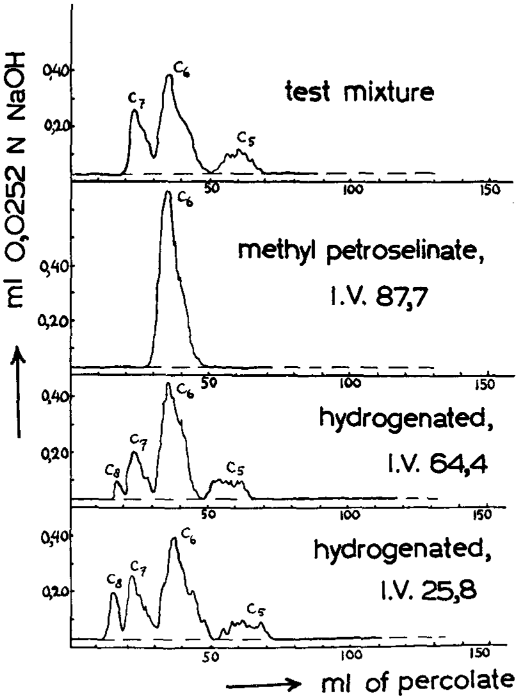

FIG. 1. Chromatographic analysis of dicarboxylic acids, obtained from partly hydrogenated methyl petroselinate.

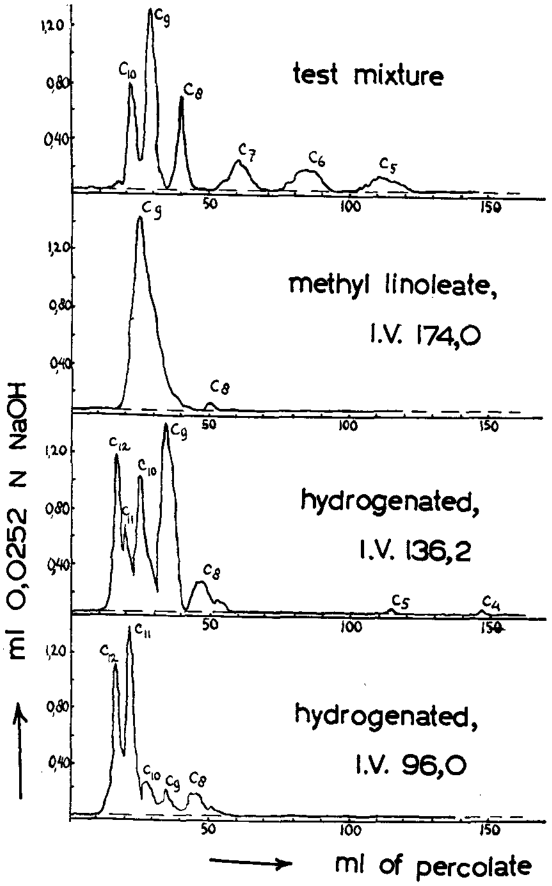

FIG. 2. Chromatographic analysis of dicarboxylic acids, obtained from partly hydrogenated methyl linoleate.

determination of saturated fatty acids in hydrogenation products of methyl esters of oleic and linoleic acid (12).

Summary

The displacement of the double bond of several unsaturated fatty acid methyl esters during hydrogenation with a nickel-kieselguhr catalyst at 180°C. was investigated. The analysis of the dicarboxylic acids (obtained by oxidation of the reaction products with $KMnO_4$ in acetic acid solution) by means of partition chromatography enabled a reliable semiquantitative determination of the position isomers formed.

During hydrogenation of methyl esters of oleic, elaidic, petroselinic, and linoleic acid formation of large amounts of position isomers was proved to occur. Migration of the double bonds in both directions took place but was in all cases strongly pronounced in a direction opposite the ester group. The place and configuration (cis or trans) of the double bonds in the starting material apparently were of little importance in this respect. It follows that hydrogenation of fatty acid esters leads to products which are far more complicated, as is generally known. This is especially of importance with respect to the application of hydrogenated fatty oils in the food industries.

Acknowledgment

The authors' thanks are due to W. v. Lookeren Campagne for assisting in the experimental part.

REFERENCES

1. Moore, C. W., J. Soc. Chem. Ind., *38*, 320 T (1919).
2. Hilditch, T. P., and Vidyarthi, N. L., Proc. Roy. Soc., London, A *122*, 552 (1929).
3. Scheffers, H. W., thesis, Delft, 1930.
4. Bauer, K. H., and Krallis, M., Z. Unters. Lebensmittel, *36*, 38 (1934).
5. Haverkamp Begemann, P., Keppler, J. G., and Boekenoogen, H. A., Rec. trav. chim., *69*, 447 (1950).
6. Gordon, A. H., Martin, A. J. P., and Synge, R. L. M., Biochem. J., *37*, 80 (1943).
7. Bertram, S. H., Rec. trav. chim., *46*, 397 (1927); thesis, Delft, 1928.
8. Bertram, S. H., Chem. Weekblad, *33*, 3, 216 (1936); Rec. trav. chim., *59*, 650 (1940).
9. Armstrong, E. F., and Hilditch, T. P., J. Soc. Chem. Ind., *44*, 43 T (1925).
10. Van Loon, J., Rec. trav. chim., *46*, 492 (1927).
11. Organic Synthesis, *22*, 75 (1942).
12. Van Vlodrop, C., thesis, Delft, 1938.

[Received June 5, 1952]

Structure of Hydroperoxides Obtained from Autoxidized Methyl Linoleate[1,2]

O. S. PRIVETT,[3] W. O. LUNDBERG,[3] N. A. KHAN,[3] WESLEY E. TOLBERG,[4] and DONALD H. WHEELER,[4] Hormel Institute of the University of Minnesota and General Mills Research Laboratories

THE course and mechanism of the autoxidation of linoleate esters have been extensively studied (3, 4, 5, 15, 16). It appears well established that the principal products formed initially under mild conditions of oxidation are monomeric monohydroperoxides, a high proportion of which contain conjugated diene systems (4, 5, 15). The geometric configurations in the double bond systems of the autoxidation products have not hitherto been established.

Previous estimates of the amount of conjugated peroxide (3, 4, 5, 15, 16) have been based on the molecular extinction coefficient for trans, trans linoleic acid (32,200 at 230-234 mμ, mole/liter, 1 cm.). The peroxides were estimated to be 70 to 75% conjugated. The remaining peroxide was assumed to be nonconjugated. However a linoleate peroxide formed at 0° with lipoxidase catalyst was reported with 97.5% conjugation on this basis (2).

The trans, trans isomers were the only pure conjugated linoleates then known. More recent work has shown that the cis, trans conjugated linoleates have lower molecular extinction coefficients, 27,400 (11) or 28,700 (17). Obviously a knowledge of the geometric

---

[1] This work was supported in part by a contract between the Office of Naval Research, Department of the Navy, and the University of Minnesota.

[2] Hormel Institute publication No. 81, and paper No. 133, Journal Series, General Mills Research Laboratories.

[3] Hormel Institute, Austin, Minn.

[4] General Mills Research Laboratories, Minneapolis, Minn.