Hydrogenation of Methyl Linolenate. II. Studies on the Structure of the Isolinoleic Acids[1]

DAMASCENE REBELLO and B. F. DAUBERT, University of Pittsburgh, Pittsburgh, Pa.

IN a previous communication (1) on the hydrogenation of methyl linolenate the isolation of fractions rich in methyl isolinoleate was reported. The purpose of this paper is to report the results of a study of the oxidation of the methyl isolinoleate fractions and identification of the oxidation products for the end in view of postulating the structure or structures of the isolinoleic acids produced on the hydrogenation of methyl linolenate under the conditions used.

Experimental

Oxidation of Isolinoleic Acid. The fraction rich in methyl isolinoleate (94.6%) was isolated as described previously (1) and subjected to an oxidation by potassium permanganate using acetone as the solvent. The method of oxidation employed was a modification of the method of Armstrong and Hilditch (2).

The ester (4.6 g.) was dissolved in 200 ml. of acetone (b.p. 55 to 56° C.) and oxidized with 28.0 g. of finely powdered potassium permanganate over a period of 14 hours. At the end of the oxidation there was no indication of non-oxidized ester. The oxidized products were subjected to a steam distillation after acidification with sulphuric acid.

The steam-volatile constituents were made very nearly anhydrous by a distillation of the sodium salts of the steam-volatile acids, over a mixture of 85% phosphoric acid and phosphorous pentoxide. The distillate obtained (0.8 g.) was fractionated in a microdistillation apparatus described by Schrader and Ritzer and nine fractions were collected. Determinations of the boiling points of the fractions indicated the presence of butyric acid in the last two fractions (b.p. 163-4° C.). Its identity was later confirmed by converting it into two derivatives (Table I). The presence of propionic acid in the initial fractions of the distillation was proved through its *p*-phenylphenacyl derivative (Table I).

The non-volatile constituents (dicarboxylic acids) were extracted with ethyl ether and crystallized from the same solvent. Oily residues of unknown composition were obtained during the recrystallizations. The solid dicarboxylic acids (1.5 g.) were extracted with cold water. The solution of water-soluble acids was evaporated to dryness and the dry solids extracted with hot benzene. The solids insoluble in benzene were crystallized from ethyl ether to give crystals of succinic acid (112 mg. m.p. 188° C.). The filtrate on concentration to a small volume and recrystallization gave a second crop of crystals. (26 mg. m.p. 186-186.5° C.). The characterization of succinic acid was done by a determination of its neutral equivalent and by means of two derivatives (Table I).

The solids soluble in benzene were crystallized from cold water. The water-soluble constituents were crystallized from chloroform; the crystals obtained melted at 135° to 150° C., thereby indicating the probable absence of glutaric acid (m.p. 98° C.) and pimelic acid (m.p. 105° C.).

The benzene-soluble solids and the water-insoluble constituents were pooled and crystallized from ethyl acetate. The crystals obtained were crystallized from water. The solids crystallized from water, as well as the dicarboxylic acids soluble in water, were subjected to counter-current extraction procedures using ethyl ether and water as the two solvents.

The water insoluble constituents were extracted in 12 separatory funnels, using 170 ml. of water and 50 ml. of ether, both solvents mutually saturated. The calculation of the quantities of the two solvents employed, was done as suggested by Bush and Densen (4). The method is based on the distribution coefficient of the dicarboxylic acids in the solvents mentioned. A total of 144 extractions were carried out and 24 fractions were collected. Each of the extract-fractions was evaporated to dryness and crystallized from benzene. The melting points of most of the crystals were determined. From a guide of the melting points of the fractions pure sebacic (6 mg. m.p. 132° C.), azelaic (152 mg. m.p. 105° C.), and suberic (89 mg. m.p. 141° C.) acids were obtained by crystallization of specific fractions from water. From the water-soluble fractions pure adipic acid was obtained by means of two counter-current extractions using 100 ml. of ether and 38 ml. of water, both mutually saturated. Five separatory funnels were employed in each set of extractions. Pure adipic acid (23 mg. m.p. 153° C.) was obtained by an initial crystallization from concentrated nitric acid of the extracts crystallized from benzene having melting points between 146° and 150° C. and subsequently from ethyl acetate.

Each of the dicarboxylic acids (azelaic, suberic, and adipic acids) was characterized by a determination of its neutralization equivalent. The identity of each of the above acids (sebacic acid included) was confirmed by its conversion to characteristic derivatives of the phenacyl type. With the exception of butyramide and di-*p*-phenylphenacyl sebacate, which were insufficient in amount, the elementary analyses of all the derivatives checked closely with those calculated for the pure esters (Table I).

Infrared Studies. Infrared spectral transmission curves were obtained for the concentrates of methyl isolinoleate (A-15, 85.4% ester; B-12-1, 95.8% ester; see previous communication (1) using a Baird Double Beam Spectrophotometer.[2] The absorption peak at 10.3 μ characteristic of a *trans*-configuration of a double bond in a straight chain molecule was obtained in both cases.

Discussion

The products of oxidation of a 94.1% concentrate of methyl isolinoleate (fraction B-10-1 Table III) (1) identified were: a) in the steam volatile fraction: propionic and butyric acids; and b) in the steam non-volatile fraction: succinic, adipic, suberic, azelaic, and sebacic acids. Attempts to ascertain the presence of glutaric and pimelic acids gave negative results.

Positional Isomerism. As reviewed earlier (1) 15 positionally isomeric isolinoleic acids are possible on

---

[1] Contribution No. 800 from the Department of Chemistry, University of Pittsburgh.

[2] Foil Miller, Department of Chemical Physics, Mellon Institute, Pittsburgh.

TABLE I

Characterization of Oxidation Products of Methyl Isolinoleate

Acid	N.E.*	Derivatives**	M.P. °C.	Formula	Elementary C	Analysis (%) H	Analysis (%) Br	Data
Propionic		p-Pp.	102^a	$C_{17}H_{16}O_3$	76.12	5.97		Calcd.
			103		76.19	5.98		Found
Butyric		p-Pp.	82,83^a	$C_{18}H_{18}O_3$	76.60	6.38		Calcd.
			84		76.60	6.24		Found
		Butyramide^b	115^a					
			113					
Succinic	59.0	Di-p-pp.	208^a	$C_{32}H_{26}O_6$	75.89	5.14		Calcd.
	58.8		207-8		76.03	5.38		Found
		Di-p-bp.	211^a		46.88	3.13	31.24	Calcd.
			211-2	$C_{20}H_{16}O_6Br_2$	46.73	2.92	31.06	Found
Sebacic		Di-p-bp.^{b}	147^a					
			146.5					
Azelaic	94.0	Di-p-bp.	130.6^a	$C_{25}H_{26}O_6Br_2$	51.56	4.47	27.48	Calcd.
	94.2		130.0		51.76	4.43	27.54	Found
		Di-p.	69.7^a	$C_{25}H_{28}O_6$	70.75	6.60		Calcd.
			69.5		71.00	6.60		Found
Suberic	87.0	Di-p-bp.	144.2^a	$C_{24}H_{24}O_6Br_2$	50.72	4.22	28.15	Calcd.
	87.3		144.2		50.95	4.04	28.09	Found
		Di-p.	102.4^a	$C_{24}H_{26}O_6$	70.24	6.34		Calcd.
			102.5		70.05	6.19		Found
Adipic	73.0	Di-p-bp.	154.5^a	$C_{22}H_{20}O_6Br_2$	48.91	3.70	29.60	Calcd.
	73.4		154.5		48.82	3.72	29.47	Found

* Neutralization Equivalent. ** p-Pp; *p*-Phenylphenacyl ester. Di-p-pp: Di-*p*-phenylphenacyl ester. Di-p-bp: Di-*p*-bromophenacyl ester. Di-p: Di-phenacyl esters.

[a] Literature values. [b] Insufficient for elementary analysis.

the hydrogenation of a single ethylenic bond in the linolenic acid molecule, assuming a shift by one carbon of either or both the remaining double bonds.

Propionic and butyric acids, found as oxidation products could result only from a cleavage of the double bonds in the 15:16 and 14:15 positions, respectively, of the isolinoleic acid isomers.

The presence of butyric acid demonstrates that a shift of the double bond in the 15:16 position has taken place towards the carboxylic end of the partially hydrogenated linolenic acid molecule. Likewise the presence of sebacic acid in the oxidation products indicates a shift of the double bond from the 9:10 to the 10:11 position. The work of van der Veen (5) in his studies on the hydrogenation of methyl linolenate clearly demonstrated this viewpoint; however this investigator did not clearly prove these shifts of double bonds to be in the resultant isolinoleic acid molecule as the oxidation studies by ozonolysis were conducted on the hydrogenated product. As such therefore the oxidation products could possibly have resulted from the various monoenoic acids present in the partially hydrogenated methyl linolenate. The present work has the advantage over the work of van der Veen in that the oxidation studies were carried out on a concentrated sample of isolinoleic acid (94.1% pure).

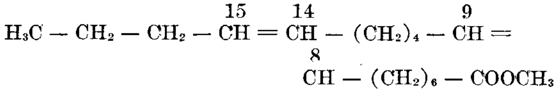
The presence of succinic acid in the oxidation products can only be accounted for on the basis of a simultaneous shift of both the double bonds in the 9:10 and 15:16 positions of the partially hydrogenated methyl linolenate towards each other. A 10,14-isolinoleic acid therefore results, whose structure is further confirmed by the presence of butyric and sebacic acids in the oxidation products.

Likewise the presence of adipic acid together with propionic and azelaic acid demonstrates the presence of a 9,15-isolinoleic acid. This acid results from a hydrogenation of the 12:13- or middle double bond of the linolenic acid molecule with no shift of the remaining double bonds.

Suberic acid could result by a fission of an octadecadienoic acid having its double bonds in the 8:9 position, assuming that the other double bond is in the 14:15 or 15:16 position. This acid could also result from the oxidation of an 8,16-isolinoleic acid. However due to the absence of acetic acid in the oxidation products, the latter isomer is not considered. Furthermore suberic acid could also result as a secondary oxidation of azelaic acid. Considering suberic acid as a product of oxidation of either or both of the 8,14- and 8,15-isolinoleic acids, the inference is that the double bond in the 9:10 position in linolenic acid has undergone a shift to the 8:9 position. As a shift of this (9:10) double bond to the 10:11 position has already been demonstrated, a shift to the 8:9 position is not entirely impossible. Pimelic acid would be the oxidation product of 8,15-isolinoleic acid. As pimelic acid was found to be absent, the presence of suberic acid can be accounted for only by the fission of an 8,14-isolinoleic acid. This is further confirmed by the presence of butyric and adipic acids, both of which could result as direct oxidation products of an 8,14-isolinoleic acid.

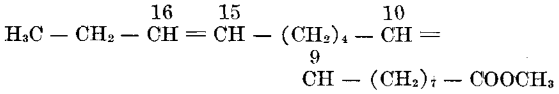
Reviewing the above, the following three isomeric isolinoleic acids (methyl esters) are shown to be formed on the hydrogenation of methyl linolenate using palladium black supported on barium sulphate as the catalyst:

8,14-isolinoleic acid:



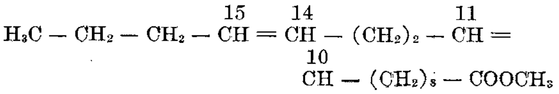
$$H_3C-CH_2-CH_2-\overset{15}{CH}=\overset{14}{CH}-(CH_2)_4-\overset{9}{CH}=\overset{8}{CH}-(CH_2)_6-COOCH_3$$

9,15-isolinoleic acid:



$$H_3C-CH_2-\overset{16}{CH}=\overset{15}{CH}-(CH_2)_4-\overset{10}{CH}=\overset{9}{CH}-(CH_2)_7-COOCH_3$$

10,14-isolinoleic acid:



$$H_3C-CH_2-CH_2-\overset{15}{CH}=\overset{14}{CH}-(CH_2)_2-\overset{11}{CH}=\overset{10}{CH}-(CH_2)_8-COOCH_3$$

It is evident from the above that the 9:10- and 15:16- double bonds of the linolenic acid undergo a shift during the hydrogenation of this acid at the 12:13-double bond, to the 8:9 and 10:11; and 14:15 positions respectively. That these shifts of both the double bonds is simultaneous is indicated by the presence of 8,14- and 10,14-isolinoleic acids.

Glutaric acid would result from the oxidation of 9,14- or 10,15-isolinoleic acids, whose presence would demonstrate the shift in part of either the 9:10- or 15:16-double bonds in linolenic acid. Glutaric acid would be oxidized to succinic acid and thus not be identified among the oxidation products. For this reason the absence of 9,14- and 10:15-isolinoleic acids is not entirely confirmed and hence these isomers may exist in a small proportion.

Configurational Isomerism. The infrared absorption spectra of two concentrates (fraction A-15, Figure 2; fraction B-12-1, Figure 3) (see paper No. 1 of this series [1]) of methyl isolinoleate revealed large absorption peaks at 10.3μ ($968\ cm^{-1}$). Lemon (6) obtained an absorption peak at the same wave length for a relatively pure sample of methyl isolinoleate, isolated by chromatographic procedures from hydrogenated linseed oil.

The peak at $968\ cm^{-1}$ has been found by various investigators for other unsaturated acids, e.g., elaidic (7) and vaccenic acid (8). It indicates a *trans*-configuration for the double bond in the unsaturated acid.

The present work confirms the work of Lemon in that at least one of the double bonds of isolinoleic acid has a *trans*-configuration. As a large number of isolinoleic acids are possible, three of which have been definitely shown to be present, it is possible that the double bonds in these octadecadienoic acids may have a *cis-cis-*, *cis-trans-*, *trans-cis-*, or a *trans-trans*-configuration.

The Twitchell lead salt-alcohol method (9) of separation gave a "solid" fraction having an iodine value (I.V., 94.4) greater than that for a monoenoic acid (theory I.V., 89.9). This seems to indicate the presence of a "solid isolinoleic" acid (17.2%) in the solid acids. It is quite likely that this acid if present has its double bonds in a *trans-trans*-configuration. The presence of a solid isolinoleic acid (12,15- isolinoleic acid) has been reported by Bauer and Ermann (7).

According to van der Veen (5), 9,15- and 10,14-isolinoleic acids are produced during the hydrogenation of methyl linolenate using palladium black as the catalyst. The present work confirms this viewpoint. The formation and presence of another isomer, 8,14-isolinoleic acid, is also indicated.

The view of various workers (1, 2, 5), that an isolinoleic acid is formed on the preferential hydrogenation of the 12:13- or middle double bond of linolenic acid is confirmed. Further it has been proved definitely that both the double bonds (9:10- and 15:16-) in the linolenic acid molecule undergo a shift by at least one carbon atom, during the partial hydrogenation of this acid. This shift in part or whole produces a *trans*-configuration in at least one of the double bonds of the isolinoleic acid isomers.

However it does not follow that other isomeric isolinoleic acids, besides the ones mentioned above (8,14-, 9,15-, 10,14-, and 10,15-octadecadienoic acids) are not formed during the hydrogenation. The isolinoleic acids which form quite a large proportion of the solid fractions crystallized at temperatures above 70° C. may have structures (positional and configurational isomers) different from the ones already proposed.

Summary

The methyl isolinoleate fraction obtained by the low temperature crystallization procedure was found to be a mixture of at least three isomers, the 8,14-, 9,15-, and 10,14- isolinoleic acids. The infrared absorption spectrum of this fraction indicated a *trans*-configuration for at least one of the double bonds of isolinoleic acid.

The Twitchell lead salt-alcohol method was found unsuitable for the determination of saturated acids, due to the presence of a "solid isolinoleic" acid in the "solid" acids separated by this method.

REFERENCES

1. Rebello and Daubert, J. Am. Oil Chemists' Soc., *28*, 177 (1951).
2. Armstrong and Hilditch, J. Soc. Chem. Ind., *44*, 43T (1925).
3. Shrader and Ritzer, Ind. Eng. Chem. Anal. Ed., *11*, 54 (1939).
4. Bush and Denson, Anal. Chem., *20*, 121 (1948).
5. van der Veen, Chem. Umschau, Fette, Olle, Wachse u Harze, *88*, 89 (1931).
6. Lemon, Can. J. Research, *27B*, 610 (1949).
7. Moore, J. Soc. Chem. Ind., *38*, 320 T (1919).
8. Rao and Daubert, J. Am. Chem. Soc., *70*, 1102 (1948).
9. Baughman and Jamieson, Oil and Fat Ind., *7*, 331 (1930).

[Received October 10, 1950]

Alkyl Hydroxyanisoles as Antioxidants

R. H. ROSENWALD and J. A. CHENICEK, Universal Oil Products Company,
Riverside, Illinois

IT has been demonstrated that the antioxidant known as butylhydroxyanisole possesses very desirable properties and is desirable in the stabilization of oils and waxes. Among these desirable properties are: a high solubility in oils, a carry-through of its antioxidant properties into baked goods, nontoxicity as witnessed by approval for use in foods (1, 2), no color, odor, or taste imparted to the substrate to which the antioxidant is added, low cost, and effectiveness in low concentrations of 0.005% to 0.02%. It has been reported that butylhydroxyanisole and the mixtures containing it more nearly meet the requirements of an ideal antioxidant than any other antioxidant studied (3).

Butylhydroxyanisole (4) is a trisubstituted benzene compound containing as substituents a butyl group, a hydroxy group, and a methoxy group. However antioxidant activity is not assured by mere presence of these three substituents for it is essential that these groups be properly arranged or oriented in the ring. Consequently it is of interest to point out the salient features so essential to obtain effec-