Conjugated Dienes and Trienes from Methyl Oleate and Methyl Linoleate[1]

THEODORE PERLSTEIN, ABNER EISNER and WALDO C. AULT,
Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Abstract

Methyl oleate and methyl linoleate were converted to conjugated dienes and trienes, respectively, by selecting and modifying the conventional procedures usually applied to the generation and characterization of fatty hydroperoxides. Conditions have been studied in the laboratory for: (a) the optimum production of hydroperoxides with a minimum of by-products, (b) the effective separation and concentration of the resulting hydroperoxide, (c) the economic reduction of the hydroperoxide mixture, (d) simple dehydration of the reduced product, and, (e) recovery of the resulting polyene-rich material. If the processing sequence is halted after the reduction step, the resulting product is a mixture of allylic hydroxy monoene or diene methyl esters. Our investigations have been extended to include studies on the methyl esters of commercial oleic acid and the mixture of methyl esters resulting from alcoholysis of lard oil. Products containing 20–25% conjugated diene and lesser proportions of conjugated triene were obtained.

Introduction

No useful process exists for the dehydrogenation of saturated fats and fatty acids to unsaturated derivatives. Theoretically dehydrogenation should be readily accomplished under suitable conditions and should afford a ready means for increasing the unsaturation of fats. However, efforts to dehydrogenate fatty materials catalytically in the presence of hydrogen acceptors, such as chloranil, have been without success (7). Moreover, efforts to introduce unsaturation by such reactions as chlorination followed by dehydrochlorination have proven impractical, partially because the specific position of the unsaturation in a fatty acid chain is usually an important factor in its properties and use. Nonspecific and random processes hold very limited promise.

In this paper we describe the results achieved by combining the reactions of autoxidation, reduction and dehydration in such a manner as to achieve a substantial conversion of monoene to conjugated diene. However, the procedure when applied to dienes was not as effective as with monoenes. The chemistry of these individual reactions is fully discussed in reviews (1,2). A flow diagram of the procedure used is shown in Figure 1.

Laboratory studies were made to determine optimum conditions for each step of the procedure when applied to the following substrates: pure methyl oleate, methyl esters of two different commercial oleic acids, lard oil, methyl esters of lard oil and methyl linoleate.

Experimental

Oxidation

In a typical experiment, 31.5 g of raffinate layer residue (7.57% peroxide) from (8A) a previous methyl oleate oxidation plus 19.2 g of fresh methyl oleate were placed in a 3-necked flask for autoxidation.

The flask was equipped with two gas dispersal tubes each entering through a side-arm and extending into the bottom. A reducing adapter tube was placed in the center arm to serve as outlet, sampling port and thermometer well.

The flask, protected from light, was immersed in an oil bath equipped with temperature controls and the bath was maintained at about 82C. Oxygen was fed into the gas dispersal tubes at a rate which was limited chiefly by foaming. Samples were taken for analysis after 6 hrs and after 22.5 hrs when the oxidation was stopped. Final analysis showed 31.65% hydroperoxide content. Liquid film infrared examination of the autoxidation product showed the hydroperoxide peak at 3400 cm^{-1} and an increase in the 970 cm^{-1} peak indicating allylic hydroperoxide and *trans*-configuration. The increase in total weight was 1.7 g, about equal to the 1.5 g increase calculated from analysis. Table I summarizes data obtained during the oxidation step with our various substrates.

Extraction

The autoxidation product obtained (51.4 g) from the above step was dissolved in 250 ml Skelly C[4] and subjected to three extractions with successive 150 ml portions of aqueous methanol (88%). The raffinate layer, when freed of solvent in a rotary evaporator, yielded 33.6 g of residue having 10.0% hydroperoxide content. It was added to 50 g fresh methyl oleate as starting material for the next experiment. The extract layer containing 17.8 g of 72.5% hydroperoxide concentrate was then ready to be reduced. Data on the extraction steps are shown in Table II.

Reduction, Dehydration and Fractionation

The extract containing the hydroperoxide concentrate was cooled in an ice-bath and 11.8 g of solid sodium bisulfite added, with stirring, over a 10-min period. Stirring was continued for 4 hr longer while the temperature of the mixture was allowed to rise to room temperature. Fifty grams of anhydrous sodium sulfate was added to the mixture which was allowed to dry overnight.

Dehydration was accomplished by refluxing in 10% V/V H_2SO_4 in methanol (3). The methanol solution of the reduced extract was freed of solid salts by filtration and the washings of filter cake were

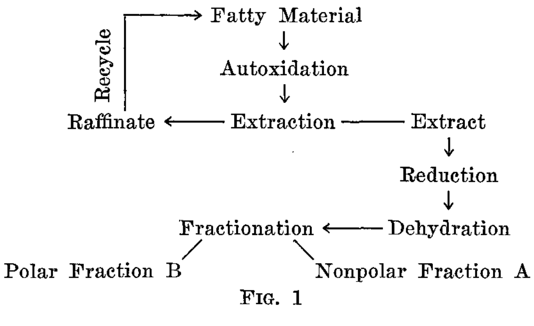

Fig. 1

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[2] E. Utiliz, Res. Dev. Div., ARS, USDA.

TABLE I

Autoxidation with O_2

Material autoxidized		Lard oil methyl esters [a]				Methyl oleate		Methyl linoleate	
Run No.		3	3E	A-1 [b]	5A	8B	9A	1	2A
Wt of starting material	g.	100.0	100.0	100.0	100.0	50.7	50.1	100.0	50.6
Hydroperoxide content	%	0.34	4.55	0.34	2.75	4.77	5.38	0.6	11.08
Wt of product withdrawn	g.	2.3	3.3	5.6	6.7	1.0	3.0	10.0	7.0
Wt of product remaining	g.	102.0	99.5	98.4	94.8	51.4	48.5	93.1	45.9
Hydroperoxide content of product	%	19.4	15.8	17.0	16.1	31.6	29.6	32.0	30.8
Hours autoxidized @ T°C		11.0 @ 82	11.0 @ 82	14.0 @ 82	23.0 @ 68	22.5 @ 82	25.0 @ 80	........[c]	10.5 @ 46

[a] Distribution in lard oil methyl ester mixture as determined by GLC was as follows: C_{14} 1.1%; C_{16} 24.9%; C_{16} monoene 4.1%; C_{18} 2.4%; C_{18} monoene 60.5%; C_{18} diene 7%. The mixture had I.V. ≅ 75, A.N. ≅ 6.2, S.N. ≅ 192.

[b] Autoxidation made with air instead of O_2.

[c] Autoxidation for 24 hr @ 38C gave only 4.2% hydroperoxide. Temp. raised to 47C and autoxidized for 15.5 hr. additional raised hydroperoxide content to 32.0%.

added to the filtrate. The volume of the extract solution was adjusted to 555 ml and 60 ml of concentrated H_2SO_4 slowly added to the stirred solution. The mixture was heated to reflux and refluxing continued for 3 hr. Nitrogen was introduced via a gas inlet tube during the refluxing period.

The cooled methanol-sulfuric acid solution of the dehydration product was extracted three times with 300 ml portions of Skelly C. The combined extracts, after being washed free of acid, dried and stripped of solvent, yielded fraction A (11.74 g). Fraction A amounted to about 70% of the total product and was composed of polyene ester isomers, plus some unreacted starting material and minor amounts of nonpolar side-reaction products. The water washes of the Skelly C extracts plus 600 ml more water were used for a threefold dilution of the methanol-sulfuric acid raffinate layer. The resulting mixture was subjected to three 300 ml methylene chloride extractions. The combined extracts, after being washed free of acid, dried and stripped of solvent, yielded fraction B (4.30 g). Fraction B, about 30% of the total product, was comprised principally of polyhydroxy esters plus small amounts of fatty acid and lactone material. Infrared examination of fractions A and B indicated the nature of the components and confirmed the effectiveness of the separation of the polar from the nonpolar components. Table III summarizes the yield data from this fraction together with those from the other experiments.

Also included in Table III are the calculated weight percent of conjugated polyene unsaturation in 3 different samples as determined by ultraviolet spectrophotometry (4). It should be realized that because of configurational isomerism, these values are approximations at best. However, in the case of autoxidized methyl oleate a more valid determination was possible. A comparison GLC analysis with known samples was made.

Autoxidation of Other Substrates

Application of the autoxidation procedure to the methyl esters of two different commercial oleic acids gave, except for a substantially longer induction period, essentially the same results as obtained with pure methyl oleate. Autoxidation of methyl esters of a distilled portion of one of these commercial oleic acids had a normal induction period suggesting that an oxidation inhibitor originally present in the commercial samples was responsible for the long induction period.

Trials with an extra winter strain commercial lard oil were not too successful. Although a 19.6% hydroperoxide content was achieved after 13 hr of autoxidation, a rise in the temperature of the substrate equal to or above that of the oil bath was observed after 4 hr of reaction time. This rise in temperature usually signified that an appreciable buildup of side-reaction products was taking place. It also indicated that the hydroperoxide decomposition rate was approaching or exceeding the rate of hydroperoxide formation. Additional difficulties were encountered with extractions. Insufficient difference in polarity between autoxidized and unautoxidized material did not permit effective fractionation. Moreover, if methanol sulfuric acid is employed in the dehydration step, alcoholysis of the glycerides takes place and the final products are methyl esters. Converting the lard oil to methyl esters (by alcoholysis with methanol using sodium methoxide as catalyst) before starting the autoxidation obviated most of the difficulties described above. The composition of the lard oil methyl ester mixture is given as a footnote to Table I.

Discussion

Although oxygen was used in most of the experiments described, other runs demonstrated that air served equally well for the autoxidations. It is generally recognized that a fixed maximum of hydroperoxide concentration can be attained and continuing the reaction serves no beneficial purpose but increases considerably, the amount of decomposition products. The problem of how to handle the unoxidized material most efficiently still remained. The adopted procedure described earlier was arrived at only after an examination of other methods. Initially

TABLE II

Extraction of Autoxidized Product from Skelly C Solution with 88%/wt MeOH–H_2O

Material autoxidized		Lard oil methyl esters				Methyl oleate		Methyl linoleate	
Run No.		3	3E	A-1	5A	8B	9A	1	2A
No. & vol. of extractions	ml.	3 × 300	2 × 300 [a]	2 × 300	3 × 300	3 × 150	3 × 150	3 × 300	3 × 150
Wt of raffinate residue	g	71.3	79.5	76.3	74.6	33.6	34.4	64.9	32.1
Hydroperoxide content	%	4.92	6.38	6.30	4.62	10.0	9.90	8.84	8.17
Wt. of extract residue	g	30.7	20.0	22.1	20.2	17.8	14.1	26.9	13.8 [b]
Hydroperoxide content	%	51.8	53.5	55.0	58.7	72.5	77.7	89.1	81.2
Percent of total hydroperoxide extracted		82.0	68.2	71.8	77.5	79.3	76.2	80.2	79.4

[a] Autoxidation product extracted with 81%/wt. EtOH–H_2O.

[b] A 25 ml sample out of 480 ml yielded 0.720 g residue. Hydroperoxide content was 81.16%.

TABLE III

Fractionation of Dehydration Products

Material autoxidized		Lard oil methyl esters				Methyl oleate		Methyl linoleate	
Run No.		3	3E	A-1	5A	8B	9A	1	2A
Wt. Skelly C extract residue Fraction A	g	18.5	14.2	12.6	13.88	11.7	8.74	10.9	6.36
Wt. CH_2Cl_2 extract residue Fraction B	g	8.3	5.7	7.7	4.30	4.3	4.00	14.8	5.82
Theory	g	29.1	18.9	20.8	18.96	16.6	12.97	24.4	11.99
Conjugated diene [a] in fraction A	%/wt	....	....	....	13.07	....	20.35[b]	....	6.60[c]

[a] Determination of conjugated unsaturation calculated from absorbance measurements obtained by UV spectrophotometry. AOCS official method Cd 7–58.

[b] From GLC data, this value is 24.8%.

[c] Also contains 7.07% conjugated triene and 1.60% conjugated tetraene calculated from UV spectrophotometry.

it was thought that it should be possible to reduce the hydroperoxide present in the mixture and then recycle the mixture of reduction products and unautoxidized material. This did not prove to be satisfactory and led to an increase in side-reaction products. Extraction of reduced autoxidation product followed by recycle of the raffinate layer also proved to be unsatisfactory. The final scheme, i.e., removal of autoxidized product from the reaction mixture by fractional extraction and recycling the raffinate layer, was found to be the most practical procedure. Moreover, the small amount of hydroperoxide left in the raffinate layer helped reduce the time required to reach maximum hydroperoxide concentration in the subsequent recycle runs.

The use of sodium bisulfite for the reduction of the autoxidation product seemed to be most practical from the standpoint of cost, convenience and effectiveness (5). Furthermore, Coleman and Swern (6) have shown that sodium bisulfite reduction of hydroperoxide results in less carbonyl and more hydroxyl formation than that obtained with any other reducing agent.

The polar fraction B obtained from the fractionation of the dehydration products contains a large amount of polyhydroxy ester. This material when utilized in a polyurethane foam formulation produced a foam that had good resistance to humid aging.

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