Summary

Variations in quantity and concentration of hydrogen peroxide were studied in epoxidation of soybean oil by using the partially preformed peracetic acid epoxidation method.

Use of a hydrogen peroxide/olefin mole ratio as low as 1.05/1 yields epoxidized soybean oil that meets the low iodine number and high epoxide content characteristics required for stabilizer-plasticizer use.

Use of a hydrogen peroxide/olefin mole ratio as low as 0.50/1 results in more than 95% hydrogen peroxide utilization and yields epoxidized soybean oil containing more than two epoxide groups per molecule. Products of this type may be of interest for recently proposed applications in alkyd, polyester, and epoxy resins.

Increasing the hydrogen peroxide concentration to 70% in epoxidation permits reduction of acetic acid usage to half that required when 50% hydrogen peroxide is used. Agitation control is also necessary for optimum results. A two-step epoxidation method can be used to avoid formation of potentially detonable mixtures in epoxidation with 70% hydrogen peroxide by the partially preformed peracetic acid method.

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[Received April 20, 1959]

Report of the Spectroscopy Committee, 1958-59

THE MAJOR ACTIVITY of the Spectroscopy Committee of the American Oil Chemists' Society during the year ending with the 50th Annual Meeting of the Society in New Orleans has been a collaborative investigation of a proposed method for the determination of *trans* isomers by means of infrared absorption. A single meeting was held during the 50th meeting of the Society in New Orleans.

Determination of trans Acids by Means of Infrared Absorption

As a collaborative test of a proposed A.O.C.S. Tentative Method for Isolated *trans* Isomers by Means of Infrared Absorption Spectrophotometry, 11 samples, including three primary standards of very high purity and eight analytical samples, were furnished each committee member as follows:

No. 1. Elaidic acid, primary standard
No. 2. Methyl elaidate, primary standard
No. 3. Trielaidin, primary standard
No. 4. Hydrogenated methyl oleate, low *trans* content
No. 5. Hydrogenated methyl oleate, high *trans* content
No. 6. Vegetable oil
No. 7. Fatty acids
No. 8. Methyl esters
No. 9. Hydrogenated soybean oil, low *trans* content
No. 10. Hydrogenated soybean oil, high *trans* content
No. 11. Hydrogenated vegetable oil

Each committee member was asked to analyze each sample at least in duplicate on as many different infrared spectrophotometers as were available to him. Results, received from all 10 members of the Spectroscopy Committee, are given in the attached table.

Committee Meeting April 21, 1959

The committee met in the Mardi Gras room of the Roosevelt hotel on April 21, 1959, with nine of the 10 committee members present (or represented), and five guests: members—Robert R. Allen, Anderson Clayton and Company; J. R. Chipault, Hormel Institute; N. D. Fulton, Procter and Gamble Company; Samuel F. Herb, Eastern Utilization Research and Development Division; William E. Link, Archer-Daniels-Midland Company; Donald E. Reid (for Robert D. Mair), Hercules Powder Company; Donald H. Wheeler, General Mills Inc.; Hans Wolff, A. E. Staley Manufacturing Company; and Robert T. O'Connor, Southern Utilization Research and Development Division; and guests—A. S. Fenton, Procter and Gamble Company; David Firestone, Food and Drug Administration; Marvin Formo, Archer-Daniels-Midland Company; Donald F. Kuemmel, Procter and Gamble Company; and Elizabeth McCall, Southern Utilization Research and Development Division.

Discussion of Results of Collaborative Tests. The recently completed collaborative work to test a proposed method for isolated *trans* isomers by infrared absorption was discussed in detail, and the following conclusions were agreed upon.

a) Inasmuch as infrared absorption measurements can and will be made with several instruments there is no object in citing a specific procedure for any one (or more) particular instrument. The proposed tentative method should be sufficiently broad to include any spectrophotometer meeting minimum requirements.

b) Inasmuch as the results on the analysis of acids do not show satisfactory agreement, the proposed tentative method should not include within its scope the analysis of acids. Acids can, of course, be analyzed by first converting them to their methyl esters.

c) Further work should be initiated to devise a satisfactory method for the direct analysis of acids. The committee feels that this analysis should also be attempted by some "baseline" type of background correction rather than a correction based on a measured oleic acid standard. Further collaborative work is recommended.

d) As the proposed infrared method is to be a general one, for use on all infrared spectrophotometers, it is not possible to supply values for absorptivities to be used in calculation of percentage of isolated *trans* (as such values differ widely for different instruments and even for the same models unless measured with exact programming). Therefore the primary standards, methyl elaidate and trielaidin, will be required for calibration of instruments by all users of the proposed tentative method. However such primary standards will not usually be readily available. Therefore the committee believes that it

TABLE I

Spectroscopy Committee Collaborative Testing for Isolated *trans* June 1959

Collaborator #	Date and/or instrument	Elaidic acid #1	Methyl elaidate #2	Trielaidin #3	Hydrogenated methyl oleate #4		Deviation from mean	Hydrogenated methyl oleate #5		Deviation from mean	Vegetable oil #6		Deviation from mean	Fatty acids #7		Deviation from mean
		a	a	a	a	% Trans.		a	% Trans.		a	% Trans.		a	% Trans.	
1	Perkin-Elmer 21	0.650	0.469	0.461	0.108	23.0	0.3	0.190	40.6	0.8	0.193	41.7	0.1	0.185[a]	36.6	0.7
2	Perkin-Elmer 21															
	2/9	0.482[c]		0.475	0.113	23.7	0.4	0.203	42.5	1.1	0.200	41.9	0.1	0.230[b]	42.1	4.8
	3/6	0.487	0.478	0.478	0.116	24.3	1.0	0.206	43.2	1.8	0.200	41.9	0.1	0.228	41.8	4.5
3	Perkin-Elmer 21															
	Inst. #451	0.409[c]	0.422	0.408	0.102	24.2	0.9	0.178	42.3	0.9	0.179	43.9	2.1	0.146[c]	35.7	1.6
	Inst. #605	0.424	0.429	0.419	0.107	25.2	1.9	0.180	42.0	0.6	0.188	45.0	3.2	0.152	35.9	1.4
4	Perkin-Elmer 21	0.661	0.452	0.458	0.108	23.4	0.5	0.190	42.1	0.7	0.196	42.8	1.0	0.201[b]	38.5	1.2
5	IR4	0.478[c]	0.464	0.455	0.108	23.8	0.1	0.196	42.4	1.0	0.189	41.4	0.4	0.148[c]	30.8	6.5
	IR5	0.448	0.454	0.442	0.099	21.9	1.4	0.176	38.9	2.5	0.181	40.8	1.0	0.152	33.9	3.4
6	1/29	0.663	0.480	0.467	0.096	20.1	3.2	0.194	40.4	1.0	0.194	41.7	0.1	0.206[b]	38.5	1.2
	IR4 1/30	0.668	0.488	0.472	0.115	23.7	0.4	0.201	41.2	0.2	0.196	41.5	0.3	0.213	39.4	2.1
	3/14	0.682	0.480	0.492	0.114	23.8	0.5	0.197	41.4	0.0	0.200	40.5	1.3	0.201	37.1	0.2
7	Perkin-Elmer	0.493[d]	0.457	0.438	0.103	22.6	0.7	0.182	39.9	1.5	0.182	41.4	0.4	0.186[d]	37.6	
	21	0.484	0.440	0.428	0.102	23.1	0.2	0.175	39.7	1.7	0.176	40.4	1.4	0.192	39.9	0.3
																2.6
8	Perkin-Elmer 21	0.651	0.457	0.447	0.106	23.2	0.1	0.188	41.1	0.3	0.186	41.7	0.1	0.196[b]	38.1	0.8
9	Perkin-Elmer 21	0.643	0.460	0.455	0.108	23.5	0.2	0.193	42.0	0.6	0.191	41.9	0.1	0.183[a]	36.6	0.7
10	Perkin-Elmer 21	0.724	0.487	0.483	0.116	23.8	0.5	0.209	43.0	1.6	0.195	40.4	1.4	0.186[b]	34.0	3.3
11	Average					23.3	0.77		41.4	1.02		41.8	0.82		37.3	2.21
12	Standard-deviation						1.10			1.20			1.19			2.83

					Methyl esters #8		Deviation from mean	Hydrogenated soybean oil #9		Deviation from mean	Hydrogenated soybean oil #10		Deviation from mean	Hydrogenated vegetable oil #11		Deviation from mean
		a	a	a	a	% Trans.		a	% Trans.		a	% Trans.		a	% Trans.	
1	Perkin-Elmer 21	0.650	0.469	0.461	0.162	34.6	0.4	0.056	12.1	0.3	0.195	42.3	1.2	0.119	25.8	0.2
2	Perkin-Elmer 21															
	2/9	0.482[c]		0.475	0.172	36.0	1.0	0.062	13.0	0.6	0.211	44.3	0.8	0.122	25.6	0.4
	3/6	0.487	0.478	0.478	0.168	35.2	0.2	0.060	12.5	0.1	0.210	44.0	0.5	0.125	26.2	0.2
3	Perkin-Elmer 21															
	Inst. #451	0.409[c]	0.422	0.408	0.151	35.8	0.8	0.054	13.4	1.0	0.186	45.7	2.2	0.112	27.4	1.4
	Inst. #605	0.424	0.429	0.419	0.158	36.7	1.7	0.054	12.8	0.4	0.188	44.8	1.3	0.111	26.5	0.5
4	Perkin-Elmer 21	0.661	0.452	0.458	0.161	35.6	0.6	0.057	12.4	0.0	0.190	41.6	1.9	0.115	25.1	0.9
5	IR4	0.478[c]	0.464	0.455	0.162	34.9	0.1	0.056	12.2	0.2	0.196	43.0	0.5	0.116	25.4	0.6
	IR5	0.448	0.454	0.442	0.152	33.7	1.3	0.054	12.2	0.2	0.188	42.5	1.0	0.110	25.0	1.0
6	1/29	0.663	0.480	0.467	0.169	35.2	0.2	0.054	11.6	0.8	0.204	43.8	0.3	0.126	27.0	1.0
	IR4 1/30	0.668	0.488	0.472	0.171	35.0	0.0	0.058	12.4	0.0	0.212	44.9	1.4	0.128	27.1	1.1
	3/14	0.682	0.480	0.492	0.169	35.2	0.2	0.061	12.4	0.0	0.212	43.2	0.3	0.125	25.5	0.5
7	Perkin-Elmer	0.493[d]	0.457	0.438	0.156	34.2	0.8	0.054	12.4	0.0	0.190	43.4	0.1			
	21	0.484	0.440	0.428	0.152	34.6	0.4	0.050	11.7	0.7	0.183	42.8	0.7	0.116	26.6	0.6
														0.110	25.7	0.3
8	Perkin-Elmer 21	0.651	0.457	0.447	0.158	34.7	0.3	0.054	12.1	0.3	0.194	43.3	0.2	0.114	25.6	0.4
9	Perkin-Elmer 21	0.643	0.460	0.455	0.161	35.1	0.1	0.057	12.5	0.1	0.200	44.0	0.5	0.120	26.2	0.2
10	Perkin-Elmer 21	0.724	0.487	0.483	0.167	34.3	0.7	0.061	12.6	0.2	0.206	42.5	1.0	0.125	25.9	0.1
11	Average					35.0	0.55		12.4	0.31		43.5	0.87		26.0	0.59
12	Standard-deviation						0.72			0.43			1.77			0.70

Absorptivity corrected by: [a] oleic acid value published; [b] oleic acid value determined by collaborator; [c] base-line technique; [d] oleic acid in reference beam.

(or some other group within the Society) should arrange to supply secondary standards which will be calibrated against the primary standards available to the committee.

e) As a general method is being described, it is not possible to specify in detail such factors as exact slit-width, scanning speed, etc. However the committee feels that the method should contain some precaution (or some reference to a standard set of requirements, for infrared quantitative absorption) *that standard procedures for quantitative* infrared spectrophotometry must be observed, *i.e.*, that slit-width must not be so large that sufficient resolution is not obtained, scanning speeds must not be so fast that accurate pen response is not obtained, etc. A reference to American Society for Testing Materials standard requirements might suffice.

f) A base-line technique requiring the drawing of a base-line tangent to the infrared spectrum is probably theoretically

preferable to a line drawn between two arbitrarily selected points. However this latter technique is much more reproducible between various laboratories and, in an analytical procedure where the same technique is applied to standards and analytical samples, is probably more reproducible and accurate than the tangent curve. It is therefore recommended for the proposed tentative method.

g) With the above factors considered and incorporated, the committee recommends that the method be submitted to the Uniform Methods Committee for inclusion as a Tentative Method in the American Oil Chemists' Society Official Methods.

The complete method, amended as suggested by the action of the committee at the New Orleans meeting, is attached to and made a part of this report.

Other Committee Discussions and Future Planning. It was announced at the April 21st meeting of the committee in New Orleans that the changes proposed by the committee in the Official Method for the Determination of Polyunsaturated Fatty Acids to insure greater safety while using this procedure (1) have been accepted by the Uniform Methods Committee and will be incorporated into A.O.C.S. Official Method Cd 7-58.

The committee decided that collaborative tests to extend the scope of the infrared absorption method for isolated *trans* to the direct analysis of long-chain fatty acids should be the next activity. It was decided also that efforts to make the secondary standards, required by users of this method, readily available should be expedited.

At a previous meeting of the Spectroscopy Committee (1) it was suggested that the committee could perform a valuable service to the fat and oil industry by acting as a central agency for the collection, examination, and dissemination of infrared spectra of fatty materials from all sources. The collection of spectra appears quite feasible, but several problems arise in connection with their reproduction and distribution.

At the April 21 meeting in New Orleans it was pointed out that the Coblentz Society has initiated a system of collection and dissemination of infrared spectra and have several "collectors" over the country. Members of the Spectroscopy Committee or any members of the Society could submit spectra to be transmitted to the Coblentz Society. In this manner the spectra would be made available to any member of the Society and to the entire fat and oil industry. It was decided that spectra should be submitted to the chairman of the Spectroscopy Committee, who is already acting as one of the collectors of infrared spectra for the Coblentz Society. The committee urges members throughout the A.O.C.S. to participate in this activity. Spectra may be submitted to the chairman of the Spectroscopy Committee and details of the plan, requirements for spectra to be submitted, etc., may be obtained from him.

Acknowledgment

The Spectroscopy Committee is aware that, particularly in its collaborative testing program, it is indebted to several individuals for assistance in making spectral measurements and computations and in offering suggestions. The service of these individuals is gratefully acknowledged. The chairman, in particular, wishes to acknowledge the considerable assistance of Miss Elizabeth R. McCall in compiling, recomputing, and arranging the collaborative data for the preparation of the table included in this report.

ROBERT T. O'CONNOR, chairman

REFERENCE

1. Report of the Spectroscopy Committee, 1957–58, J. Am. Oil Chemists' Soc., *35*, 593–596, 1958.

A.O.C.S. Tentative Method

Isolated Trans Isomers

Infrared Spectrophotometric Method

Definition. In most naturally-occurring vegetable fats and oils, unsaturated constituents contain only isolated, *i.e.*, nonconjugated, double bonds in the *cis* configuration. These *cis* bonds may be isomerized to the *trans* configuration during extraction and processing procedures. Oxidation and partial hydrogenation promote isomerization from the naturally-occurring *cis* to the *trans* isomers. Animal and marine fats may contain measurable amounts of naturally-occurring *trans* isomers. Isolated *trans* bonds are measured in an infrared spectrophotometer. An absorption band with maximum at about 10.3 μ, arising from a C-H deformation about a *trans* double bond, is exhibited in the spectra of all compounds containing an isolated *trans* group. This band is not observed in the spectra of the corresponding *cis* and saturated compounds. Measurement of the intensity of this absorption band under analytically controlled conditions is the basis for a quantitative method for the determination of isolated *trans* content.

Scope. This method is applicable to the determination of isolated *trans* bonds in natural or processed long-chain esters and triglycerides which contain only small amounts (less than 5%) of conjugated materials. The spectra of long-chain fatty acids exhibit a band of medium intensity at about 10.6 μ, arising from a vibration of the carboxyl group. The method as described is not applicable to these materials. Long-chain fatty acids can, of course, be analyzed by converting them to their methyl esters prior to infrared measurements. This method is not applicable, or is applicable only with specific precautions, to fats and oils containing large quantities (over 5%) of conjugated unsaturation, such as tung oil; to materials containing functional groups which modify the intensity of the C-H deformation about the *trans* double bond, such as castor oil containing ricinoleic acid or its geometrical isomer ricinelaidic acid (12-hydroxy-9-octadecanoic acid); to mixed glycerides having long and short chain moieties, such as diacetostearin, nor, in general, to any materials containing constituents which have functional groups which give rise to specific absorption bands at or sufficiently close to interfere with the 10.3 μ band of the C-H deformation of the isolated *trans* double bond.

A. *Apparatus*

1. Infrared spectrophotometer covering the spectral region about 9 to 11 μ, with wavelength scale readable to 0.01 μ, and equipped with cell compartment for holding 0.02 to 2.00-mm. cells.

Any of several commercially available infrared spectrophotometers are satisfactory. The analysis is probably most conveniently performed by use of an automatic recording instrument of the split-beam type, such as the Perkin-Elmer Model 21, Beckman Models IR-4 or IR-7, Baird Atomic Model 4-55, or of the memory type of recording, such as Beckman Instruments Models IR-3 or IR-2-T. The analyses can

be made satisfactorily also with the smaller model instruments available from these companies or on nonrecording or null-type instruments available, such as the Perkin-Elmer Model 12-C or Beckman Instruments Model IR-2. Whichever instrument is selected should be checked for wavelength and photometric-scale accuracy by the manufacturer's instructions. The absorptivities of the primary standards (see D below) must be established for the specific instrument used for the determination. Once established, these values can be used for a period of time without further checking although it is advisable, for highest quantitative accuracy, to remeasure the absorptivities from time to time by using the appropriate standard.

2. *Absorption Cells:* Fixed thickness absorption cells with NaCl or KBr windows from 0.2 to 2.0 mm. For use in null type of instruments pairs of cells matched to within 0.01 absorbance units are required. In the split-beam type of instruments electronic balance of the two beams with both cells filled with the CS_2 solvent to within these limits should be attained.

3. *Volumetric Flasks:* 5-ml. and 10-ml. volume accurately calibrated.

4. *Hypodermic Syringes:* With blunted needles for filling absorption cells.

5. *Chart Paper:* Linear in either wave number or wave-length, depending upon the instrument used and calibrated in either transmittance or absorbance.

6. *Analytical Balance:* Capable of weighing 0.2 g. to an accuracy of ± 0.0002 g.

B. *Reagents*

1. *Carbon Disulfide:* Dry, A.C.S. grade (Note 1).

2. *Primary Standards, Methyl Elaidate and Trielaidin:* As the entire quantitative accuracy of the procedure depends upon the absorptivity values obtained from the primary standards, these materials must be of highest possible purity, 99+%.

3. *Secondary Standards:* As samples of sufficiently pure methyl elaidate and of trielaidin are not readily available, secondary ester and triglyceride standards may be used. These secondary standards are materials containing a known proportion of the *trans*-isomer calibrated against the primary standard (Note 2).

C. *Preparation of Solutions of Samples and Standards*

Weigh accurately to ± 0.0002 g. approximately 0.2000 g. of standard or sample into a glass-stoppered, 10-ml. volumetric flask. Dilute to volume with carbon disulfide, and mix thoroughly. Concentrations should be adjusted so that with the absorption cells selected a transmittance between 20 and 70% at the *trans* absorption maximum will be obtained.

Solid fats must be melted on a steam bath and mixed before sampling. Samples that appear cloudy must be filtered. If the diluted sample appears cloudy because of the presence of water, add a small quantity of anhydrous sodium sulfate, mix, and allow to settle before removing the sample for analysis.

D. *Procedure*

Fill a clean absorption cell with carbon disulfide solvent and a matching cell with the prepared sample or standard solution, using a hypodermic syringe. With the cell in an upright position inject the sample from the bottom, allowing any trapped air bubbles

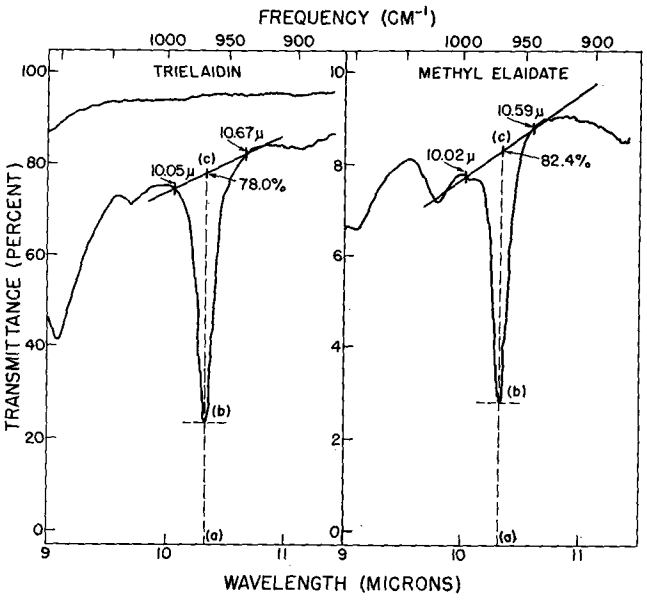

FIG. 1.

to pass up through the cell. Place the cell in the sample holder of the spectrophotometer. Measure the transmittance or absorbance (Note 3) over the region 9 to 11 μ. The exact programming of the instrument to obtain this curve will depend upon the particular instrument selected. The basic principle is that once the transmittance (or absorbance) curve is obtained for the primary standard, all samples subsequently analyzed must be measured with the same instrument with all programming controls set at identical positions. It is not practical to attempt to specify any exact operating conditions for the numerous infrared spectrophotometers commercially available and suitable for measurements for these analyses. However the analyst is cautioned that established techniques must be employed in any method for quantitative analysis by means of infrared absorption spectra. For example, the slit-widths must not be too wide to permit sufficient resolution; the scanning speeds must not be so fast as to prevent adequate pen response, etc. (Note 4).

Once a curve has been obtained for the required standard, it need not be repeated as long as the same instrument can be used with the same programming controls. However, for highest accuracy control, it is recommended that the standard be rechecked from time to time, especially if any adjustment in the instrument has been made necessary, *i.e.*, replacement of glower, detector, etc. If, for any reason, the exact programming cannot be duplicated when measuring a specific sample, the calibration curve from the standard must be repeated and new values read from it must be used for analyses.

The transmittance (or absorbance) curves are obtained for each sample in the same manner as for the standard. If esters are being analyzed, a curve of the ester standard is required. If triglycerides are being analyzed, the trielaidin standard should be used to obtain the standard curve.

Analysis of Esters and Triglycerides: From the charts of the primary standard methyl elaidate and/or trielaidin or the appropriate secondary ester and/or triglyceride standard, and for each sample

read the transmittance at the 10.36 μ maximum, convert to absorbance, and calculate the absorptivities. On the charts draw a line through the absorption peak from 10.02 μ to 10.59 μ for methyl esters (or from 10.05 μ to 10.67 μ for triglycerides). Measure the distance from the zero line of the recorder chart to the absorption peak (ab, Figure 1). Calculate the fractional transmission (bc) as the distance to the absorption peak (ab) divided by the distance to the base line (ac), convert to absorbance, and calculate the "background corrected absorptivity." Calculate the *% trans* isomer as methyl elaidate (or trielaidin) from the equation:

$$\%\ trans \text{ as methyl elaidate (or trielaidin)} = \frac{[a]\text{sample (background corrected)}}{[a]\text{methyl elaidate (or trielaidin)}} \times 100$$
(background corrected)

where a = absorptivity = A/bc

A = absorbance = log 1/T

b = internal cell length in centimeters

c = concentration of solution in g./l.

NOTE 1. Prolonged breathing of CS_2 vapors is dangerous. This solvent should be handled only under conditions which provide adequate ventilation, preferably under a chemical hood.

NOTE 2. Samples of these secondary standards will be made available through the Society. Questions regarding them should be addressed to the chairman of the Spectroscopy Committee, A.O.C.S., Box 19687, New Orleans 19, La.

NOTE 3. All nomenclature and symbols used throughout this method and those suggested by the Joint Committee on Nomenclature in Applied Spectroscopy (Anal. Chem., *24*, 1349–1354 [1952]) and as adopted by the American Society for Testing Materials "Tentative Definition of Terms and Symbols Relating to Absorption Spectroscopy" (F-131-57-T).

NOTE 4. For this purpose reference is made to the American Society for Testing Materials, Committee E-13, on Absorption Spectroscopy publication, "Proposed Recommended Practices for General Techniques of Infrared Quantitative Analysis," copies of which may be obtained from A.S.T.M. Headquarters, 1916 Race street, Philadelphia 3, Pa.

Cyclization of Linolenic Acid by Alkali Isomerization[1]

C. R. SCHOLFIELD and J. C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois

ALTHOUGH the conjugated dienoic acids formed by alkali isomerization of linoleic acid are rather stable upon further heating with alkali, the products from linolenic acid are not. Prolonged heating of alkali-isomerized linolenic acid decreases the ultraviolet absorption in both the diene and triene regions. For example, Bradley and Richardson (1) showed that with linseed oil triene conjugation reaches a maximum and decreases during heating with NaOH in ethylene glycol, diethylene glycol, or water. Mitchell *et al.* (6) reported that in the low concentration used for analytical determinations the absorption resulting from linolenic acid at both 234 mμ and 268 mμ decreases after about 15 min. at 180°.

Kass and Burr (3) isolated pseudo-eleostearic acid (10,12,14-octadecatrienoic acid) from linseed oil isomerized with alkali. Previously unpublished work of this laboratory (4) suggested the presence of a cyclic monomer. Pseudo-eleostearic acid is however the only compound that has been obtained in a pure state from alkali-isomerized linolenic acid, and the nature of the other products has not been determined. In this paper it is shown that prolonged treatment of linolenic acid with alkaline ethylene glycol produces a large amount of cyclic monomeric material together with small amounts of dimeric and other products. The monomer is believed to be similar to the one MacDonald (5) obtained from linseed oil and to those Paschke and Wheeler (10) and Rivett (11) obtained from eleostearates by heat treatment.

Experimental

Preparation and Isomerization of Methyl Linolenate. A concentrate containing 85% of methyl linolenate was prepared from perilla oil esters by the urea complex separation procedure of Parker and Swern (9). Pure methyl linolenate was prepared from this concentrate by countercurrent distribution between acetonitrile and pentane-hexane. Details of this preparation will be described in another paper (12). The resulting product contained 100% methyl linolenate as measured by analytical alkali-isomerization. Gas chromatography indicated only a trace of impurity (<0.01%), which was probably linoleate.

A mixture of 30 g. of methyl linolenate, 30 g. of potassium hydroxide, and 125 ml. of ethylene glycol was heated for 7 hrs. at 200°C. under nitrogen. After cooling to 100°C., water was added and the reaction was refluxed for a short time. The reaction mixture was cooled and acidified with dilute H_2SO_4. The acids were dissolved in ethyl ether, washed free of H_2SO_4 with water, and dried over sodium sulfate. This procedure was repeated with another 30-g. portion of methyl linolenate, the two ether solutions were combined, and diazomethane was added to form methyl esters. After the evaporation of the solvent the yield was 55.8 g. (93%).

Fractionation of Isomerized Esters. A solution of 90 g. of urea in 300 ml. of methanol was added to the isomerized esters, and the mixture was warmed to reflux and allowed to cool to room temperature. The urea adduct was removed by filtration on a Buchner funnel and washed with ethyl ether. This ether was collected separately from the methanol filtrate. The three fractions were treated with water containing a small amount of hydrochloric acid, and the esters were recovered by extraction with ethyl ether. The ether solutions were washed with water until neutral and dried over sodium sulfate. The solvent was removed under vacuum. The weights of material recovered in the fractions were: adduct, 2.40 g.; methanol filtrate, 36.20 g.; ether wash, 14.50 g. Infrared and ultraviolet absorptions of the fractions recovered from the methanol filtrate and ether wash were quite similar, and these fractions were combined. This combined material was again treated

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