tometric method, the errors introduced from this source in the analysis of ordinary samples are undoubtedly insignificant. Thus the amounts of oxidized linolenate likely to be present in animal fats are so small that their contribution to the total observed tetraenoic absorption after isomerization could hardly affect the value obtained for arachidonic acid. In the ordinary analysis of vegetable oils high in linolenic acid, observed tetraenoic conjugation after isomerization may be simply discounted, except as an index of the state of oxidation of the oil.

Fortunately, the amount of triene conjugation realized for even relatively large amounts of oxidized linoleic acid on alkali isomerization is low and contributes only small errors to the amounts of spectrophotometrically determined linolenic acid. The development of these bands is probably of analytical significance only in the analysis of pure preparations of polyunsaturated acids and their compounds, where it may erroneously indicate the presence of linolenic or a tetraenoic acid. The more highly unsaturated fractions obtained by crystallization or distillation techniques may similarly be in error when spectrophotometrically analyzed. In these cases some evaluation of the amount of conjugated absorption contributed by the oxidized components may be obtained by observing the degree of development of the bands on heating in the absence of alkali.

No interference from anomalous tetraenoic conjugation, arising from oxidized constituents of vegetable oils on alkali-isomerixation, is to be expected in the previously cited test of Beadle *et al.* (7) for the detection of lard in admixture with hydrogenated vegetable oil shortenings since hydrogenation should completely destroy such constituents. In compounded shortenings containing unhydrogenated or mildly hydrogenated vegetable oils, some measure of the amounts of tetraenoic conjugation contributed by the vegetable oil fraction may be obtained by subjecting the fatty acids of the sample to the heating test.

While the findings reported here are of only minor importance in the everyday analysis of vegetable oils, they may be of considerable significance in special studies, for example on autoxidation behavior, stability, and flavor constituents.

Summary

It has been shown that the low-intensity absorption bands characteristic of conjugated tetraenoic and trienoic fatty acids frequently encountered in the ultra-violet spectra of alkali-isomerized vegetable oils prepared by ordinary commercial or laboratory extraction techniques have their probable origin in oxidation products of linolenic and linoleic acid, respectively. Similar bands are found in the spectra of mildly autoxidized preparations of pure linolenic and linoleic acids after either alkali-isomerization or heating at 180°C. in neutral ethylene glycol.

Tetraenoic and trienoic conjugation formed from oxidation products of linolenic and linoleic acids during alkali-isomerization can be differentiated from the tetraenoic and trienoic conjugation produced by alkali-isomerization of arachidonic and linolenic acids, respectively, by spectrophotometric examination of the sample after heating in neutral ethylene glycol. Essentially equal amounts of conjugation are formed from the fatty acid oxidation products on heating and on alkali-isomerization while no conjugation is obtained from arachidonic and linolenic acids on heating in the absence of alkali.

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Report of the Refining Committee 1948-1949

THE activities of the Refining Committee during the past year have been largely concerned with a further investigation of the centrifuge method as applied to degummed soybean oil and an attempt to improve the results by the standard A.O.C.S. Refining Method on degummed soybean oil. The different projects may be summarized as follows:

At the New Orleans meeting it was suggested that a demonstration of the centrifuge method of refining be scheduled and that those members of the Refining Committee who were interested either be present or send representatives. In August a meeting was held in the Hammond laboratories of Lever Brothers Company, at which the centrifuge method was demonstrated by C. J. Carmack. Attendance at this meeting was excellent, and those individuals present made a number of constructive suggestions.

In October the Northern Regional Laboratory sent out a series of four degummed soybean oils, two of the expeller type and two of the solvent extracted type for collaborative refining by the members of the committee. A total of 11 laboratories reported on this collaborative work, and the general results were about the same as those previously observed. It was found, however, that many of the members had considerable difficulty in refining the degummed expeller oils by the standard A.O.C.S. Method, which was used as a comparison with the centrifuge results.

At the New Orleans meeting Mr. Mays had reported on a modification of the centrifuge method which depends upon the refining of the oils by the standard A.O.C.S. procedure, separating the foots, and centrifuging them in the Servall machine. A committee, under the chairmanship of J. R. Mays, was appointed and some work with this method was carried out. A report was submitted at the New York meeting.

N. W. Ziels and his small subcommittee presented a report at the New York meeting covering work with the cone-type agitator in the centrifuge method as well as a proposed modification in which both the refining and bleaching work would be carried out at room temperature. The results indicated that while it appeared possible to refine with the cone agitator with temperatures of 100° F. and below, the cold bleaching was not successful.

The results of the work on the two types of agitators during the year indicated that both gave reproducible results and that low temperature refining with the cone agitator gave reproducible results. At the New York meeting Mr. Ziels exhibited a multiple paddle machine fitted with cone agitators to be used with the centrifuge method, and Mr. Cole, the designer and builder, was present. It was decided that experimental work would be carried out with this machine in the Lever Brothers laboratories and a report made to the committee at a later date. This work is still under way, and it is not intended to make a formal report at the New Orleans meeting.

In view of the difficulty with the standard A.O.C.S. Method on degummed expeller oils, three members of the committee volunteered to check this method and to investigate the use of an intermediate excess (0.15% as 12° lye) in the refining. Mr. Mays' committee on the modified centrifuge method also agreed to run check tests on the samples of degummed expeller oils. A report covering this work, together with the results of a referee sample of degummed expeller oil in which the intermediate excess was also employed, were reported to the committee in a report issued March 24, 1949. The results showed clearly that the method was considerably improved by the use of the intermediate excess.

As a result of a vote of the members the Refining Committee recommends to the Uniform Methods Committee that a new tentative method for the refining of degummed expeller soybean oils only be established in which the excesses to be used are 0.15% and 0.20% NaOH as 12° lye.

E. M. James.

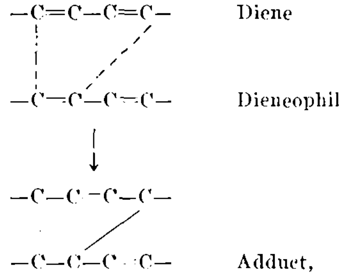
Thermal Polymerization of Unsaturated Fatty Esters Normal Methyl Linoleate*[1]

R. F. PASCHKE and D. H. WHEELER, General Mills inc., Minneapolis, Minn.

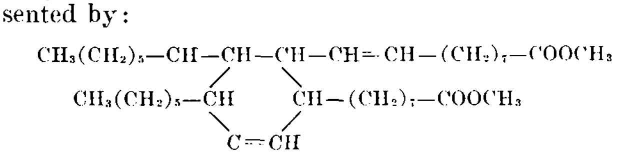
Introduction

THE knowledge of the reactions involved in the thermal polymerization of drying oils has increased considerably during the past 10 years. This has been largely due to the study of the thermal polymerization of the simple monohydric alcohol esters of the unsaturated esters of the drying oil acids. The earlier work of Kino (1), Kappelmeier (2), Steger and Van Loon (3), and Brod, France, and Evans (4) all pointed to the formation of a polymer which was largely dimer when the methyl or ethyl esters of polyunsaturated acids were polymerized by heat.

Bradley and Johnston (5) confirmed dimerization as the principal polymerization reaction of the methyl esters from olive, dehydrated castor, soybean, linseed, and tung oils. These same workers (6) subsequently isolated a methyl linoleate dimer from the polymerized methyl ester of dehydrated castor oil acids. Bradley and Richardson (7) followed the development of conjugation during thermal polymerization and found that conjugation reached a low equilibrium value when non-conjugated esters were used as starting material. This fact, together with the properties of the dimers from non-conjugated esters, was considered by Bradley and Johnston to be confirmation of the Scheiber (8) theory that non-conjugated linoleic and linolenic esters are changed to the conjugated forms before they polymerize and that the dimerization was by way of a modified 1,4-diene or Diels Alder addition, as proposed by Kappelmeier (9) for eleostearate, between two molecules of the conjugated forms. In such a diene addition, one of the conjugated systems acts as the diene, while a double bond in another molecule acts as the dieneophile. According to this theory,



the dimers from conjugated and non-conjugated esters would be essentially identical. The dimer of conjugated or non-conjugated linoleate was represented by:



this being a dimer of 9,11-methyl linoleate.

Another possibility which was not considered, or at least has not been emphasized, is that the dimerization might be a modified 1,4-diene addition between a conjugated form and a non-conjugated form with a double bond of the non-conjugated form acting as dieneophile. This would result in a structure similar

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[1] Paper No. 97, Journal Series, Research Laboratories, General Mills inc.