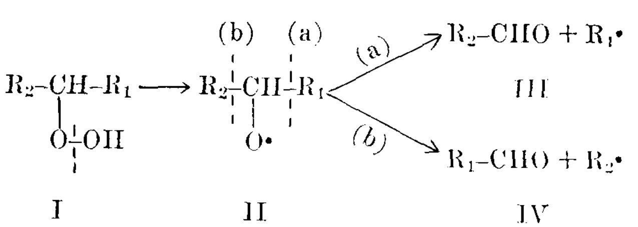
• *Letter to the Editor*

Formation of Methyl Azelaaldehydate on Autoxidation of Lipids

THE FORMATION of aldehydes by decomposition of fat hydroperoxides has been extensively studied in recent years because aldehydes contribute to the flavor deterioration of fat-containing foods. The mechanism suggested involves cleavage of isomeric hydroperoxides (I) to the alkoxyl radical (II), which undergoes carbon-to-carbon fission (a) to form the aldehyde (III) (1).



R_1 = Ester end. R_2 = Hydrocarbon end.

Evidence for the formation of normal aldehydes like III from decomposition of fat hydroperoxides was reviewed by Lea (5) and Morris (6). Cleavage of II at site (b) would give the semialdehyde ester (IV). Although the formation of semialdehydes on autoxidation of fats was previously suggested (2,9), evidence for their presence was not established. However a recent Japanese report indicates that semialdehydes form by autoxidation of oleic acid, linolenic acid, and sardine oil (7) and attributes the discoloration of fish oils on contact with ammonia or amines to these aldehydes. The present communication deals with the identification by gas chromatography of methyl azelaaldehydate in autoxidized lipids.

During gas chromatographic analyses of soybean oil methyl esters at different levels of autoxidation, a prominent peak appeared in the autoxidized samples in the vicinity of methyl palmitate. The substance responsible for this peak was a carbonyl since it could be removed by treating the sample with 2,4-dinitrophenyl hydrazine. The carbonyl compound was characterized by its emergence either before or after methyl palmitate, according to the stationary phases used in the column.[1] The same behavior was exhibited by methyl azelaaldehydate obtained by reductive ozonolysis of methyl oleate (8).[2]

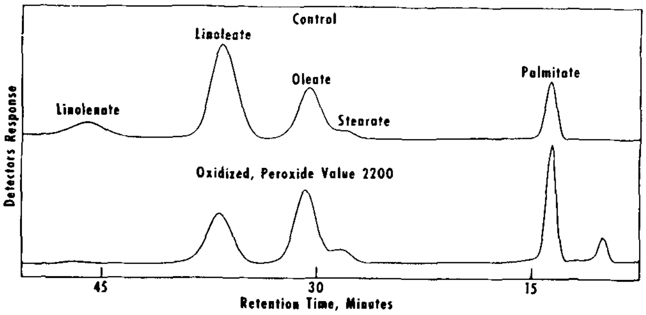


FIG. 1. Gas chromatographic analysis of soybean oil methyl esters before and after autoxidation. (Conditions: "Pye" instrument with 4 ft. x ¼-in. column; 10% Craig polyester succinate on Chromosorb W 60/80; 174°C.; argon flow 25 cc./min.)

When a Craig polyester succinate was used as the stationary phase for oxidized soybean oil methyl esters, the peak came before methyl palmitate (Figure 1). With ethylene glycol succinate the peak came after (Figure 2). The retention time of this peak corresponds to that of methyl azelaaldehydate. The relative retention times (methyl palmitate = 1.0) of methyl azelaaldehydate in four different stationary phases were 0.85, 0.78, 0.76, and 1.3 with polyvinyl acetate (172°C.), Resoflex LAC 2R-446 (175°C.), Craig polyester succinate (174°C.), and ethylene glycol succinate (155°C.), respectively. Similar evidence showed the presence of methyl azelaaldehydate in autoxidized methyl oleate, linoleate, linolenate, and linseed oil methyl esters.

Methyl azelaaldehydate would be expected from the decomposition of methyl hydroperoxide esters with hydroperoxy groups in the C_9 position by cleavage (b) of the C_9-C_{10} bond. The formation of C_9 hydroperoxides has indeed been established on autoxidation of methyl oleate, linoleate (6), and linolenate (4). Except for the 8 and 9 hydroperoxide isomers, all other hydroperoxides produce unsaturated semialde-

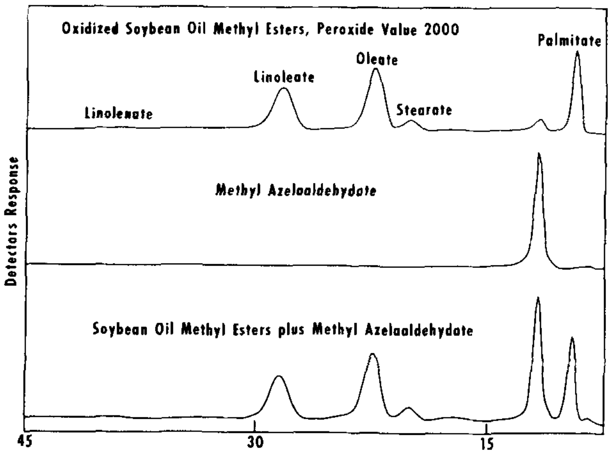


FIG. 2. Gas chromatographic analysis of a) autoxidized soybean methyl esters, b) methyl azelaaldehydrate, and a) + b). (10% Ethylene glycol succinate; 153°C.; argon flow 43 cc./min.)

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[1] S.F. Herb (Eastern Regional Research Laboratory, Philadelphia, Pa.) in a private communication also observed a similar carbonyl peak in autoxidized fatty esters. He suggested that the position of this peak in relation to palmitate is related to the effect of aging on the polarity of the stationary phase.

[2] E. H. Pryde kindly supplied the methyl azelaaldehydate.

hydes. The absence of semialdehydes higher than azelaaldehydate may indicate that the resulting unsaturated semialdehydes decompose under the conditions of gas-liquid chromatography. Evidence for higher semialdehydes than azelaaldehydate was recently obtained by hydrogenating decomposition products of autoxidized methyl linolenate. A more detailed account of this work is being prepared.

The evidence for a type (b) cleavage during autoxidation of fats leads one to expect a new series of substances that may contribute to the color and flavor components of fat-containing foods. According to scheme (b), the alkyl radical $R_2\bullet$ may be expected to combine with hydrogen or hydroxyl radicals to give low-molecular-weight hydrocarbons or alcohols, respectively. Unpublished evidence has been obtained in this laboratory (3) that hydrocarbons and alcohols may be constituents of the volatile fraction of reverted soybean oil.

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ABSTRACTS . . . . R. A. REINERS, Editor

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• Fats and Oils

SYNTHESIS OF TRANS-10-HYDROXY-2-DECENOIC ACID. Masahiro Fujii, Nobuko Koga, Yoshio Osawa, and Isso Chuman (Tsurumi Chem. Labs., Yokohama). *Nippon Kagaku Zasshi* **81**, 1782 (1960). This acid, present in royal jelly from queen bees, was synthesized from ricinoleic acid, through 10-hydroxydecanoic acid, 10-acetoxydecanoic acid, 10-acetoxy-2-bromodecanoic acid, and debromination. Infrared spectrum is presented.

INTERMOLECULAR HYDROGEN BONDING OF HYDROXYSTEARIC ACIDS. I. 10-HYDROXYSTEARIC ACID. Isokichi Nakajima and Yoshiyuki Toyama (Nagoya Univ.). *Nippon Kagaku Zasshi* **81**, 1472–4 (1960). The infrared absorption spectrum was similar for crystalline 10-hydroxystearic acid and its methyl ester in the range of vibrating OH (3290–3380 cm^{-1}). Thus the OH formed H bonding with the OH of the adjacent molecule in rectangular direction to the fatty acid C chains. The OH forming H bonding in the mixed crystals of 10-hydroxystearic and stearic acids was proportional to the square of hydroxystearic acid content.

II. D-12-HYDROXYSTEARIC ACID. I. Nakajima and Y. Toyama. *Ibid.*, 1474–76. The infrared absorption of vibrating OH of D-12-hydroxy stearic acid appeared in much lower frequency than that of OH in the H bonding of the type OH . . . OH. Thus COOH might be involved with intermolecular H bondings.

FORMATION OF PERACETIC ACID. Koichi Murai, Giichi Akazome, and Yasuto Murakami (Sansuiso Fats & Oils Inds. Co., Fushimi, Kyoto). *Kôgyô Kagaku Zasshi* **63**, 1233–5 (1960). This is Part VI of the studies on epoxy-fatty acid esters. Peracetic acid is often used in synthesizing epoxy unsaturated fatty acids. The equillibrium const. in the formation of peracetic acid from acetic acid and H_2O_2 was $K = 3.26$ in the range of 25–45°. The activation energy was 11.7 kcal./mole with H_2SO_4 as the catalyst.

REACTIONS BETWEEN UNSATURATED FATTY ACIDS OR AROMATIC CARBOXYLIC ACIDS AND SODIUM HYDROXIDE AT HIGH TEMPERATURE. Kenjiro Takeshita (Kyûshû Univ., Fukuoka). *Kôgyô Kagaku Zasshi* **63**, 2159–63 (1960). Reactions with NaOH at high temperatures (200–500°) were studied of acrylic, methacrylic, oleic, cinnamic, hydrocinnamic, phenylpropionic, benzoic, phenylacetic, and propionic acids. These reactions could be well interpreted by the following general formula:

$$RCH_2CH_2COONa + 3NaOH + H_2O \longrightarrow$$
$$RH + CH_4 + 2H_2 + 2Na_2CO_3.$$

UREA-INCLUSION COMPLEXES IN FATS. B.B.L. Srivastava (Banaras Hindu Univ.). *Indian Oil & Soap J.* 3, 51–55 (1960). The use of urea adducts to separate mixtures of fatty acids, esters, and waxes is discussed.

THE USE OF SILICONE RUBBER GUMS OR GREASE IN LOW CONCENTRATION AS STATIONARY PHASE FOR THE HIGH TEMPERATURE GAS CHROMATOGRAPHIC SEPARATION OF LIPIDS. N. Nicolaides (Dept. of Food Science and Technology, Univ. of California, Berkeley, Calif.). *J. Chromatography* **4**, 496–9 (1960). Silicone rubber gums and grease were used at low concentrations (5% of substrate) and at high temperatures (240–300°) as stationary phase of gas-liquid chromatography. The retention times at 5% liquid phase in 5-foot column are about one-third those at 25% and this occurs at no loss in resolution. Methyl esters of fatty acids, waxes, sterols, and tocopherols were chromatographed.

RHEOLOGY OF COCOA BUTTER. III. CRYSTALLINE CHANGES DURING STORAGE AT VARIOUS TEMPERATURES. C. Sterling (Dept. of Food Science and Technology, Univ. of California, Davis, Calif.). *Food Research* **25**, 770–6 (1960). Oxidation of purified cocoa butter results in decreased crystalline organization and increased amorphous fraction, in a direct dependence upon temperature. Potentiality of organization of normal (α, β', β) crystals is progressively decreased, but at some stage in oxidation, probably involving a large amount of dimer formation, the crystalline form suddenly changes. It is speculated that a new type of crystal (ω) is produced. This is gradually superseded by a less crystalline, gel-like structure as oxidation continues.

CHEMICAL CHANGES IN ANIMAL AND VEGETABLE FATS DURING HEAT TREATMENT AND REFLECTIONS ON THE EVALUATION OF THEIR PHYSIOLOGICAL PROPERTIES. J. Wurziger and H. Ostertag (Health Inst., Hamburg). *Fette Seifen Anstrichmittel* **62**, 895–903 (1960). The authors have studied the relationship between the chemical and physiological properties of heat treated fats, and have determined the changes which occur in fats heated for 12 hours at 180°. Soybean oil, lard, hydrogenated soybean oil, and hydrogenated lard were employed in the study; and acid number, epoxide, carbonyl value, and iodine value were measured. Values determined and in the above mentioned order for soybean oil, lard, hydrogenated soybean oil and hydrogenated lard, respectively, were: 0.9, —, 6.0, 119; 1.6, —, 3.4, 57.6; 0.9, —, 3.0, 24.0; 0.6, —, —, 3.6. After heating these oils in the absence of oxygen for 12 hours at 180°, the values were: 0.9, —, 13.6, —; 1.7, —, 14.8, 55.4; 1.0, —, 15.0, 23.5; 0.7, 1.3, —, 3.4. Heating for 12 hours at 180° in the absence of air reduced the polyunsaturated fatty acid content somewhat. When these oils were heated under the same conditions in the presence of air the following values were obtained: 2.0, 56.1, 582.7, 79.6; 16.0, 180.2, 178.2, 13.2; 21.7, 160.3, 204.4, 15.6; 52.1, 48.2, 25.8, —. The content of linoleic acid and linolenic acid decreased from the initial values of 52.4, 10.2; 12.5, 0.5; 5.7, 0.25; and .006, — to 36.7, 3.3; 1.4, —; 0.6, —; 0.7, —. Rats were fed the various oxidized fats at the 10–20% level and the animal fats examined for carbonyl compounds. The carbonyl value of the rat body fat was 0.04–0.13. The authors have shown that carbonyl compounds from highly oxidized fats are deposited in rat carcass fat.