SYMPOSIUM: THERMAL OXIDATION AND POLYMERIZATION IN FATS

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Introduction: Studies on Heated Fats

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DURING THE LAST TWO decades more than 100 publications have appeared in the literature on the chemical and nutritional aspects of heated fats. Perkins (1) reviewing the most pertinent literature up to 1960, concluded that sufficient data exist to justify the suspicion that the use of heated unsaturated oils may not be desirable from the nutritional standpoint. Seven papers presented at the symposium on Lipids and Their Oxidation (2) reported on the biological significance of auto-oxidized lipids.

Various symptoms of toxicity ranging from growth depression to death have been observed as a result of feeding oxidized fats to laboratory animals (1,3–6). Potentiation of known carcinogens fed to animals with heated oil fractions has also been reported (7,8). Some experimental evidence also exists to indicate that the edible fats in normal usage do not produce toxic products (9,10).

Oils and fats are normally processed at temperatures lower than those which will cause polymerization or any excessive degradation, but in frying where reuse of the oil occurs in commercial establishments a hazard might exist (11,12).

During frying, oil is heated to temperatures between 180C and 200C. Mechanisms involved during frying involve thermal oxidation and polymerization in presence of air. The three main groups of products formed are (a) hydroperoxides (b) secondary degradation products which include carbonyl compounds. Epoxy-, and hydroxy fatty acids and (c) polymers. Cyclized products may also be formed in the absence of air.

In strongly heated fats hydroperoxides do not accumulate and the toxicity is generally attributed to the degradation products and the polymeric material. Although some progress has been made on the study of separated fractions from heated fats, the evidence is not enough to arrive at any definite conclusions.

In a recent study on heated corn oil (13), the author fractionated corn oil heated at 200C into 8 fractions. The first four fractions, constituting about 62% of the original oil, were found to be triglycerides. The remaining 4 fractions constituted polymeric and degraded products with molecular weights ranging from 1320 to 4800. A number of hydroxyacids and short chain fatty acids were also identified in the polymeric fractions.

When heated to high temperatures in the absence of air, fatty acids, particularly the poly unsaturated acids, can cyclize without increase in molecular weight to form 1,2 di-substituted cyclohexanes. Polymerization can also occur through a Diels-Alder reaction which also gives rise to a 1,2 di-substituted cyclohexane. No evidence is available to indicate the presence of such hydro-aromatic systems which would be formed if polymerization occurred by Diels-Alder reaction in edible oils.

In the presence of air, decomposition of initially formed hydroperoxides at temperatures below 100C gives rise to oxygen linked polymers. While at higher temperatures carbon linked polymers predominate.

Questions that still remain unanswered are: (i) whether or not thermal polymers are in fact formed in

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frying oils during normal processing. (ii) what particular fractions are toxic and (iii) what are the effects of long term feeding of oxidised fats.

The papers presented at this symposium are not intended to review all the work but to present further observations to elucidate the questions.

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Chromatographic Studies on Oxidative and Thermal Fatty Acid Dimers[1]

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Abstract

A chromatographic study was carried out to investigate the nature of polymeric products in edible oils. Dimers from low-temp oxidation of methyl linoleate were compared with thermal dimers from high-temp polymerization of conjugated methyl linoleate. The distilled dimers were subjected to liquid-partition chromatographic separations on silicic acid columns as methyl esters, as free acids, and as methyl esters prepared by saponification and reesterification. Chromatographically isolated dimer fractions were also rechromatographed before and after each treatment.

When thermal dimer esters are saponified and reesterified, chromatographic recoveries are quantitative, and the expected changes in polarity result; whereas, with oxidative dimer esters, gross changes in polarity occur. Chromatographic separations of dimer esters or their acids fractionate into distinct areas of increasing polarity.

Introduction

POLYMERIC MATERIALS in glyceride oils may result from thermal treatment, oxidation, or a combination of both. Some of the most effective catalysts that cause dimerization of fatty acids are those that generate free radicals. UV light, peroxides, anthraquinones and metals in the presence or absence of air induce polymerization. High temps and the absence of air are required to form thermal polymers. Although the composition and structure of the thermal and dehydro fatty acid polymers have been well characterized, the structure of polymers formed during active oxidation is unknown and their composition varies. Studies designed to characterize oxidative polymers have relied upon distillation, solvent fractionation, selective adsorption or chromatographic separations to isolate a homogeneous material suitable for analysis.

Polymer formation in edible fats concerns the oil processor, the food technologist, the nutritionist and the consumer because of the changes polymers induce in the properties and characteristics of the fat. In 1960 Perkins (19) reviewed the literature on the chemical and nutritional changes that occur in heated fats. Firestone (9) in 1963 reviewed the methods for the determination of polymers in fats and oils. A method for the determination of 0.01 to 1.0% thermal dimer was published by Rost (21,22); but he states that it is not suitable for the determination of oxidatively derived polymers in fats, and cautions that oxidation of the thermal polymer through exposure to air must be avoided. We have described a method of partition chromatography using silicic acid to separate either thermal or oxidative polymeric fatty acids from the unaltered natural acids (12). Structural differences between the thermal and oxidative type of polymers and the presence of polar groups in the oxidative-type polymer indicate that a difference in chromatographic polarity should exist. The ability to distinguish between thermal and oxidative polymers would contribute to a better understanding of the behavior of fats and oils in industrial and edible applications.

The present paper describes chromatographic studies designed to distinguish between thermal and oxidative dimers by the analysis of their methyl esters, the free dimeric acids obtained by saponification of the esters, and the esters obtained by reesterification of isolated dimeric acids.

Experimental

Materials. Methyl linoleate used for the preparation of the oxidative dimer was obtained by esterification of a linoleic acid conc obtained from safflower fatty acids through Podbielniak extraction with furfural and hexane (3). The fraction boiling at 147–150C at 0.5 mm was used, which by gas-liquid chromatography (GLC) showed a purity of 98.8% and the presence of 1.2% methyl oleate. The alkali-conjugated methyl linoleate was prepared from safflower fatty acids obtained through crystallization in hexane at −40C. Isomerization was conducted for 45 min at 190–200C in an ethylene glycol solution containing 15% potassium hydroxide. The acids were methylated in methanol and H_2SO_4 and purified by distillation at 144–150C 0.4 mm. The conjugated methyl linoleate esters have an absorptivity of 76.9 at 232 mμ, indicating a conjugation of 82%. Soybean methyl esters were prepared from refined soybean oil by transesterification with sodium methoxide. At the start of each experiment esters were freshly distilled.

Autoxidation. Methyl linoleate was oxidized without catalyst at 25C in a closed oxygen system at atmo-

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