Formation of γ and δ Lactones in Irradiated Beef

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ABSTRACT

Formation of γ and δ lactones by irradiation in beef has been recently reported. This paper provides evidence for their presence and postulates a mechanism for their formation.

INTRODUCTION

The formation of relatively short chain lactones (C_8-C_{12}) as a result of heat treatment has been indicated in various food products (1-3). The presence of γ and δ lactones up to C_{12} chain length was also indicated in the steam distillate of milk fat irradiated in vacuum (4). In general, the formation of lactones in these studies was shown to be mainly associated with oxidative changes or thermally induced oxidation processes.

In recent studies of the formation of radiolysis products in model lipid systems (5) and irradiated beef (6), several radiolytic compounds were identified among which were long chain gamma and delta lactones. These compounds have not been previously identified or reported in irradiated beef fat or triglycerides. No evidence was given in the earlier papers for their identification.

This paper describes the conditions under which they have been observed, the evidence for their identification, and a possible mechanism for their formation.

EXPERIMENTAL PROCEDURES

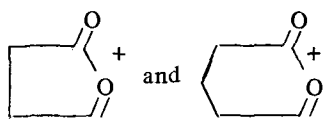
The sample and procedures used in this investigation are the same as described in a previous study (5).

Identification of the lactones was based on a comparison of the gas chromatographic retention times and mass spectra with those of the authentic compounds, where available. In other cases, the identification was based on extrapolation of GC retention data and a correlation of the mass spectra with other known spectra of lactones. Gamma and delta lactones (C_8-C_{12}) used for correlation were purchased from ICN/K&K Labs. Gamma – palmitolactone and gamma – stearolactone were obtained through the courtesy of Dr. J.S. Showell of Eastern Regional Research Laboratory, US Department of Agriculture and Dr. M.J. Diamond of Western Reg. Res. Lab, US Department of Agriculture, respectively.

RESULTS AND DISCUSSION

As reported in the prior studies (5,6) long chain lactones were found in every case to be formed both in irradiated beef and model systems of pure fatty acids and triglycerides. The lactones identified in these studies consisted of γ and δ palmitolactones, γ and δ stearolactones, and γ and δ oleolactones corresponding to the major fatty acids. For the purpose of comparison, only the γ lactones found in the pure fatty acids and triglycerides were quantified: 1.4 mg/g of γ-palmitolactone from tripalmitin and 1.8 mg/g from palmitic acid; 0.11 mg/g of γ-oleolactone from triolein and 0.09 mg/g from oleic acid. Gamma lactones were present in greater quantities than the corresponding delta isomers.

The lactones found in these studies were separated by gas chromatography and identified by mass spectrometry. Gas chromatographic analysis of the radiolysis products from beef fat revealed their presence and demonstrated an adequate resolution between the two isomers. A typical chromatogram is shown in Figure 1. The mass spectral data for these compounds are presented in Figure 2. The major peaks produced in the mass spectra of γ and δ lactones correspond to ions of



giving rise to m/e 85 and 99, respectively. In addition, peaks at m/e 114 and (M-18) are typical of lactones and appear in relatively great abundance in the spectra. The mass spectra of the lactones from the irradiated lipids were identical to the authentic compounds and those given in the literature (7,8).

The formation of lactones has been associated mainly with the presence of hydroxy fatty acids in the natural product. The reaction of the hydroxy group with carbonyl carbon has been suggested to be the mechanism by which lactones are formed from hydroxy acids. However, in the study of model systems (5) a variety of γ and δ lactones were identified in irradiated triglycerides and fatty acids. Since hydroxy acids are absent in the model systems, and, when present in beef, are found only in trace quantities, a free radical reaction involving the fatty acid side chain must be responsible for the production of lactones by radiolysis.

A study of meat fat heated in air (3) has suggested a peroxide mechanism which involves decomposition to a hydroxy acid as a possible route for the formation of lactones. However, it should be noted that in the study of milk fat irradiated in vacuum (4), formation of short chain

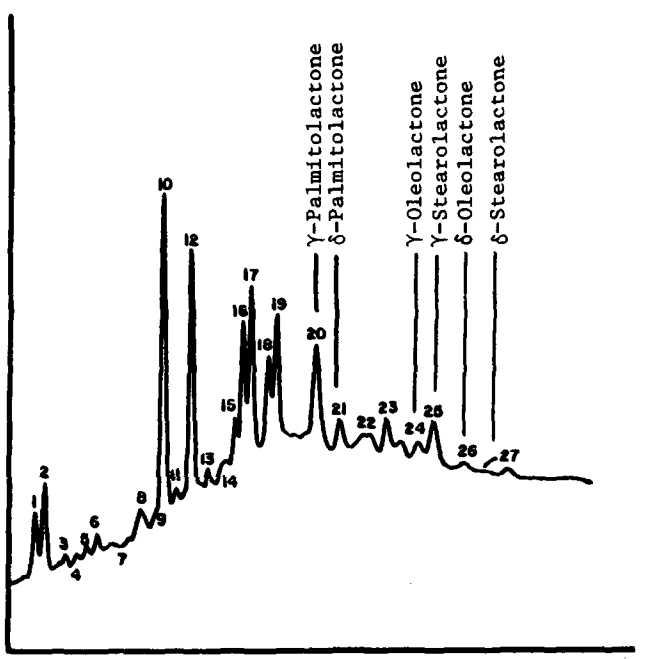


FIG. 1. Portion of gas chromatogram of fraction III from GPC of irradiated beef fat. Column: 7' x 1/8"-3% Dexil 300. Temperature: 100 C-330 C (8 C/min). Attenuation: 32 x 100.

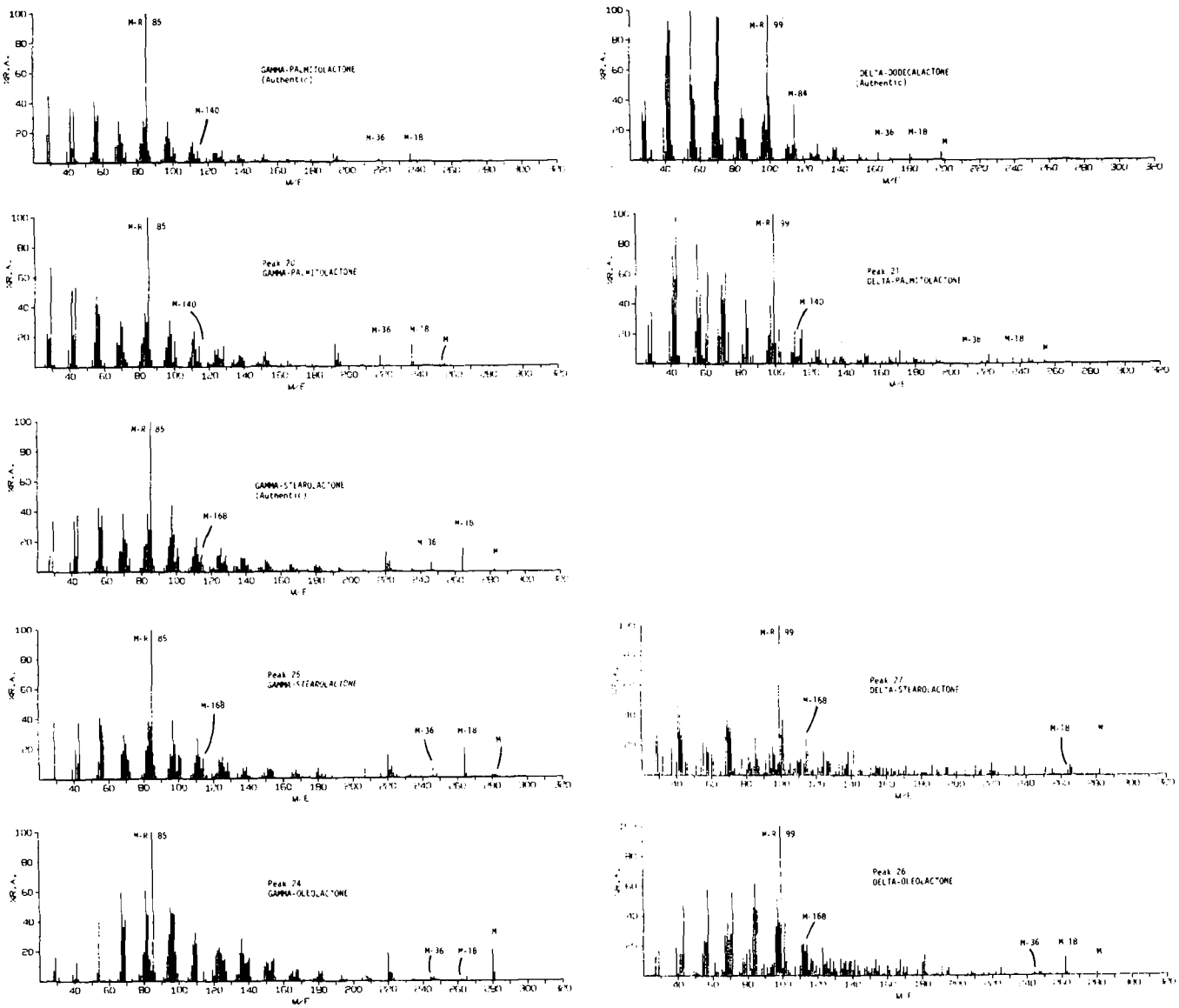
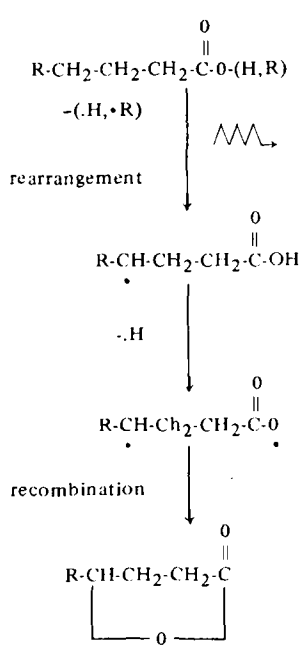


FIG. 2. Mass spectra of γ and δ lactones.



(Scheme 1)

lactones was observed in the absence of oxygen. Therefore, as a result of these findings, a possible mechanism is suggested for the formation of lactones in irradiated lipids as depicted in Scheme 1.

We believe that the formation of lactones in samples under vacuum is mainly associated with the free radical mechanism. However, in the presence of oxygen, oxidative processes as well as the free radical mechanism may be operative for the formation of lactones in lipids. Presently, studies are in progress to establish the effect of oxygen on the formation of lactones in fatty acids and triglycerides.

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