The effect of amino acids on the carbonyl content of irradiated lard was more apparent at a dose of 2 megarads than at 10 megarads. In either case however it was apparent that the presence of amino acids during the irradiation affected the quantity and type of carbonyls formed.

Discussion

While lard is quite rich in oleic acid, it is not surprising that nonanal and decanal comprise only 9.9-mole percentage of the volatile carbonyl compounds isolated in this study. During *gamma* irradiation, as during autoxidation, it is the linoleic acid that is principally attacked and degraded. Hexanal, pentanal, and propional have been previously isolated from oxidized linoleate (5). Forss, Pont, and Stark (9) have isolated the hexa- to undecadienals from milk and cite linoleic acid as the common source of this series of compounds.

Swift *et al.* (22) isolated 2,4-decadienal from cottonseed oil while Stapf and Daubert (20) found the same compound in soybean oil. Forss *et al.* (8) found heptadienal and nonadienal to be the most abundant dienals in milk. No simple explanation is available for the observation that the principal degradation product of linoleic acid varies from fat to fat. Our data would seem to suggest that under the influence of *gamma* radiation the principal site of oxidation in lard is the 8 position of linoleic acid.

Starting from the observation that amino acids influence the quantity and type of carbonyl compounds found in irradiated lard, the interaction of sulfur compounds and *alpha-beta* unsaturated aldehydes was investigated (23). These condensation products were suggested as important precursors for the development of the typical odors noted in irradiated meat. It has been long recognized that *alpha-beta* unsaturated aldehydes are important constituents of off-odor and flavor in oxidatively rancid fats and oils. Now, in the case of irradiated meat, it seems possible that the acrolein and crotonal derived from the meat fat may combine with the degradation products of the protein to contribute significantly to the off-odor and flavor of the meat product.

Summary

The volatile carbonyl compounds from irradiated lard were isolated and characterized qualitatively and quantitatively as the 2,4-dinitrophenylhydrazones. Propional, butanal, pentanal, hexanal, nonanal, decanal, acrolein, crotonal, and 2,4-undecadienal were identified by paper chromatography and spectrophotometric analysis.

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Preparation of Esters and Anhydrides from Long Chain Fatty Acid Chlorides[1]

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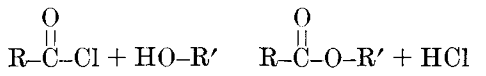
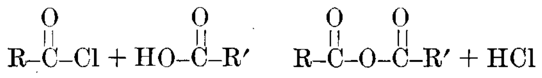
Fatty acid chlorides combine with alcohols to form esters according to the following general reaction:



$$R\text{–}\overset{\overset{O}{\|}}{C}\text{–}Cl + HO\text{–}R' \quad R\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}R' + HCl$$

Substitution of a free acid for the alcohol results in anhydride formation (1).



$$R\text{–}\overset{\overset{O}{\|}}{C}\text{–}Cl + HO\text{–}\overset{\overset{O}{\|}}{C}\text{–}R' \quad R\text{–}\overset{\overset{O}{\|}}{C}\text{–}O\text{–}\overset{\overset{O}{\|}}{C}\text{–}R' + HCl$$

These reactions can be made substantially quantitative by removing the HCl formed during the reaction. This has been accomplished in the past almost exclusively by the addition of a tertiary amine, such as pyridine, quinoline, or trimethylamine, to the reaction mixture. The amine also acts as a solvent for the reactants, either alone or in conjunction with an inert solvent, such as chloroform.

This paper describes the preparation of a number of esters and anhydrides from acid chlorides, in which the reactants are mixed directly and the HCl is stripped from the reaction mixture by operating at reduced pressure. This method is, of course, only applicable to the higher fatty acid chlorides and alcohols of low volatility. Reaction for 1 hr. at 100°C. and 2-mm. pressure gave excellent results. Yields of the order of 90% of the recrystallized product of high purity were obtained for the following compounds, tristearin, pentaerythritol tetrastearate, α-methyl-glucoside tetrastearate, monosaturated triglycerides, stearic anhydride, palmitic anhydride, and a mixed stearic-palmitic anhydride.

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[1] This paper was awarded an honorable mention in the 1957 Fatty Acid Producers' Award Competition administered by the American Oil Chemists' Society.

The procedure is well suited to industrial applications as it eliminates the need for the comparatively expensive tertiary amines, gives high yields in a short reaction time, and results in a product that is easily purified. Coupled with an improved procedure for preparation of long chain fatty acid chlorides described in an earlier paper (2), this opens the way to a much wider industrial use of fatty acid chlorides as acylating agents. The use of acid chlorides is of particular advantage in the preparation of materials such as mixed anhydrides and synthetic glycerides containing more than one type of acid radical.

Experimental

The fatty acid chlorides were prepared as described earlier (2). A typical example is the preparation of stearoyl chloride. Twenty grams of stearic acid were dissolved in 200 ml. of Skellysolve F,[2] and 15 g. of phosphorous pentachloride were added. The mixture was refluxed for 1 hr., cooled to room temperature, and washed twice with ice water. The Skellysolve phase was dried with anhydrous sodium sulphate, and the solvent was removed under vacuum. Infrared analysis of the product showed less than 1.5% free acid.

Preparation of Tristearin. Stearoyl chloride and freshly distilled glycerol, in a molar ratio of 3 to 1, were heated to 100°C. at a pressure of 2 mm. The glycerol was not soluble in the acid chloride so the reaction was initially heterogenous and a magnetic stirrer was used to keep the glycerol dispersed. After one hour all visible evolution of gas had ceased and a homogenous, pale yellow product was obtained. A single crystallization from acetone gave a 92.5% yield of material containing no measurable free acid. The crystallized material on a heating stage microscope showed phase transitions at 54.5 and 65.5° C. and melted at 71.0°C. The reported melting points (3) of the three polymorphic forms of tristearin are 54.5, 65.0, and 71.5°C.

Preparation of Pentaerythritol Tetra-stearate. Stearoyl chloride and pentaerythritol in a molar ratio of 4 to 1 were heated for 1 hr. at 100°C. and 2-mm. pressure. The reaction, which was initially heterogenous, gave a homogenous, pale yellow product. Crystallization from chloroform gave a 92.6% yield of material having a melting point of 73 to 74°C. The crystallized material contained no measurable free acid, and the determination of acetyl values by the method of West *et al.* (4) showed no free hydroxyl groups.

Preparation of α-Methyl-glucoside Tetra-stearate. Stearoyl chloride and α-methyl-glucoside in a molar ratio of 4 to 1 were heated for 1 hr. at 100°C. and 2-mm. pressure. Again the reaction, which was initially heterogenous, gave a homogenous product. Crystallization from acetone gave a 91.6% yield of material melting at 74.5 to 75.5°C., which contained no free acid or free hydroxyl groups. A methoxyl determination gave a value of 2.51. The calculated value for the tetra-ester is 2.48.

Preparation of Monosaturated Triglycerides. A mixture of monosaturated triglycerides was prepared by reacting monostearin with a mixture of oleoyl and linoleoyl chlorides. The monostearin was prepared as described by Malkin *et al.* (5) by using the isopropylidine group as the blocking agent. A mixture of oleoyl and linoleoyl chlorides was prepared from a mixture of these acids obtained from safflower oil. Monostearin and the acid chlorides were combined in a molar ratio of 1 to 2.2 and heated under reduced pressure as before. Crystallization from acetone gave an 85.0% yield of material with an iodine value of 100.7 and linoleic acid content of 49.4%. A mixture of only stearodiolein, stearooleolinolein, and stearodilinolein containing 49.4% linoleic acid would have an iodine value of 100.2. The presence of any unreacted monostearin or any tristearin or distearins resulting from intermolecular interchange during reaction would lower the iodine value. The product was therefore essentially monosaturated glycerides.

Preparation of Stearic Anhydride. Stearic acid and stearoyl chloride in a molar ratio of 1 to 1.1 were heated under reduced pressure as before. Crystallization from acetone gave an 89.5% yield of material melting at 69.8 to 70.5°C. The reported melting point for stearic anhydride (3) is 70.7°C. Infrared analysis of the crystallized material showed 0.9% free acid.

Preparation of Palmitic Anhydride. Palmitic acid and palmitoyl chloride in a molar ratio of 1 to 1.1 were heated to 100°C. for 1 hr. at 2-mm. pressure. Crystallization from acetone gave a 96.0% yield of material containing 1.5% free acid and having a melting point of 62.8 to 63.6°C. The reported melting point for palmitic anhydride (3) is 63.9°C.

Preparation of Stearic-palmitic Anhydride. Palmitic acid and stearoyl chloride in a molar ratio of 1 to 1.1 were reacted as above. Crystallization from acetone gave an 87.5% yield of material containing 2% free acid and having a melting point of 60.8°C. The long crystal spacings, determined by X-ray diffraction, for the three anhydrides were stearic 40.4 Å, palmitic 36.2 Å, and stearic-palmitic 42.2 Å. The fact that the spacing for the mixed anhydride is different from the two simple anhydrides indicates that it is a mixed anhydride and not a mixture of anhydrides.

Conclusions

The use of reduced pressure to remove the HCl formed in the reaction of acid chlorides with alcohols and acids appears to be generally applicable to reactants of low volatility. The lowest yield of recrystallized product obtained was 85.0%, and in most cases tested the yield was more than 90%. Any side reactions occurring are apparently minor as a single crystallization gave products of high purity.

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[2] Petroleum solvent with boiling range of 35 to 58°C.