by manipulation of natural rations. From a practical standpoint it does not seem feasible to attempt to improve the keeping qualities of pork fat by increasing the tocopherol content of the diet, unless means can be found to bring about more economical storage of diet tocopherol in adipose tissues.

Furthermore, while tocopherol and the degree of saturation may be the only important factors in determining the keeping quality of rendered hog fat, other factors probably influence to a large extent the keeping qualities of the fat present in refrigerated, frozen or cured pork. Among such contributing factors may be mentioned the lipoxidases present in muscle and adipose tissue, the effect on such oxidases of salt, pH, etc. (9), and possible variations in synergistic antioxidants present in muscle tissue. Further work along these lines will be reported at a later date.

Summary

1. Fat from hogs on several natural rations became rancid more rapidly than fat from similar hogs on purified rations with or without added tocopherol.

2. Feeding of tocopherols to hogs on purified and natural rations resulted in small decreases in the susceptibility of their fat to oxidative rancidity. The magnitude of the protective action of dietary tocopherol was too small to be of practical significance.

3. Subcutaneous injection of a distillation mixture of tocopherols resulted in no added protection to the fat, probably because of lack of absorption.
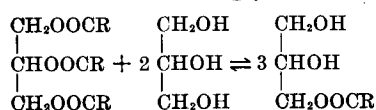
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The Stability and Constitution of Monoglycerides

JOHN ROSS, A. C. BELL, C. J. ARROWSMITH, and A. I. GEBHART

Colgate-Palmolive-Peet Company, Jersey City, N. J.

IT has long been reported in the literature (1) that glycerol and fatty acid triglycerides will react at temperatures of 180-290° C. to form mono- and di-esters of glycerol. It has been commonly accepted and more recently reported (2) that conversely, glycerol and triglycerides are formed when distillation is attempted of mono- and diglycerides in vacuo.

$$CH_2OOCR \quad CH_2OH \quad CH_2OH$$
$$CHOOCR + 2\ CHOH \rightleftharpoons 3\ CHOH$$
$$CH_2OOCR \quad CH_2OH \quad CH_2OOCR$$

As stated in a recent review (3) it is generally acknowledged that these reactions "can be considerably speeded up if catalysts are used." However, we feel that it would be more useful to adhere to the restricted view that such reactions between polyhydric alcohols and polyhydric alcohol esters proceed at an appreciable rate only in the presence of catalysts. The earlier chemists realized the value of catalysts in promoting reaction rates but later chemists have neglected to recognize the possible catalytic effect of impurities on the reversibility of these reactions and upon the stability of their products.

We have found that pure anhydrous glycerol and fatty acid triglycerides do not react appreciably below decomposition temperatures but will do so readily in the presence of water or other catalysts. We have also found (4) that pure mono- and di-esters of fatty acids and glycerol can be distilled without disproportionation.

In this discussion the words "pure," "catalyst," and "appreciable" are used in a limited sense and not with their absolute meanings. Thus a preparation is described as pure when it contains no decomposition or reversion catalyst, or when such catalyst is inhibited.

Reaction Between Glycerol and Triglycerides

In Table I can be seen the results of heating glycerol (0.2 moles) and a triglyceride (0.1 mole coconut oil) with and without water in an agitated autoclave.

The refined coconut oil used had been refined by bleaching and so-called "caustic refining" and thus contained 0.013% of soap. The "pure" coconut oil was prepared by treating an ether solution of this refined coconut oil with acetic acid, washing with water and finally drying, removing the solvent and

TABLE I.

	Weight Oil	Weight Glycerine	Weight Water	Temperature	Time	% Free Fatty Acid	Acetyl Value	Calculated Approx. % Monoglyceride
	g.	g.	g.	°C.	hrs.		%OH	%
Refined coconut oil	66.0	18.4	2.0	270	2	5.6	....	50
Refined coconut oil	66.0	18.4	None	270	2	0.5	2.16	24
Pure coconut oil	66.0	18.4	2.0	240	2	6.3	....	50
Pure coconut oil	66.0	18.4	None	240	2	0.6	0.45	3

recovering the oil. The reaction mixture from the autoclave was washed with water to remove glycerol and the oil fraction analyzed, by determination of acid, acetyl, and saponification values. The hydroxy-ester content is expressed as monoglyceride calculated from these figures.

It is seen from the table that anhydrous, soap-free coconut oil does not show appreciable reaction with glycerol under the experimental conditions at 240° C. However, water or soaps can act as catalysts.

Distillation of Monostearin

Monostearin was prepared by the method of Hil-ditch and Rigg (5); 175 g. pure methyl stearate (b.p. 178°/3 mm. I.V.=0), 175 g. phenol, and 550 g. glyc-erol were heated together in a current of nitrogen to 160° C. and then 1.0 g. caustic soda added and the temperature gradually raised to 230° C. so that the total time of heating was 3 hours. Methanol distilled off during reaction. Five g. of glacial acetic acid was added and the main part of the excess glycerol and phenol was removed by distillation up to 150° C./3 mm. The residue was taken up in ether and washed once with 5% acetic acid in water, then several times with distilled water and finally dried. After remov-ing the ether, the product was distilled at 0.2 mm. pressure from a Claisen flask. The fraction boiling 200-226° C. was redistilled and the cut boiling 186-200°C./0.2 mm. was crystallized from ether. In this way 56.0 g. of pure monostearin m.p. 80.5° C. (sa-ponification equivalent = 356) was obtained.

Forty g. of this pure crystallized ester was distilled from a pyrex Claisen flask at 0.2 mm. pressure and 30.8 g. collected in three fractions, see Table II.

TABLE II.

	Weight g.	b.p. °C./0.2 mm.	m.p.°C.* of distillate	Saponifi-cation Equiva-lent
I.	17.0	190-191	74	358
II.	10.0	191-200	74	357
III.	3.8	200-225	67	357
Residue	7.0		67	347

* Daubert and Clarke, J.A.C.S. 60, 690 (1944), have shown the existence of four forms of l-mono-stearin, transition points 48.5°, 75.4°, 78.0°, and 81.8° C. The analysis and not the melting point is therefore the indication of purity of composition. Crystallization from solvents appears to give the highest melting and most stable form.

Analysis of the residue in the flask indicated that it could be 80% monostearin. Upon recrystallization from, ether, 4.9 g. of pure monostearin m.p. 80.5° were obtained. It therefore appears that the decom-position or disproportionation of the monostearin amounted to less than 5%. It is possible that better results would be obtained in quartz vessels. Young and Black (2) reported that they could isolate no monoglyceride when they attempted to distill their preparation of monostearin and concluded that dis-proportionation was almost complete.

Under these conditions of distillation at low pres-sures it is very difficult to measure the exact pressure near the thermometer where the distillation occurs and to maintain constant distillation rates. Conse-quently, boiling points do not have the significance that is associated with them at higher pressures.

Other monoesters of glycerol have been prepared and distilled. Their boiling points are given in Table III below. The melting points given are for materials after crystallization from solvent (ether or ligroin). In all cases before distillation, steps were taken to remove or inhibit the catalysts used in the prepara-tion and when so prepared these monoglycerides can be distilled with none or very slight reversion.
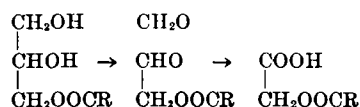
TABLE III.

	m.p.°C.	b.p.°C.
Monocaprin*	49°	175°/1 mm.
Monolaurin*	60°	186°/1 mm.
Monomyristin	71°	199°/1 mm.
Monopalmitin*	70°	211°/1 mm.
Monostearin	80.5°	190°/0.2 mm.
Mono-olein*	40°	186°/0.2 mm.

* Made from commercial acids.

The Constitution of Monoglycerides

It has been previously shown (5) that esters pre-pared by esterification of glycerol with fatty acids can be almost quantitatively oxidized with lead tetra-acetate and it was therefore concluded that they must be mainly α-monoglycerides. More recently periodic acid oxidation has been applied (6) to the estimation of monoglycerides. Using periodic acid we have iso-lated and identified the various stages of oxidation in the case of monomyristin and this definitely proves the constitution as α-monoglyceride

$$
\begin{array}{ccc}
CH_2OH & CH_2O & \\
| & | & \\
CHOH & \rightarrow CHO & \rightarrow COOH \\
| & | & | \\
CH_2OOCR & CH_2OOCR & CH_2OOCR
\end{array}
$$

Oxidation of Monomyristin

Myristic monoglyceride was prepared by the action of excess glycerol upon pure methyl myristate using a small amount of caustic soda as catalyst. The crude product was made acid with acetic acid, washed with water and distilled and finally recrystallized from petroleum ether. This material melted at 71° C. and had b.p. 199° C./1 mm.

To a solution of 10 g. of monomyristin in 50 ml. of methanol was added 53 ml. of a solution of periodic acid in 90% methanol containing 0.162 gm. H_5IO_6 per ml. (total weight added=8.6 g. H_5IO_6). After stand-ing at 30° C. for 45 minutes the oxidation was com-plete as indicated by titration of excess periodic acid in a small control experiment. The reaction mixture was poured into 500 ml. of water and the myristyl glycolic aldehyde extracted with ether. Ten g. of this aldehyde was recovered as an oil which solidified on cooling but was liquid at room temperature. This crude aldehyde was used for preparation of the semi-carbazone and oxime.

Myristyl glycolic aldehyde oxime recrystallized from benzene m.p. 85.5° C.

Calc. for $C_{16}H_{31}O_3N$ % N = 4.92%.
Found N = 5.17%.

Myristyl glycolic aldehyde semicarbazone crystal-lized from alcohol m.p. 126° C.

Calc. for $C_{17}H_{33}O_3N_3$ % C = 62.33 % H = 10.17.
Found % C = 62.32 % H = 10.20.

A portion of 3 g. of crude myristyl glycolic aldehyde was heated for half an hour on the steam bath with peracetic acid mixture prepared from 3 ml. 30% hydrogen peroxide and 8 ml. of glacial acetic acid. After standing overnight the oxidation mixture was diluted with water and the myristyl glycolic acid

collected on a Buchner. funnel. The dry acid, 2.2 g., was crystallized twice from benzene m.p. 80° C.

Calc. for $C_{16}H_{30}O_4$ % C = 67.13 % H = 10.55.
  Neutral Equiv. = 286.
  Saponification Equiv. = 286.
Found % C = 66.94 % H = 10.63,
  Neutral Equiv. = 289.
  Saponification Equiv. = 287.

A portion of the above acid ester was saponified with alcoholic caustic potash. After a few minutes warming, a quantity of granular crystals separated. These were filtered off and washed with 95% alcohol to remove potassium myristate and recognized as potassium glycolate by conversion to the p-nitro benzyl ester m.p. 107° and comparison with a known specimen of p-nitro benzyl glycolic ester (7).

Summary

1. It has been shown that pure anhydrous glycerol and fatty triglycerides do not react appreciably below decomposition temperatures, but that water or an alkaline material such as soap will catalyze reaction.

2. It has been shown that fatty monoglycerides when free from soap or alkaline material can be distilled in vacuum with only slight reversion in the higher members of the series.

3. The monoglycerides produced by the action of glycerol on methyl esters of fatty acids using caustic alkali as catalyst have been shown by periodic acid oxidation to have a-mono glyceride structure.

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Modification of Vegetable Oils

VI. The Practical Preparation of Mono- and Diglycerides

R. O. FEUGE and A. E. BAILEY [1]
Southern Regional Research Laboratory [2]
New Orleans, Louisiana

TECHNICAL mono- and diglycerides are prepared by the reaction of fat or fatty acids with glycerol in the presence of an alkaline catalyst (4, 6, 8). These materials not only find wide use in such industrial applications as the manufacture of "high-ratio" shortenings and oil-modified resins, but are also potentially important as intermediates for the preparation of so-called "tailor-made" fats.

The reaction product of fatty acids or fat with an excess of glycerol consists invariably of a mixture of mono-, di-, and triglycerides with unreacted glycerol. No systematic investigation has been made of the reaction in terms of the composition of the reaction product. However, various investigators (8, 9, 11, 12, 15) have reported that the composition is dependent upon such factors as the temperature, the reaction time, and the amount and nature of the catalyst used, as well as the proportions of fatty acids and glycerol in the reaction mixture.

In the case of a fat reacted with a very small excess of glycerol and a suitable catalyst there is strong evidence (2) that the fatty acid radicals become rearranged to an ultimate state of random distribution amongst the triglyceride molecules. Since in technical mono- and diglyceride manufacture there exist conditions equally favorable to acyl interchange, it seems surprising that the composition of the product should depend upon the temperature or similar conditions of reaction. In a homogeneous material in which the reaction has been carried to equilibrium it would ap-

pear more reasonable to expect that the proportions of triglycerides, diglycerides, monoglycerides, and free glycerol would conform to a pattern of random distribution with respect to OH groups esterified.[3] In such a material the composition would depend solely upon the proportions of fatty acids and glycerol reacted, and would be calculable by statistical methods (2).

The present investigation was undertaken to generally elucidate the manner of mono- and diglyceride formation and decomposition, and particularly to test the above-mentioned hypothesis of random distribution.

Experimental

The fat used in the experiments consisted of refined cottonseed oil which had been hydrogenated to an iodine value of 0.7. The average molecular weight of the (tri-) glycerides, calculated from the neutralization value of the fatty acids, was 876.2. This corresponds to a molecular weight of 614.9 for the diglycerides and 353.5 for the monoglycerides. Calculated glycerol contents for the tri-, di-, and monoglycerides were 10.51%, 14.98%, and 26.05%, respectively.

Reaction between the fat and glycerol was carried out in the stirred glass vessel described previously (7), under an atmosphere of hydrogen. In all cases sodium hydroxide equivalent to 0.1% of the weight of the fat was used as a catalyst.

The reaction product was analyzed for total content of free and combined glycerol by the official A. O. C. S. bichromate method (1), after alcoholic