and had a neutral equivalent of 283.8. Its melting point showed no depression on mixing with pure stearic acid (m. p. 70–71°, neut. equiv. 284.3); hence the reduced acid was stearic acid.

Anal. Calcd. for $C_{18}H_{36}O_2$: C, 75.95; H, 12.76. Found: C, 76.19; H, 12.82.

Oxidation of a small amount of the liquid acids with alkaline permanganate[10] yielded a mixture of dihydroxy- and tetrahydroxystearic acids. The dihydroxystearic acid was extracted from the crude mixed acids with chloroform. After crystallization from alcohol it melted at 129–130°. No depression was observed in the melting point on admixture with authentic 9,10-dihydroxystearic acid.

Anal. Calcd. for $C_{18}H_{36}O_4$: C, 68.26; H, 11.47. Found: C, 67.99; H, 11.48.

The acid insoluble in chloroform was crystallized from alcohol and melted at 171–172°. A mixed melting point with authentic tetrahydroxystearic acid showed no depression and established the substance as tetrahydroxystearic acid.

Anal. Calcd. for $C_{18}H_{36}O_6$: C, 61.99; H, 10.42. Found: C, 62.29; H, 10.21.

Another sample of the unsaturated acids was brominated in cold light petroleum ether. The precipitate which formed was crystallized from petroleum ether yielding a white crystalline acid melting at 113–114°. It was proved by the mixed melting point method to be tetrabromostearic acid,

Anal. Calcd. for $C_{18}H_{32}O_2Br_4$: Br, 53.29. Found: Br, 53.01.

The substance remaining in the petroleum ether after removal of the tetrabromostearic acid was a light brown oil. It was probably dibromostearic acid.

Anal. Calcd. for $C_{18}H_{34}O_2Br_2$: Br, 36.15. Found: Br, 38.21.

The above data show the presence in the acetone-soluble fat of both oleic and linoleic acids. Since no substance insoluble in ethyl ether was found on bromination, it appears that no higher unsaturated acids were present,

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Summary

1. The chemical composition of the lipids of the pathogenic fungus, *Blastomyces dermatiditis*, has been determined. The lipids make up about eight to ten per cent. of the weight of the whole dried cells.

2. The lipids were separated into approximately one-third phosphatide and two-thirds acetone-soluble fat.

3. The phosphatide on hydrolysis with aqueous sulfuric acid gave glycerophosphoric acid, choline, ethanolamine, and fatty acids. These substances were isolated and the first three identified. The fatty acids probably consisted of palmitic, stearic, oleic and linoleic acids. A small amount of carbohydrate was obtained on saponification.

4. The acetone soluble fat gave on saponification glycerol, ergosterol, and palmitic, oleic and linoleic acids. These were isolated and identified. Stearic acid probably was present also.

5. These results are compared with the data on tubercle bacilli and certain striking differences noted.

DURHAM, N. C. RECEIVED AUGUST 22, 1938

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[10] Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, SWIFT & COMPANY]

The Reversibility of the Reaction between Triglycerides and Glycerol

BY HARLAND H. YOUNG, JR., AND HOWARD C. BLACK

The fact that triglycerides react with glycerol at high temperatures has been known for several years. The products obtained by such a reaction have been described in the literature[1] and more recently have become of commercial importance as emulsifying agents for water-in-oil emulsions. Many of the products reported have been prepared from natural fats and oils and necessarily have been complex mixtures. The designation of these as mixtures of mono- and diglycerides has been based upon saponification numbers, acetyl values and their marked solubility in the lower alcohols.[1a,c] Grün[1b] reported the formation of di- and triglycerides when monoglycerides were heated but did not identify the products completely. Fischer[2] prepared α-dibenzoylglycerol by the vacuum distillation of α-monobenzoylglycerol. More recently Hurd[3] has described the formation of glycerol triphenyl-

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[1] (a) Bellucci, *Gazz. chim. ital.*, **42**, II, 283 (1912); (b) Grün, *Chem. Umschau Fette, Öle, Wachse, Harz.*, **32**, 225 (1925); (c) Tsuchiya and Akiyama, *J. Soc. Chem. Ind. Japan*, **36**, Suppl. binding, 233 (1933).

[2] Fischer, Bergmann and Bäwind, *Ber.*, **53**, 1589 (1920).

[3] Hurd, *et al.*, THIS JOURNAL, **59**, 1952 (1937).

methyl di- and triethers by heating the α-monoether to 190 and 260°, respectively.

This research has resulted from the observation that commercial monoglycerides, as prepared from natural fats and glycerol, do not hydrolyze when deodorized with steam at high temperatures and reduced pressures, but lose glycerol and are converted into the original fat. In the present investigation, pure synthetic triglycerides have been treated with glycerol in the presence of catalysts. The reaction products have been separated and identified. Their behavior during vacuum distillation with and without the aid of steam has been studied.

Experimental

α-Monoglycerides.—Monolaurin, monopalmitin and monostearin were prepared by Fischer's method as described by King and co-workers.[4] In the purification of these compounds by numerous crystallizations, it was noted that rate of crystallization is an important factor in obtaining the high melting points reported by King. Saponification values were used as the best criterion of purity.

Triglycerides.—Trilaurin, tripalmitin and tristearin were prepared by the action of a slight excess of the fatty acid chlorides on anhydrous glycerol in the presence of quinoline or pyridine. This procedure is a modification of that described by King.[4] After one crystallization from ether and two from an alcohol–chloroform mixture (70:30 by volume) the white crystalline compounds melted sharply and had the theoretical saponification values.

Ethylene Dipalmitate.—Three and one-tenth grams (0.05 mole) of redistilled ethylene glycol and 16 g. of quinoline were placed in a glass-stoppered bottle and cooled in an ice-bath. Twenty-eight g. (0.10 mole) of palmityl chloride was added and the mixture shaken vigorously until it set to a hard mass. After standing at room temperature for two or three days, the product was taken up in 1200 cc. of ether and 400 cc. of 0.5 N sulfuric acid. Successive washings with additional 0.5 N sulfuric acid, 10% sodium bicarbonate and water removed most of the impurities. After drying over anhydrous sodium sulfate, the ether solution was allowed to stand at −26°. Light yellow plates separated which were redissolved in 500 cc. of ether, decolorized with carbon and recrystallized at −26°: yield 20.0 g.; m. p. 68.7–68.9°. This compound, as prepared in another way, has a reported m. p. of 68.7°.[5]

Reaction of Triglycerides with Glycerol.—The reaction between trilaurin and glycerol is described as typical of the procedure. Ten grams of glycerol, 10 g. of trilaurin and 0.2 g. of trisodium phosphate were refluxed for fifteen minutes at the boiling point of glycerol under anhydrous conditions in an atmosphere of nitrogen. One layer formed after five minutes of boiling. After the flask had cooled, some of the excess glycerol was held in solution in the solid fatty layer, but 4 g. of it separated into a clear liquid lower layer. The solid product was dissolved in 100 cc. of anhydrous ether, leaving behind all of the excess glycerol, most of the catalyst and a trace of soap. The ether solution was dried over anhydrous sodium sulfate, decolorized with carbon and crystallized at −26°. The gummy precipitate was recrystallized from 150 cc. of ether and then from 50 cc. of alcohol at −26°: yield 3 g.; m. p. 60.5–61.0°; sap. value 204.2, calcd. for monolaurin, 204.6; mixed m. p. with monolaurin was 60.5–61.0°. With no alkaline catalyst thirty minutes boiling was necessary for the formation of one layer and only 1.0 g. of pure monolaurin was isolated. A small quantity of another compound was separated from the uncatalyzed reaction mixture. This melted at 54.5–55.0°; reported melting point for α,α'-dilaurin 56.6°.[4] The amount obtained was insufficient for saponification value determination. When 0.2 g. of sodium carbonate was used as a catalyst, 0.5 g. of crystalline material was separated: m p. 54.5–55.0°; sap. value 236.4, calcd. for dilaurin, 245.8.

Ten grams of tripalmitin treated in the same way gave 1.0 g. of crystals: m. p. 75.0–75.5°; mixed m. p. with pure monopalmitin 75.0–75.5°; sap. value 171.0, calcd. 169.8. With no alkaline catalyst, a five-hour boiling period failed to cause the formation of one layer and no crystalline product could be isolated. The amorphous nature of many of these products is probably due to the formation of polyglycerol ethers and their esters.

In the case of tristearin 0.5 g. of crystals melting at 79.5–80.0° was isolated when trisodium phosphate was used as catalyst: mixed m. p. with pure monostearin 79.5–80.0°; sap. value 156.0, calcd. 156.6.

Several recrystallizations were required in the isolation of pure reaction products from the reësterification of tripalmitin and tristearin. The low yields of pure monoglycerides obtained are not indicative of the completeness of the reaction. In every case, the saponification value of the reaction mixture, after complete removal of excess glycerol, was only slightly above the calculated value for the pure compound. The loss occurred in the several crystallizations necessary for the removal of last traces of di- and triglycerides.

Decomposition of α-Monoglycerides when Heated in Vacuo.—The distillation of α-monopalmitin is described as typical of this procedure. Five grams of monopalmitin was distilled at 0.5 mm. With an oil-bath temperature of 200°, material was distilled at 189–190°. Distillation stopped after half the material came over. Nothing more distilled even by raising the temperature to 225°. The non-volatile residue, when purified by successive crystallization from alcohol–chloroform mixtures, was tripalmitin and melted at 63.5–64.0°. The distillate was extracted with ether to separate the fatty material from glycerol. Seven-tenths gram of material was isolated from the distillate melting at 74.0–75.0°; mixed m. p. with pure monopalmitin 74.0–75.0°.

Similar treatment of α-monolaurin resulted in the distillation of a large portion of the monolaurin unchanged, b. p. 171–172° (0.5 mm.). A very small amount of glycerol was found in the distillate. The residue in the flask was purified and yielded 0.5 g. of trilaurin. α-Monostearin was transformed into tristearin with only a trace of the

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(4) Averill, Roche and King, THIS JOURNAL, **51**, 866 (1929).

(5) Rutan and Roebuck, *Trans. Roy. Soc. Canada*, [3] **9**, June (1915).

monoglyceride distilling unchanged at 184–86 (0.3 mm.). An appreciable quantity of glycerol which distilled with the trace of fatty material made isolation of the small amount of monoglyceride impossible.

Reaction of Ethylene Dipalmitate with Ethylene Glycol.—Ten grams of ethylene glycol (redistilled and dry) was refluxed at its boiling point with 10 g. of ethylene dipalmitate and 0.2 g. of anhydrous trisodium phosphate. The reaction proceeded for fifteen minutes, one layer being formed after ten minutes of boiling. The esters were separated from excess ethylene glycol by means of dry ether extraction. Impure crystals were obtained by holding the ether solution at −26°. These, after being filtered, were dissolved in 250 cc. of hot alcohol. As the solution cooled to room temperature, crystals of unreacted dipalmitate separated, m. p. 68.6–68.9°; yield 2 g. The mother liquor, when cooled to 2°, yielded 5 g. of β-hydroxyethyl palmitate, m. p. 51.2–51.5°. Rutan and Roebuck[6] reported the melting point of β-hydroxyethyl palmitate and ethylene dipalmitate as 51.5 and 68.7°, respectively. This method for the preparation of the monoester is an improvement over earlier methods. With no alkaline catalyst the interesterification did not take place during three hours of refluxing at the boiling point of ethylene glycol.

Decomposition of β-Hydroxyethyl Palmitate when Heated in Vacuo.—Five grams of the palmitate was distilled as described previously for the α-monoglycerides. About half the material distilled at 155–160 (2 mm.). From the residue there was separated 1.5 g. of pure ethylene dipalmitate, m. p. 68.5–68.9°. The distillate was separated and purified by fractional crystallization from alcohol. A trace of the crude dipalmitate, melting at 66–67°, separated at room temperature. The mother liquor at 2° yielded 1.5 g. of pure β-hydroxyethyl palmitate, m. p. 51.5–52.0°.

Steam Distillation of α-Monoglycerides in Vacuo.—The distillation procedure already described was repeated with a rapid current of steam being used. A vacuum of 2 mm. was maintained. The same general reaction was obtained in every case; *i. e.*, some of the monoglyceride and glycerol distilled, the triglyceride remaining in the residue. At no time was there found more than minute traces of free fatty acid in the distillates from the steam distillation. This is noteworthy because much steam was used, and during the removal of glycerol and the transformation to triglyceride one might expect any free acyl groups to react with the steam as rapidly as with monoglyceride. In the presence of steam, decomposition of mixed monoglycerides, as prepared from natural fats, to triglycerides and glycerol takes place at a much lower temperature (140°) than under the condition of ordinary vacuum distillation (170°).

Discussion

The reaction between triglycerides and glycerol is reversible. The reaction between the higher diesters of ethylene glycol and the glycol is also reversible. Alkaline catalysts promote the formation of the monoesters but seem to have no accelerating effect upon their decomposition during vacuum distillation with or without steam. Temperatures required for formation of mono- from polyesters are appreciably higher than for the reverse decomposition. The catalytic effect of the alkaline salts used may be due either to the alkalies themselves or to the soaps formed during the reaction. Approximately 90–95% of the alkaline salt catalysts are recovered when anhydrous reactants are used, but small traces of soap are always found in the reaction mixture.

Summary

1. The products obtained by the interaction of triglycerides with glycerol have been isolated in pure state. These products are chiefly α-monoglycerides.

2. There has been effected the reverse of this reaction, namely, the formation of triglycerides from the mono- or diglycerides by distillation *in vacuo* with or without steam.

3. A new method of preparation for β-hydroxyethyl palmitate has been described as well as a method for its separation from ethylene dipalmitate.

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