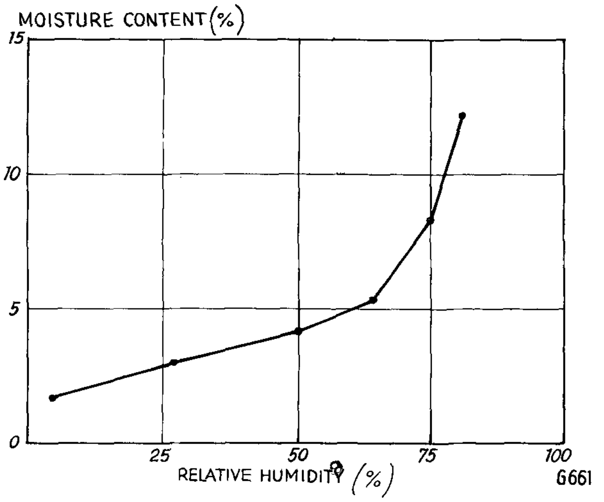

FIG. 10. Relation between moisture content and relative humidity at 55°C. of Dutch shortbread.

TABLE III

Peroxide Value of Powdered Dutch Shortbread, Stored at 37°C. and 22°C., with and Without BHT for Eight Months

Storage time	At 37°C.		At 22°C.	
	Control	With BHT	Control	With BHT
(days)				
30	0.5	0.7	0.7	0.6
58	0.9	0.7	1.5	—
73	1.1	0.6	—	—
159	1.7	1.0	0.8	0.5
252	3.1	1.6	1.0	0.6

TABLE IV

Peroxide Value of Dutch Shortbread, Stored in Tins Lined with Untreated and BHT-Treated Packing Paper at 22°C. for Eight Months

Storage time	Control		BHT-treated shortbread	
	Untreated paper	Treated paper	Untreated paper	Treated paper
(days)				
30	0.7	0.7	0.6	0.6
73	0.9	0.9	1.2	0.6
252	1.3	1.3	0.7	0.7

The vanillin component especially was characteristic. As to the powders stored at 22°C. hardly any difference could be tasted.

Even after eight months of storage all the samples qualified as very good. One may say that BHT, incorporated in the shortbread, had some slightly depressing effect on the formation of peroxides. The similarity between the peroxide values of the samples packed in BHT-treated and in untreated paper indicated that during the storage period BHT had no effect.

From results obtained with shortbread stored under different conditions, the conclusion may be drawn that BHT can afford good protection against peroxide formation as well as against flavor deterioration.

Summary

Investigations on the use of the gallic acid esters, butylated hydroxyanisole, and butylated hydroxytoluene as antioxidants in animal fats, vegetable oils, margarine, and bakery products are described. It was found that the gallates and BHT were highly effective in lard; BHA was of lesser importance.

In vegetable oils scarcely any effect was observed although some antioxidants might be able to suppress peroxide formation in these products; the flavor evaluations however are not always in accordance with these findings.

In margarine it was found that some antioxidants had a promising effect on the peroxide formation but only a slight effect on the flavor. Mixtures of antioxidants however could exercise a synergistic effect on the organoleptic qualities.

In bakery products, *e.g.*, Dutch shortbread, BHT can afford good protection against flavor deterioration.

Mention is made of the fact that the dissociation of peroxides is governed primarily by their concentration and that fats with a peroxide value of 25 to 50 meq/kg. are very stable on heating at 100°C. without air-passage.

REFERENCES

1. Ault, W. C., Weil, J. K., Nutting, G. C., and Cowan, J. C., J. Am. Chem. Soc., *69*, 2003–2005 (1947).
2. Bergel, F., Chemistry and Industry, *1944*, 127–128.
3. Boehm, E., and Williams, R., Pharm. J., *151*, 53 (1943).
4. Carr, D. S., and Harris, B. L., Ind. Eng. Chem., *41*, 2014–2015 (1949).
5. Engel, C., and Tollenaar, F. D., private communication to K. J. H. van Sluys, Food Manuf., *26*, 99–101 (1951).
6. Esch, G. J. van Voeding, *16*, 683–686 (1955).
7. Hilditch, T. P., Chemistry and Industry, *1944*, 67–71.
8. Kaufmann, H. P., Thieme, J. G., and Volbert, F., Fette, Seifen, Anstrichm., *58*, 1046–1056 (1956).
9. Kerk, G. J. M. van der, Verbeek, J. H., and Cleton, J. C. F., Rec. Trav. Chim., *70*, 277–284 (1951).
10. Morris, S. G., and Riemenschneider, R. W., J. Am. Chem. Soc., *68*, 500–501 (1946).
11. Mossel, D. A. A., and Kuyk, H. J. L. van, Food Research, *20*, 415–423 (1955).
12. Tollenaar, F. D., Intern. Dairy Congr. Stockholm, 1949; Proc. XIIth Congr., *2*, 357–367 (1949); *7*, 73–74 (1951).
13. Tollenaar, F. D., Centr. Inst. Nutrition Research T.N.O., Rept. R307 (1952), 10 pp.
14. Tollenaar, F. D., IXth Intern. Congr. Agricult. and Food Inds., Rome, 1952, T. P. 9.
15. Tollenaar, F. D., Olearia, *7*, 5–14 (1953).
16. Tollenaar, F. D., Deut. Lebensm.-Rundschau, *52*, 307–313 (1956).
17. Tollenaar, F. D., and Vos, H. J., Fette, Seifen, Anstrichm., *58*, 112–118 (1956).
18. Tollenaar, F. D., Fette und Seifen, *55*, 3–7 (1953).
19. Vos, H. J., Wessels H., and Six, C. W. Th., Analyst, *82*, 362–367 (1957).

[Received June 26, 1957]

Preparation of 3-Stearoyl-D-Glucose—A Bread-Softening Agent

F. H. OTEY and C. L. MEHLTRETTER, Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois

BREAD STALING has long been a problem to the baking industry. One important aspect of bread staling is the increase in firming of the crumb, and it is desirable to develop products which will prolong crumb softness and thus shelf life of bread (4). To find more effective softening agents acceptable for use in bread a study was made of the relationship of bread-softening action to the chemical structure of compounds derived from glucose (6). Of the products synthesized and evaluated, the most promising was 3-stearoyl-D-glucose. This substance was found to have a high crumb-softening action comparable to that of polyoxyethylene monostearate (4), one of the most effective bread softeners available. Improved machinability of doughs and increased water absorption of doughs, both desirable properties to the baker, were also obtained with 3-stearoyl-D-glucose. Because the product is a simple ester of glucose and stearic acid, it probably would be acceptable as a food additive.

Esterification of the hydroxyl group at position 3 in the D-glucose structure was accomplished by reacting stearoyl chloride with 1,2:5,6-diisopropylidene-D-glucose in the presence of chloroform (or dimethylformamide) and pyridine.

Subsequent hydrolysis of the intermediate 3-stearoyl-1,2:5,6-diisopropylidene-D-glucose with mineral acid eliminated acetone and gave the desired 3-stearoyl-D-glucose. In an alternate method for preparing the ester in higher yield and purity the 1,2:5,6-diisopropylidene-D-glucose was reacted with sodium dispersed in toluene prior to esterification with stearoyl chloride in the same solvent. The products obtained by the sodium method had a higher melting point than that prepared in pyridine, but paper chromatography, mixed melting point, and optical rotation indicated that the products were structurally alike.

In view of the possibility of acyl group migration (3) during deacetonation of the intermediate, confirmation of the 3-stearoyl structure was sought. Acetonation of the ester followed by saponification produced 1,2:5,6-diisopropylidene-D-glucose in high yield and showed that little or no migration of the stearoyl group had occurred.

Experimental

Materials. The 1,2:5,6-diisopropylidene-D-glucose was prepared as described in a previous paper (5). Toluene was found to be a satisfactory solvent for extraction of the compound from water in a sufficiently pure state for direct esterification.

Stearoyl chloride was prepared in 90% yield from Hystrene S-97[1] stearic acid by the method of Ralston and Selby (7) and was purified by distillation.

Esterification in Pyridine. Sixty-five grams (0.25 mole) of 1,2:5,6-diisopropylidene-D-glucose were dissolved in 100 ml. of dry pyridine. Gradually added to this solution were 50 ml. of chloroform containing 83.3 g. (0.275 mole) of stearoyl chloride. The reaction mixture, protected from air moisture, was stirred at room temperature for 24 hrs. After the solvent was removed *in vacuo* at 60°C., the residual crude 3-stearoyl-1,2:5,6-diisopropylidene-D-glucose was deacetonated in 700 ml. of diethyl ether by stirring while 700 ml. of concentrated hydrochloric acid were added in small portions as rapidly as possible (1). A rise in temperature above 20°C. was avoided by chilling the mixture. After stirring for 2 hrs., 1 liter of ice water was added, and stirring was continued for 2 hrs. The floating precipitate was filtered, washed free of acid with water, and dried at 50°C. Yield of crude product was 85 g. (76%). Extraction with boiling ether (acetone may also be used) yielded 58 g. of product that was sufficiently pure for bread-softening tests. Recrystallization from ethanol gave a melting point of 125–130°C.; $[\alpha]^{25}_{D}$ + 66.5° (c, 3.9; pyridine [after 10 min.]).

Anal. calcd. for $C_{24}H_{46}O_7$: C, 64.54; H, 10.38. Found: C, 64.12; H, 10.33.

Munson and Walker method (2): Found: Theoretical amount of D-glucose.

Esterification with Sodium. To a suspension of 15 g. of "bird shot" sodium in toluene were slowly added 54.6 g. (0.21 mole) of 1,2:5,6-diisopropylidene-D-glucose dissolved in 350 ml. of toluene. After stirring for 20 hrs., the solution was decanted from excess sodium. To this sodium was added dropwise, with stirring, 64.4 g. (0.212 mole) of stearoyl chloride over a period of 1.5 hrs. The remaining operations were essentially the same as those described in the pyridine procedure. Yield of crude 3-stearoyl-D-glucose was 78.5 g. (84%). Extraction with ether or acetone yielded 61 g. of final product, which melted at about 110°C. Recrystallization from alcohol produced platelets melting at 135–139°C.; $[\alpha]^{25}_{D}$ + 66.9° (c, 3; pyridine [after 30 min.]).

Anal. calcd. for $C_{24}H_{46}O_7$: C, 64.54; H, 10.38. Found: C, 64.14; H, 10.37.

Munson and Walker Method: Found: Theoretical amount of D-glucose.

Proof of Structure. Three grams (0.0067 mole) of 3-stearyl-D-glucose (which was prepared in pyridine) were added to a cooled solution of 40 ml. of acetone containing 1 ml. of concentrated sulfuric acid. The mixture was stirred for 4 hrs. at 20–25°C., and the unreacted product (0.1 g.) was recovered by filtration and washed with acetone. The combined filtrate and washings were chilled and carefully neutralized with concentrated aqueous sodium hydroxide. After removing precipitated sodium sulfate, the solution was concentrated to dryness *in vacuo* at 15–20°C. The oily residue was crystallized from acetone by the addition of water and again from aqueous ethanol. Yield of 3-stearoyl-1,2:5,6-diisopropylidene-D-glucose was 2.45 g. (71.6%); melting point 32–34°C.

Anal. calcd. for $C_{30}H_{54}O_7$: C, 68.40; H, 10.33. Found: C, 68.29; H, 10.07.

The 3-stearoyl-1,2:5,6-diisopropylidene-D-glucose (1.40 g., 0.0027 mole) was refluxed in alkaline ethanol for 20 min. After removal of ethanol *in vacuo* the residue was dissolved in water and extracted with toluene. The toluene extract was concentrated to dryness *in vacuo* to yield 0.65 g. (94%) of crude product, which after recrystallization from water melted at 109–110°C. Mixed melting point and paper chromatography proved the substance to be 1,2:5,6-diisopropylidene-D-glucose.

Repetition of this procedure with 3-stearoyl-D-glucose prepared by the sodium method also produced 1,2:5,6-diisopropylene-D-glucose in good yield.

Summary

In previous work 3-stearoyl-D-glucose was found to have superior bread softening action. This paper describes its synthesis by reaction of stearoyl chloride with 1,2:5,6-diisopropylidene-D-glucose and subsequent deacetonation of the intermediate stearoyl diisopropylidene-D-glucose. Acetonation of the product, followed by saponification of the acyl group, produced 1,2:5,6-diisopropylidene-D-glucose and indicated that the substance is 3-stearoyl-D-glucose.

Acknowledgment

The authors wish to thank Bonita R. Hopson and Clara E. McGrew of this Division for the elemental analyses.

---

[1] The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or products not mentioned.

REFERENCES

1. Baer, E., and Fischer, H. O. L., J. Biol. Chem., *128*, 475–489 (1939).
2. Bates, F. J., "Polarimetry, Saccharimetry, and the Sugars," Circ. C440, Natl. Bur. Standards, p. 174, Washington, D. C., U. S. Government Printing Office, 1942.
3. Doerschuk, A. P., J. Am. Chem. Soc., *74*, 4202–4203 (1952).
4. Kent-Jones, D. W., and Amos, A. J., "Modern Cereal Chemistry," 5th ed., p. 301, Liverpool, England, The Northern Publishing Company, 1957.
5. Mehltretter, C. L., Alexander, B. H., Mellies, R. L., and Rist, C. E., J. Am. Chem. Soc., *73*, 2424–2427 (1951).
6. Ofelt, C. W. Mehltretter, C. L., MacMasters, M. M., Otey, F. H., and Senti, F. R., Cereal Chem., *35*(2), 142–145 (1958).
7. Ralston, A. W., and Selby, W. M., J. Am. Chem. Soc., *61*, 1019–1020 (1939).

Differential Thermal Analysis. III. Melting Curves of Oils and Fats

J. HANNEWIJK and A. J. HAIGHTON, Unilever Research Laboratory, Vlaardingen, The Netherlands

IN THE FIRST PART of this series (1) the principle, apparatus, and procedure of the differential thermal method for the analysis of fats are described. In addition, examples of melting curves of water and of some fats are included. In the second part (2) a description of melting curves of a number of pure glycerides is given. In the present paper the various factors influencing the shape of the melting curves are discussed in detail. These factors may be based on the apparatus (height and diameter of fat layer, rate of heating), but they can be kept constant, and therefore the manner in which crystallization takes place is of much greater importance. The pretreatment of the fats is also considered. Reproducibility of the measurements is checked, using different sample holders and thermocouples. Finally some DTA curves of natural oils and fats are given.

Influence of Cooling and Tempering on DTA Curves

In order to be able to draw the base line of a melting curve the determination should start from about 10° to 20°C. below the temperature at which melting sets in. Cooling to this temperature may be performed in the following ways.

a) The fat or fatty mixture is introduced into the sample holder and is rapidly cooled. The melting curve obtained gives information about the fatty portion as such. Figure 1a shows the curve of a chocolate with cocoa butter and a curve of chocolate with a substitute.

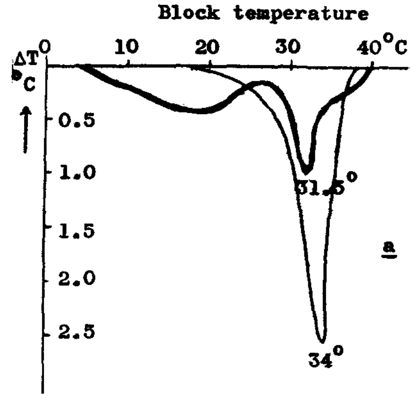

FIG. 1a. ——— pure chocolate, fat phase = 100% cocoa butter
▬▬▬ chocolate, fat phase = 50% cocoa butter, 50% substitute (hardened fat).

b) The sample holder, filled with premelted fat, is placed in the copper block, which is rapidly cooled subsequently until the fat is completely solid. In this way often metastable crystals will be formed, resulting in exothermic transformation peaks (maxima) in the curve. This method is particularly suitable for studying the polymorphic behavior of fats. The positions of these peaks can be useful for the identification of pure triglycerides and of fats and oils. The curves for such unestablished fats are drawn as dotted lines.

c) The liquid fat is introduced into the sample holder and stabilized at a given temperature. On stabilizing, the following takes place. If a fat with a number of triglycerides of different melting points is rapidly cooled, a great variety of mixed crystals will be formed, resulting in a regular melting range (Figure 1b, dotted line). If such an unstabilized fat is tempered at, *e.g.*, 29°C., part of the mixed crystals will melt, and the more saturated glycerides will be reassociated to form new series of mixed crystals, having higher melting points. This is illustrated by two minima in Figure 1b (at 27° and 37°C.). Hence, by the selective stearin formation during tempering, the final melting point is increased from 39° to 42°C., and the initial melting point is decreased

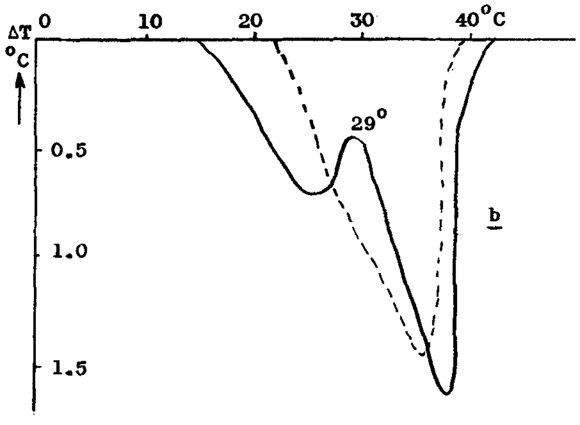

FIG. 1b. Cocoa butter substitute (based on coconut oil):
-------- rapidly cooled.
——— tempered at 29°C.

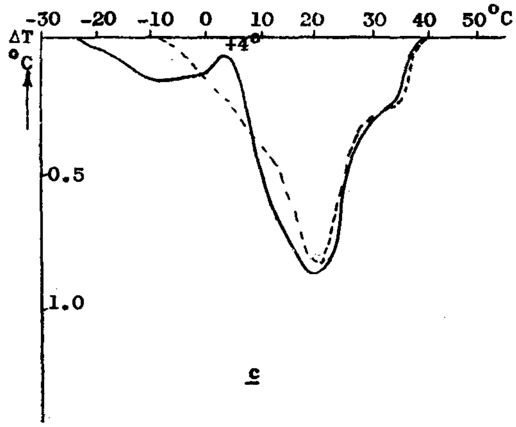

FIG. 1c. Margarine fat blend:
-------- rapidly cooled (directly after Votator)
——— after 1 hr. of tempering at 5°C.