On the Configuration of Cocoa Butter

E. S. LUTTON, Research and Development Department, Procter and Gamble Company,
Miami Valley Laboratories, Cincinnati, Ohio

THE GLYCERIDES OF COCOA BUTTER have been stated to be approximately as follows: (1) 2% trisaturated, 20% 2-oleoyldistearin, 55% 2-palmitoyloleoylstearin (OPS), 5% oleoyldipalmitin, 18% monosaturated. All three possible configurations have been proposed for the principal glyceride, but the present study shows that it is actually 2-oleoylpalmitoylstearin (POS)[1] for which the earlier evidence was limited (3).

By a procedure modelled closely after that of Hilditch and Stainsby (4) a "middle half" was separated from commercial cocoa butter by fractional crystallization from acetone in 11 steps. Five fractions of intermediate solubility, grouped according to refractive index, totalled 605 g. out of an original 1,200. Data for the cocoa butter and the selected "POS portion" are compared with theory and literature values in Table I.

A 71.6-g. charge of methyl ester of the "POS portion" was fractionally distilled. Calculations from sapon. nos. of the six fractions indicated 0.6% methyl myristate, 31.2% palmitate, and the remainder C_{18} (theory for POS, 31.2% palmitate).

X-ray examination of the "POS portion" showed alpha-2, beta prime-2, and beta-3 forms of m.p., respectively; 17°, 27°, and 35.5° with short spacings (Å) 4.22 S; 4.33 S, 4.11 S, 3.83 M-diff.; 5.43 W, 5.14 VW, 4.61 S, 4.00 W, 3.85 VW, 3.74 W, 3.64 W, where S is strong, M is medium, W is weak, VW is very weak, diff. is diffuse. Long spacings (Å) were, respectively, 48, 44, and 64.3. These values compare well with POS values (5), but the metastable beta prime-3 form found for POS was not observed.

A cooling curve of a 75-g. sample of completely hydrogenated "POS portion" showed the rapid rise from the minimum expected for PSS as compared with the long flat at the minimum typical of SPS (6). Determinations of m.p. and x-ray data of alpha, beta prime, and beta forms were in good correspondence with those of PSS (7).

Subjecting the "POS portion" to enzymatic hydrolysis by pancreatic lipase, which removes fatty acids from 1- and 3-positions to leave 2-monoglyceride (8), yielded fatty acids of iodine value 5 and monoglycerides of iodine value 89; this indicates saturated acids in 1- and 3-positions and unsaturated in the 2-position.

The combination of evidence shows that the predominant glyceride of cocoa butter is POS, which largely determines the character of cocoa butter, *e.g.*, its beta-3 phase. Compatible cocoa butter extenders should therefore be of symmetrical, disaturated configuration to promote beta-3 formation instead of unsymmetrical, disaturated configuration, for which the stable form is beta prime-3. Dilatometric and enrobing studies indicate a compatibility of fractions from such fats as aceituno oil, Borneo tallow, and palm oil and the incompatibility of "OPS fractions" from lard.

The present conclusion with regard to the major component of cocoa butter adds to the considerable evidence in the literature that the disaturated glycerides of vegetable fats are symmetrical. Further support is given to the idea that triglycerides of specific configuration are characteristic of natural fats rather than triglycerides formed by random fatty acid distribution.

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Summary

It is concluded from x-ray diffraction, thermal curve, and enzymatic hydrolysis that the predominant glyceride of cocoa butter is 2-oleoyl palmitoyl stearin (POS) instead of 2-palmitoyl oleoyl stearin (OPS), the configuration which has been rather generally accepted. Accordingly it is suggested that a fully satisfactory cocoa butter extender should be largely of symmetrical, disaturated configuration since only thus is the characteristic beta-3 form of cocoa butter likely to be preserved.

An important aspect of this finding is that all disaturated vegetable glycerides which have been well characterized are of symmetrical, disaturated configuration. This not only supports the idea of the formation of specific glycerides in natural fats as opposed to random fatty acid distribution but also points to some important common feature in vegetable glyceride metabolism.

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[1] Since the manuscript for this paper was submitted, it has come to the author's attention that the POS configuration has been recently proposed by others on the basis of similar evidence (2).

TABLE I

Analytical and Physical Data on Cocoa Butter and "POS Portion"

	Cocoa butter	"POS portion"	Theory and Lit. (4) for		
			POS	OPS	OSP
Iodine No.	40.0	31.4		32.8	
Sapon. No.	191.7	195.6		195.2	
% Saturated acids	54.7	62.6		62.8	
% Oleic acids	37.4	31.4		32.8	
% Linoleic acids	3.2	1.6			
Rapid complete M.P. (7)		17.0°	18.2°	25.3°	26.3°
Complete M.P.		33–35.5°	38°	37–40°	39.8°
Phase (from solvent)		Beta-3	Beta-3	Beta Prime-3	Beta Prime-3
Complete M.P. of completely hydrogenated sample (7)		64.8°	65.2°	68°	65.2°

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• Oils and Fats

Isomerization of unsaturated fatty-acid esters. I. Effect of catalysts on double-bond migration. J. J. A. Blekkingh, H. J. J. Janssen and J. G. Keppler (Unilever Res. Lab., Vlaardingen, Neth.). *Rec. trav. chim.* **76**, 35–48(1957). Methyl esters of oleic, elaidic, erucic, petroselenic, physeteric, 10-hendecenoic, 12-acetoxy-9-octadecenoic, and linoleic acids were isomerized by stirring 4 to 10 g. with 0.4 to 1.0 g. nickel catalyst (containing sulfur) in carbon dioxide atmosphere for 8 hours at constant temperature. With nickel catalyst migration of the double bonds occurs predominantly toward the methyl group. No migration was observed with elaidinization catalysts (sulfur dioxide, selenium, nitrogen trioxide) or with alkali isomerization. During simultaneous hydrogenation with platinum catalyst, migration of the double bond in methyl oleate occurred only after reduction of the main portion of the ester.

II. Location of double bonds by oxidative degradation methods. J. G. Keppler. *Ibid.* 49–57. Oxidative degradation methods for location of double bonds based on potassium permanganate in acetic acid, ozonolysis, sodium dichromate and chromic oxide were investigated. A procedure using ionization followed by treatment with silver oxide in alkaline medium was preferred. Analyses of the fission products were by chromatographic methods. (*C. A.* **51**, 10927)

Esterified olive oil and tests for peanut oil. V. Gazzi (Lab. chim. provinciale, Bologna, Italy). *Boll. lab. chim. provinciale (Bologna)* **7**, 150–4(1956). The presence of peanut oil in rectified B grade olive oil cannot be determined by the usual A.O.A.C.-1955 test or its variations, by Allavena's method, nor by Blanc's method. (*C. A.* **51**, 10786)

Peroxide estimation in fats. L. Hartman (D.S.I.R., Wellington). *J. New Zealand Inst. Chem.* **20**, 132–6(1956). A review. (*C. A.* **51**, 10925)

Spectrophotometric estimation of chlorophylls and pheophytins in olive oil. Mariano M. Lorenzo. *Anales inst. nacl. invest. agron. (Madrid)* **5**, 295–307(1956). Maximum coefficients of absorption of chlorophyll a, chlorophyll b, pheophytin a, and pheophytin b occur at wave lengths 6700, 6525, 6775, and 6625 Å., respectively. Beer's law holds at these wave lengths for concentrations of between 0 and 10 p.p.m. Thus, by determining the absorption coefficients for these wave lengths on a sample of olive oil, the contents of the chlorophylls and the pheophytins can be determined by use of equations. A table of absorption coefficients is presented in the original. (*C. A.* **51**, 10927)

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Polymerized components in sulfur-olive oil. J. Gracián Tous, E. Vioque, and P. de la Maza (Inst. Gras y Sus Derivados, Servilla, Spain). *Fette, Seifen Anstrichmittel* **58**, 353–6(1956). Sulfur-olive oil foots contain polymerized compounds which could be decomposed by strong hydrolysis. (*C. A.* **51**, 10928)

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Nonsaponifiables from deep-fry fats. Dolores Torres, Toni Trinchese, Sister Emeran Foley and J. V. Karabinos (College of St. Francis, Joliet, Ill.). *Trans. Illinois State Acad. Sci.* **49**, 205–6(1956). Seven vegetable, animal, and mixed fats which had been used 10–180 days for deep fat frying foods and an unused corn oil were analyzed for nonsaponifiables. The unused corn oil gave 1.5% of nonsaponifiables which gave a strong Lieberman-Burchard test, while the others gave 0.3–1.3% of nonsaponifiables with negative to slightly positive Lieberman-Burchard test. (*C. A.* **51**, 10786)

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