80° petroleum ether. The pure material melted at 99.5–100.5° after two recrystallizations from petroleum ether. *Anal.* Calcd. for $C_{10}H_{17}O_2N$: C, 65.57; H, 9.38; N, 7.65. Found: C, 65.98; H, 9.36; N (Dumas), 7.66. Attempts to hydrolyze this cyanohydrin by the procedure given for phenylacetonitrile (use of hydrogen chloride dissolved in alcohol)[13] gave only a few per cent. of recovered cyanohydrin.

4-Hydroxy-2,6-dimethylcyclohexanone cyanohydrin (VII) was prepared in 20% yield from 5.6 g. of VI in 20 ml. of 95% ethanol saturated with hydrogen chloride by allowing the reaction mixture to stand overnight, removing the ammonium chloride by filtration, and then heating the filtrate in a sealed tube on the steam-bath for two hours. The reaction mixture was concentrated to a sirup, dissolved in a few ml. of water and an unidentified halogen containing solid, m. p. 170–175°, filtered off. Dropwise addition of 10% sodium hydroxide solution to the filtrate precipitated the dihydroxy compound, m. p. 169–171° after recrystallization from 60–80° petroleum ether. *Anal.* Calcd. for $C_9H_{15}O_2N$: C, 63.88; H, 8.92; N, 8.27. Found: C, 63.82; H, 9.15, N (Dumas), 8.41. Heating VII with dilute sodium hydroxide solution and ferrous ammonium sulfate followed by acidification gave a strong Prussian blue test.

Heating VI with five times its weight of concentrated hydrochloric acid on a steam-bath two hours gave 25% of unchanged VI and 6% of VII, isolated as above. The use of 48% hydrobromic acid gave erratic results.

1-Acetyl-2,6-dimethyl-4-methoxycyclohexanone cyanohydrin was prepared by mixing 12.1 g. of VI, 50 ml. of acetic anhydride and 1 ml. of concentrated sulfuric acid and refluxing for three hours. The reaction mixture was diluted with water, neutralized with sodium acetate and potassium carbonate, extracted with ether, and the ether layer dried with potassium carbonate and distilled. There was obtained 6 g. (40% yield) of the acetoxy compound, b. p. 103–107° (1.5 mm.). The material was inert to bromine dissolved in carbon tetrachloride and to aqueous potassium permanganate solution. Heating with sodium hydroxide solution and a ferrous salt followed by acidification gave a Prussian blue test. *Anal.* Calcd. for $C_{12}H_{19}O_3N$: C, 63.97; H, 8.50; $-OCH_3$, 13.77. Found: C, 64.04; H, 8.30; $-OCH_3$, 13.62.

Summary

Hydroquinone monomethyl ether can be converted into 2,6-dimethyl-4-methoxyphenol, the corresponding 2,6-dimethyl-4-methoxycyclohexanol and 2,6-dimethyl-4-methoxycyclohexanone, and the cyanohydrin of the latter. The cyanohydrin forms readily in spite of the methyl groups adjacent to the carbonyl group.

COLLEGE PARK, MD. RECEIVED JANUARY 21, 1950

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(13) Kimball, Jefferson and Pike, ref. 10, p. 284.

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE CO.]

The Polymorphism of Synthetic and Natural 2-Oleyldipalmitin

BY E. S. LUTTON AND F. L. JACKSON

Introduction

Oleyldipalmitin and oleyldistearin have been isolated from various vegetable oils. In several cases it has been indicated that these glycerides were symmetrical, *i. e.*, 2-oleyldistearin (SOS)[1,2,3] and 2-oleyldipalmitin (POP).[4,5] A comparative polymorphic study of synthetic and natural SOS by X-ray and thermal techniques has been reported.[3] The present paper describes a similar study for POP.

Since the completion of this work, the polymorphism of SOS and POP, among other glycerides, has been discussed by Malkin, *et al.*[6] The results differ in important respects from those obtained in this Laboratory.

Experimental

Synthesis of POP.—The synthesis of POP was carried out by recognized procedure, namely, reaction of 1,3-dipalmitin with oleyl chloride in the presence of pyridine. The reaction product was purified by six crystallizations, four from alcohol–ether mixtures and two from Skellysolve B. Final yield of POP was 76%. Table I gives analytical constants for starting materials and product.

Isolation of Natural POP from Stillingia Tallow.—A sample of stillingia tallow was obtained from Irving R. Boody and Co., Inc., New York, N. Y. It showed an acid value of 0.5 and iodine value of 56, the high I. V. being evidence of some admixture of stillingia oil, which however, introduced no difficulty in the separation of POP. A 500-g. portion of the tallow was crystallized from acetone (1:5) at 21°, and the 11% of largely trisaturated precipitate was discarded. A 16° precipitate representing 45% of the sample was largely disaturated. Three more crystallizations of this fraction at 16° yielded 25% of "natural POP," iodine value 30.0 and complete m. p. 36.9°.

TABLE I

ANALYTICAL CONSTANTS FOR STARTING MATERIALS AND PRODUCT

Material	M. p., °C.	Saponifcn. value Exptl.	Theory	Hydroxyl value Exptl.	Theory	Iodine value Exptl.	Theory
1,3-Dipalmitin	72.8	197.4	197.2	99	98.6	0.0	0.0
Methyl oleate	..	189.3	189.3	..	..	84,2	85.6
POP	38.3	...	...	..	..	30.6	30.5

Isolation of Natural POP from Piquia Fat.—Twenty pounds of piquia nuts were obtained from Boody and Co. After shelling, there were twelve pounds of hard pericarp and kernel which were crushed; large fibers were separated. Since pericarp and kernel fat are reported to be very similar, no further separation of nut portions was made. The fat bearing portions were extracted with warm hexane. (Innumerable spines in the pericarp introduce difficulties.) After Wesson refining of the extracted glycerides, there was 430 g. of dark fat. This was fractionally crystallized as in the case of stillingia tallow. A total of 0.25% of higher melting material (largely trisaturated) was removed at 21 and 16°. At 10°, 46% of largely disaturated glycerides was obtained. Two further crystallizations of this fraction at 16° gave 31% of another "natural POP," iodine value 29.8, complete m. p. 36.9°.

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(1) Meara, *J. Chem. Soc.*, 22 (1945).

(2) Filer, *et al.*, THIS JOURNAL, **68**, 167 (1946).

(3) Lutton, *ibid.*, **68**, 676 (1946).

(4) Hilditch, "Chemical Constitution of Natural Fats," 2nd Ed., 1947, p. 281.

(5) Meara, *J. Chem. Soc.*, 773 (1947).

(6) Malkin and Wilson, *ibid.*, 369 (1949).

TABLE II

DETAILED X-RAY DATA FOR SYNTHETIC POP

hkl	Alpha-2 d/n	Alpha-2 I	Sub beta prime-2 d/n	Sub beta prime-2 I	Beta prime-2 d/n	Beta prime-2 I	Beta-3 d/n	Beta-3 I
Long spacings								
001	45.0	VS	42.4	VS	(45.0)	VS	(63.2)	S−
002	23.0	VW	21.4	W	21.2	W	30.3	S
003	15.15	M	14.2	M	14.2	M	20.5	VW−
004								
005	9.20	VW			8.45	VW	12.1	M
006	7.65	VW			7.06	VW	10.15	W
Average d	45.7		42.6		42.5		60.9	
Short spacings								
							8.00	W+
							6.92	W
	4.14	S	5.27	VW	6.08	VW	6.05	VW
	2.43	VW−	4.34	S	4.95	W	5.42	W+
			4.13	S	4.27	VS	4.56	VS
			3.84	M	3.97	S	4.04	M
			3.45	VW	3.61	W	3.85	W
			2.56	VW	3.41	W	3.65	M+
			2.34	VW−	3.23	W	3.28	W
					2.95	VW	2.85	VW
					2.63	W	2.58	M
					2.40	W−	2.39	VW
					2.18	VW	2.27	W
					1.98	VW−	2.18	W
							2.04	VW

TABLE III

COMPARISON OF THERMAL DATA FOR SYNTHETIC AND NATURAL POP'S

Treatment	Synthetic POP (I. V.[b] 30.6) Form[a]	M. p., °C.	Stillingia POP (I. V. 30.0) Form[a]	M. p., °C	Piquia POP (I. V. 29.8) Form[a]	M. p., °C.
Melt, chill 0°	Alpha-2	18.1	Alpha-2	18.9	Alpha-2	19.1
Melted, 20 min. 19°	Sub beta prime-2	26.5	Sub beta prime-2	27.0	Sub beta prime-2	26.0
Melt, chill, 1 day 27°	Beta prime-2	33.5	Beta prime-2	32	Beta prime-2	33.0
Solvent crystallized from acetone	Beta-3	38.3	Beta-3	36.9	Beta-3	36.9

[a] By X-ray diffraction. [b] I. V. = iodine value.

Physical Examination.—Thermal and X-ray examinations were performed as previously described.[7] Thermal points of metastable forms were obtained by a "thrust-in" technique, complete melting being observed in the case of the lowest melting forms, softening point being observed for the intermediate melting forms. Complete m. p. on solvent crystallized and "stabilized" samples was obtained at a heating rate of 0.2° per minute.

The lowest melting alpha form was obtained by melting and chilling the glyceride at 0°. The next form, here called sub beta prime-2, was obtained by crystallizing from the melt at 19°, just above the alpha m. p. (or by transforming alpha). The beta prime-2 form was obtained by crystallizing from the melt at 27° or by transforming sub beta prime; a simple procedure was to melt, chill and hold one day at 27°. The beta form was obtained by solvent crystallization or, in the cases of the synthetic sample and the POP from piquia fat, by transformation of beta prime near its m. p. The POP from stillingia tallow was not transformed to beta under similar conditions.

The nomenclature used in this report is in keeping with that previously adopted[8]; thus "alpha" forms show only one strong short spacing which is near 4.2 Å., "beta prime" shows strong spacings near 4.2 and 3.8 Å., while "beta" shows a strong spacing near 4.6 but none near 4.2 Å. The new term sub beta prime refers to the lower melting of two forms, both of which fit the beta prime designation; similarly for sub beta in the case of SOS. This development in nomenclature avoids undue multiplication of form types where similarities in pattern exist.

Detailed diffraction data for synthetic POP are given in Table II; comparative thermal data for natural and synthetic POP appear in Table III. The unrecorded X-ray spacings for natural samples agree in detail (within experimental error) with those for synthetic POP.

Further confirmation of the identity of POP from stillingia tallow was obtained by complete hydrogenation of a small portion. The product's alpha softening point of 47°, complete m. p. of 68.2°, and 90% beta prime (10% beta) pattern on hexane crystallization prove it to be almost entirely 2-stearyldipalmitin which shows corresponding values of 46.5 and 68.6°, and alone of the saturated C_{16}–C_{18} triglycerides gives beta prime from hexane.[7]

Discussion

In presenting evidence on the behavior of related glycerides, it is advisable to group the glycerides according to their behavior as much as possible. This should not be done to the extent of obscuring significant major differences in behavior. For instance, the differences in the mixed saturated C_{16}–C_{18} triglycerides are more interesting

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(7) Lutton, Jackson and Quimby, THIS JOURNAL, **70**, 2441 (1948).

(8) Lutton, *ibid.*, **70**, 248 (1948).

TABLE IV

COMPARATIVE DATA FOR FORMS OF POP AND SOS

POP								SOS			
Lutton and Jackson				Malkin and Wilson				Lutton			
Form	M. p., °C.	S. S.	L. S.	Form	M. p., °C.	S. S.	L. S.	Form	M. p., °C.	S. S.	L. S.
				Vitreous	12.0						
α-2	18	4.14S	45.7	α	21.5	Not stable at r. temp. according to Malkin		α-3	22.4	4.19VS	80
Sub β′-2	26.5	4.34S 4.13S 3.84M	42.6	β′	35.0	4.35S 4.14M 3.88M	42.1	β′-3[a]	35	4.59W 4.40W 4.21M 4.07M 3.76M	68
β′-2	33.5	4.27VS 3.97S	42.5	β″	29.0	5.21W 4.74S 4.42M 3.87VS 3.58M	68.5	Sub β-3[b]	37	5.22M− 4.74S 4.55M− 4.23W 3.88VS 3.60M+	73
β-3	38.3	5.42W+ 4.56VS 4.04M 3.65M+	60.9	β	37.5	5.45M 4.56VS 4.0M 3.8W 3.7M	60.7	β-3	44.3	5.44M 4.62VS 4.01M 3.86W 3.78M 3.64M	64

[a] New data from this Laboratory; this form (which appears only from rapidly cooled solvent) previously reported by Filer, *et al.*[2] [b] Formerly called X-3, here called sub beta-3 on the basis of a strong line near 4.6 Å.

perhaps than the similarities. Likewise POP and SOS have shown major differences in polymorphic behavior which have not been brought out by Malkin, *et al.*[6] This is illustrated in Table IV.

In particular, it is seen in Table IV that the characteristic intermediate form (from melt) for SOS is sub beta-3 while the two characteristic intermediate forms of POP are both of double chain length beta prime-type structure.

Malkin, *et al.*,[6] report diffraction patterns corresponding to both sub beta prime-2 and sub beta-3 (called by them β′ and β″, respectively) for POP (and also for SOS). They report no beta prime-2 (nor beta prime-3) pattern, in terms of the present nomenclature. Moreover, their sub beta prime-2 form (called β′) is assigned a m. p. which is 8–9° high; this indicates confusion with beta prime-2 which is clearly a separate form. There is agreement that the stable form of POP (as well as that of SOS) is triple chain length beta.

In support of the polymorphic forms reported here for POP, it is significant that the same four polymorphic forms were found for each of four separate preparations of POP, two synthetic[9] and two isolated from natural sources. Moreover, the synthetic and natural samples were examined at different times by different individuals. Each of the four forms reported here for POP was readily reproducible, but no trace of either Malkin's β″ or his vitreous form was found in spite of careful search.

In attempting to account for the discrepancies between two sets of observers, the present authors point to the fact that their X-ray and thermal examinations were performed on identical capillary samples treated in a carefully prescribed manner. Malkin and Wilson neither describe sufficiently their X-ray sample treatment nor do they establish the comparability of their X-ray and thermal samples. According to the present authors' experience, the lower beta melting point and higher alpha m. p. of Malkin and Wilson are evidence of lower purity; this is not thought to account, however, for their failure to observe beta prime-2, for their high m. p. for sub beta prime-2, nor for a readily obtained sub beta-3, easy indeed to obtain for SOS.

It is of interest that Malkin, for the first time in the case of triglycerides, properly associates alpha pattern and alpha m. p. His lower "m. p." ascribed to a vitreous form (his usual term for the lowest melting form) very likely was obtained from a cooling curve and represents a clouding point, for a clouding point of 14.5° was obtained for POP by the present authors. The non-existence of a "vitreous form" was demonstrated by distinct long and short spacings for samples melted and chilled as low as −50°. (Unfortunately Malkin's proper association of alpha pattern and alpha m. p. did not extend to the SOS case where again a "vitreous form" is assigned the alpha m. p.)

Comparison of Synthetic with Natural POP.—The data of Table III are sufficient proof that the oleyldipalmitin of stillingia tallow and piquia

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[9] Including a capillary tube sample obtained through the courtesy of Drs. Longenecker and Daubert of the University of Pittsburgh.

fat are symmetrical. Polymorphic data for the one synthetic and two natural oleyldipalmitins here reported are extremely similar except for rate of transformation of beta prime-2 to beta-3 as illustrated in Table V.

TABLE V

FORMATION OF BETA-3 IN POP

Treatment	Synthetic POP	Stillingia tallow POP	Piquia fat POP
Melt, chill, 2–3 weeks 32°	β-3	β'-2	β'-2 and β-3
Melt, chill, 1 day each 27, 32, 35°	β-3	β'-2	Mainly β-3
Solvent crystallized from acetone	β-3	β-3	β-3

This suggests that the POP from piquia fat was more nearly pure than that from stillingia tallow. In this connection, it might be added that beta prime-2, as in the case of other glyceride forms, has been observed to increase in m. p. on storage. This was particularly evident for the form from stillingia tallow which remained beta prime on 32° storage although its m. p. rose above 35°.

Since the only identified oleyldistearins of nature are symmetrical, as are the present oleyldipalmitins, it would be of considerable interest to establish how general is the occurrence of symmetrical disaturated glycerides in nature.

Summary

The polymorphism of synthetic 2-oleyldipalmitin (POP) has been studied by X-ray and thermal means and compared with that of oleyldipalmitin from two natural sources, namely, stillingia tallow and piquia fat. Results confirmed the conclusions of previous workers, based on thermal examination, that these two natural oleyldipalmitins are symmetrical.

The following forms were obtained for POP: alpha-2 (m. p. 18.1°), sub beta prime-2 (26.5°), beta prime-2 (33.5°), and beta-3 (38.3°). These results differ in important details from both thermal and X-ray evidence of others. Much of the difficulty involves the question of the existence of so-called vitreous forms of fats, unconfirmed in this Laboratory for POP or any other glyceride.

In contrast to the implications of earlier workers, POP was found to show a number of characteristic differences from 2-oleyldistearin which has shown, on crystallization from the melt, alpha-3, sub beta-3 (formerly called X-3) and beta-3 forms.

CINCINNATI 17, OHIO RECEIVED SEPTEMBER 29, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Solubilities of Dodecylammonium Chloride and its N-Methyl Derivatives in *n*-Hexane, Benzene and 95.0% Ethanol[1]

BY F. K. BROOME AND H. J. HARWOOD

A recent paper[2] has reported the conductivities of aqueous solutions of dodecylammonium chloride and its N-methyl derivatives. The present paper extends the study of this group of salts to their solubilities in one polar and two non-polar organic solvents. Earlier studies from this Laboratory[3,4] have considered the solubilities of the primary salt in two of these solvents, but the present work has extended the range of concentrations somewhat, and has uncovered new information on the polymorphic behavior of this salt.

Experimental

Preparation of Materials.—The preparations of the dodecylammonium chloride[5] and the methyl and dimethyl derivatives[2] used herein have been described. Trimethyldodecylammonium chloride, prepared as previously described,[6] was further dried over phosphorus pentoxide *in vacuo*. Because of its hygroscopicity, this compound was handled in a desiccated box equipped with a window and sealed-in rubber gloves.

The *n*-hexane used was Phillips Technical *n*-hexane purified by treatment with sulfuric acid, fractionation in a Stedman-packed column, and drying with sodium wire. Thiophene-free benzene was dried over sodium. Commercial absolute ethanol was diluted to 95.0% by weight with conductivity water. Its content of ethanol was checked with a pycnometer.

Procedures.—The procedures are essentially those described elsewhere.[3,7,8] Weighed portions of salt and solvent were sealed in small glass tubes, dissolved by heating, thoroughly mixed, and then cooled below the crystallization point. Solution temperatures were observed during slow heating of these samples, rotated in a regulated water- or oil-bath. Temperatures up to 100° were estimated to 0.01° on a thermometer checked against a similar thermometer calibrated by the National Bureau of Standards, and were reproducible within a few hundredths of a degree. Temperatures above 100° were measured to 0.1° with an iron–constantan differential thermocouple calibrated against a certified platinum resistance thermometer, and were reproducible within less than 0.1°.

Where polymorphic forms were detected, the lower liquidus was obtained by cooling a homogeneous sample below the higher liquidus, chilling the tip of the tube with Dry Ice to induce crystallization, and immediately plunging the tube back into the regulated bath. Repeated trials at slightly varying temperatures sufficed to establish

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[2] Ralston, Broome and Harwood, THIS JOURNAL, **71**, 671 (1949).

[3] Hoerr and Ralston, *ibid.*, **64**, 2824 (1942).

[4] Sedgwick, Hoerr and Ralston, *J. Org. Chem.*, **10**, 498 (1945).

[5] Ralston and Eggenberger, THIS JOURNAL, **70**, 436 (1948).

[6] Reck, Harwood and Ralston, *J. Org. Chem.*, **12**, 517 (1947).

[7] Ralston, Hoffman, Hoerr and Selby, THIS JOURNAL, **63**, 1598 (1941).

[8] Harwood, Ralston and Selby, *ibid.*, **63**, 1916 (1941).