TABLE I

MAIN X-RAY SPACINGS OF *n*-HEXADECANOL AND *n*-OCTADECANOL

	n-Hexadecanol						*n*-Octadecanol					
	Alpha		Sub alpha		Beta		Alpha		Sub alpha		Beta	
Long spacing (C sin β), Å.	44.3		44.9		37.2		49.0		49.7		41.8	
Literature[5]			44.84		36.84				49.57		40.96	
	d/n	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*
Short spacings, Å.	4.17	VS	4.09	VS	4.30	M	4.19	VS	4.09	VS	4.30	M
			3.73	M	4.08	VS			3.73	M	4.08	VS
			3.64	S	3.62	S			3.64	S	3.62	S

though very similar in major features are different in detail from those of sub alpha (see Table I).

Acknowledgment.—The authors are grateful to the members of this Laboratory who have given advice and experimental assistance.

CINCINNATI 17, OHIO RECEIVED MAY 21, 1951

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER AND GAMBLE COMPANY]

The Polymorphism of the Disaturated Triglycerides—OSS, OPP, POS, OPS and OSP

BY E. S. LUTTON

Two groups of disaturated triglycerides have been studied, (1) the unsymmetrical diacid compounds—1-oleyldistearin (OSS) and 1-oleyldipalmitin (OPP) and (2) the triacid compounds—2-oleylpalmitylstearin (POS), 2-palmityloleylstearin (OPS) and 2-stearyloleylpalmitin (OSP). They are compared with previously reported SOS and POP. All 1-oleyl compounds are beta prime-3 stable from solvent; OSS and OPP also give beta prime-3 as the stable form from melt; OPS gives sub-beta prime-3; OSP gives beta prime-2. All 2-oleyl compounds (POS, SOS and POP) are beta-3 stable from solvent and melt. OSS, OPP and SOS exhibit alpha-3 forms at the lowest m.p., while POS, OPS and POP show alpha-2, but OSP shows sub-alpha-2. All show sub-alpha forms when their melts are chilled to low temperatures (except OPP, not tested below 0°). The highly individualistic behavior should serve as a basis for identifying predominant disaturated components of many natural fats.

Of the seven oleyl disaturated triglycerides possible to prepare with palmitic and stearic acids, only for SOS[1,2,3] and POP[3,4] have detailed studies of crystallization behavior been reported. In this paper is described a comparable study on the other five glycerides which may be divided into two groups—(1) the unsymmetrical diacid glycerides, OSS and OPP and (2) the triacid glycerides—POS, OPS and OSP.

Preliminary work on OSS and OPP was performed with small capillary tube samples of preparations synthesized by Daubert, *et al.*[5] These were obtained through the courtesy of Profs. Longenecker and Daubert of the University of Pittsburgh. Actually these samples yielded the main features of polymorphic behavior. Final observations were made on samples synthesized in this Laboratory.

The difficultly synthesized triacid glycerides—POS, OPS and OSP[6] were made available in 1-g. amounts through the generosity of Prof. P. E. Verkade.

Experimental

The glycerides OSS and OPP were synthesized in 15-g. amounts by Mr. R. G. Folzenlogen from 1-monoölein, prepared by Dr. F. J. Baur using directed rearrangement[7] and the corresponding fatty acid chlorides. The triglycerides were purified by crystallization once from Skellysolve B and three times from acetone. Analytical data and constants for starting materials and products appear in Table I.

TABLE I

ANALYSES AND CONSTANTS FOR STARTING MATERIALS AND PRODUCTS

	M.p., °C.	S.p., °C.	Iodine value Exptl.	Iodine value Theory	Monoglyceride,[a] %
1-Monoölein	35.3[b]		70.9	71.2	104
Stearic acid		69.2			
Palmitic acid		62.5			
OSS	43.5[c]		27.7	28.5	
OPP	35.2[d]		29.9	30.5	

[a] W. D. Pohle and V. C. Mehlenbacher, *J. Am. Oil Chem. Soc.*, **27**, 54 (1950). [b] M. G. R. Carter and T. Malkin, *J. Chem. Soc.*, 554 (1947), m.p., 35.0°. [c] Ref. 5, m.p. 38.5°. [d] *Ibid.* m.p. 34.5°.

Thermal examination was carried out with samples in capillary tubes, as previously described.[2,4] In Table II appear methods of preparing the various forms along with characteristic thermal data for each form.

X-Ray examination was performed with a G.E. XRD unit, CuKα radiation, 5- or 10-cm. sample to (flat) film distance. For metastable forms samples were held in a cold block. X-Ray diffraction data appear in Table III.

A comparison of forms and melting points for the various disaturated triglycerides, including SOS and POP, appears in Table IV.

Discussion

OSS and OPP exhibit melting points corresponding to two forms each, both forms having triple-chain-length structure. They are called alpha and beta prime on the basis of their short spacings.[8] The OSS sample synthesized here melts 5° above the previous preparation[5] and along with this shows

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[1] L. J. Filer, S. S. Sidhu, B. F. Daubert and H. E. Longenecker, THIS JOURNAL, **68**, 167 (1946).

[2] E. S. Lutton, *ibid.*, **68**, 676 (1946).

[3] T. Malkin and B. R. Wilson, *J. Chem. Soc.*, 369 (1949).

[4] E. S. Lutton and F. L. Jackson, THIS JOURNAL, **72**, 3254 (1950).

[5] B. F. Daubert, H. H. Fricke and H. E. Longenecker, *ibid.*, **65**, 2142 (1943).

[6] P. E. Verkade, *Rec. Trav. Chim.*, **62**, 393 (1943).

[7] E. W. Eckey and M. W. Formo, *J. Am. Oil Chem. Soc.*, **26**, 207 (1949).

[8] E. S. Lutton, THIS JOURNAL, **70**, 248 (1948).

TABLE II

DETAILED THERMAL DATA AND TREATMENT FOR OBTAINING FORMS[a]

Form		Treatment	OSS	OPP	POS	OPS	OSP
Sub-alpha		Melted, chilled	Modification A at 0° Modification B at 20°, transforms to alpha below 27°	Not (observed (as low as 0°)	Below 5°C.	Below 0°	Below 20° 20° up to m.p.
Alpha		Melted, chilled (m.p. by "thrust in" technique)	30.4	18.5	18.2	25.3	(Sub-alpha-2) 26.3
Sub-beta prime-3		Melted, chilled, 1 week 32°				37 (apparently stable)	
Beta prime-2		Melted, chilled, 1 week 32°			?		40.2 (apparently stable)
Beta prime-3	a	Solvent crystallized (acetone)	43.5	35.2		40.2 (40–41[b])	39.8 (39.5–40.5[b])
	b	Melted, chilled, 1 day 32°			33		
	c	Melted, crystallized 30 min. 19–20°					
	d	Melted, chilled, 1 week 32°		34.8			
	e	Melted, chilled, 1 week 38°	42.5				
Beta-3	a	Solvent crystallized (acetone)			37.3 (36.5–37.5[b])		
	b	Melted, chilled, 1 week 32°			39 (stable)		

[a] Complete m.p., °C. given, unless otherwise specified. [b] Ref. 6.

TABLE IIIA

DIFFRACTION DATA FOR OSS AND OPP

		OSS				OPP	
	hkl	Sub-alpha-3 Modification A	Sub-alpha-3 Modification B	Alpha-3	Beta prime-3	Alpha-3	Beta prime-3
	001						
	002	42.1 VS[a]	41.6 VS	39.3 VS	35.5 VS	39.2 VS	33.0 VS
	003		26.8 W	29.8 M−	23.4 M	25.7 VW	21.8 M−
Long spacing, Å.	004	21.1 W			17.6 W		
	005		16.1 M	16.0 M	14.3 M	15.3 M	13.1 M
	006	14.1 W	13.9 VW			13.1 W	11.0 W
	007						9.23 W
	008		10.3 VW	9.95 VW	8.81 M−		8.22 W
	009						7.17 W
Avg. d.		84	82	80	70.8		65.3
					7.37 W−		5.94 W
					5.50 W		5.51 W+
Short spacings, Å.		4.13 VS	4.16 S	4.13 VS	5.10 W	4.13 VS	4.99 W
		3.71 S−	3.84 M		4.64 M		4.65 M
					4.39 W		4.42 W
					4.23 W+		4.20 W+
					4.06 S		4.05 S+
					3.79 S		3.77 S

[a] VS—very strong, S—strong, M—medium, W—weak, VW—very weak, (diff.)—diffuse.

a sub-alpha form existing as high as 20° although the previous sample showed alpha at 0°. The present sub-alpha, like the previous alpha, shows modifications A at 0° and B at 20° which differ in the relative intensities of their long spacings. Such a difference has not been encountered hitherto and is unexplained. The point was not tested but presumably sub-alpha transforms reversibly to alpha. OPP showed no sub-alpha form but it was not examined below 0°. The triple-chain-length structure calls for a "chair"[9] type of arrangement for these unsymmetrical molecules (Fig. 1) comparable to that previously reported for certain unsymmetrical saturated glycerides.[8]

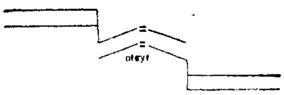

Fig. 1.—Proposed chain arrangement for 1-oleyl disaturated glycerides.

A comparison of the unsymmetrical glycerides with the corresponding symmetrical compounds (Table III) shows higher stable form melting points for the latter and greater m.p. spread between highest and lowest melting forms.

With the triacid glycerides the situation is more complicated. Perhaps their behavior can be best classified by considering the seven aforementioned disaturated glycerides together as in Table IV. The 2-oleyl glycerides uniformly show triple-chain-length beta-3 as the stable form. The 1-oleyl glycerides show stable forms of beta prime type, uniformly beta prime-3 from solvent (and from melt for OSS and OPP); but sub-beta prime-3 from melt for OPS; and beta prime-2 for OSP. The apparently stable OPS form from melt, though similar in diffraction pattern to the form from solvent, shows definite short spacing differences and is lower melt-

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(9) Postulated "chair" and "tuning fork" arrangements for triglycerides involve no claims of detailed structural accuracy. They merely show how, in the "chair," the chains in the 2- and 3-positions probably extend in the opposite direction from the chain in the 1-position while in the "tuning fork" the 1- and 3-chains are opposite the 2-chain.

TABLE IIIB

DIFFRACTION DATA FOR POS, OPS AND OSP

		POS					OPS				OSP			
	hkl	Sub-alpha-3	Alpha-2	Beta prime-2	Beta prime-3	Beta-3	Sub-alpha-2	Alpha-2	Sub-beta prime-3	Beta prime-3	Sub-alpha-2	Sub-alpha-3	Beta prime-2	Beta prime-3
Long spacings, Å.	001		48.0 VS	44 VS	(60) M		40.0 S	(37) VS			(39.5) VS		43.9 VS	
	002				33.1 VS	30.3 VS	20.0 W	19.95 M	34.2 VS	33.5 VS	20.3 W	38.5 VS	22.3 VW	34.2 VS
	003	(40 VS diff.)	15.85 S	13.7 M	22.3 M	21.2 W	13.7 W−	13.5 M	22.3 M−	22.3 M	13.6 W−	25.0 VW	14.5 S−	22.0 VW
	004					15.8 W								17.1 VW
	005	15.0 VW (diff.)	9.53 VW		13.4 S	12.7 M			13.75 S	13.3 S		15.5 S	8.69 M	13.5 M
	006					10.6 W			11.7 W	11.15 VW		13.0 VW	7.25 M−	
	007					8.7 VW			9.86 W	9.56 VW				
	008				8.37 W	7.95 S−			8.53 W	8.35 M		9.6 VW		
	009				7.47 W	6.97 M			7.64 W	7.53 VW				7.56
	0010									6.71 VW				
Avg. d.		75	47.8	44	66.8	63.1	40.3	40.3	68.5	66.9	40.6	77	43.6	67.6
Short spacings, Å.					6.06 W−					6.21 VW				
					5.56 W	5.42 M			5.35 W	4.63 W+				6.13 VW
					4.56 M−	5.15 W			4.99 W	4.23 M				5.48 M
					4.36 M	4.53 VS			4.65 W+	4.17 VS				5.21 VW
		4.1 S	4.16 VS	4.30 M	4.11 S+	4.24 VW	4.13 S	4.13 VS	4.36 W	4.02 W			4.35 M	4.38 M−
		3.7M		4.03 S	3.84 S	4.05 M	3.70 M		4.08 VS	3.78 M	4.12 VS	4.15 VS	4.19 S+	4.20 VS
				3.77 M	3.63 VW	3.86 M			3.75 S	3.66 M	3.68 M	3.80 S[a]	3.86 S	4.03 M
						3.72 S								3.82 S
						3.51 W								3.56 W

[a] Diffraction line splits below 15°, spacing value increases above 15°.

TABLE IV

COMPARISON OF DISATURATED TRIGLYCERIDE FORMS AND M. P.'S (°C.) (OMITTING SUB-ALPHA EXCEPT FOR OSP)

2-OLEYL DISATURATED

POP[4]		POS		SOS[3]	
Alpha-2	18.1	Alpha-2	18.2	Alpha-3	22.4
Sub-beta prime-2	26.5	Beta prime-2	?	Beta-prime-3	35[a]
Beta prime-2	33.5	Beta prime-3	33	Sub-beta-3	36.2
Beta-3	38.3	Beta-3	38	Beta-3	44.3

1-OLEYL DISATURATED

OPP		OPS		OSP		OSS	
Alpha-3	18.5	Alpha-2	25.3	Sub-alpha-2	26.3	Alpha-3	30.4
Beta prime-3	35.2	Sub-beta prime-3	37	Beta prime-2	40.2	Beta prime-3	43.5
		Beta prime-3	40[a]	Beta prime-3	39.8[a]		

[a] Obtained from solvent only.

ing; whether very long storage would convert sub-beta prime-3 to beta prime-3[10] is not known.

With regard to forms stable at the lowest melting point, alpha-3 is observed for three of the four di-acid compounds—SOS, OSS and OPP; alpha-2 for POP and OPS; but apparently sub-alpha-2 for OSP.

Once sub-alpha type forms had been discovered for triglycerides, as for the behenyl compounds,[11] it was observed that they could be obtained by chilling the melt to low temperatures for nearly all triglycerides including those of the present study, except OPP which was not investigated below 0°. The normal relationship appears to be a reversible transformation between sub-alpha and alpha forms,

[10] It should be pointed out that common designation as beta prime-3 for the solvent-crystallized forms of the 1-oleyl glycerides does not imply complete identity of crystal structure, for it may be that beta prime-3 of OSS is more closely related to sub-beta prime-3 of OPS than to the solvent-crystallized form of the latter.

[11] F. L. Jackson and E. S. Lutton, THIS JOURNAL, **72**, 4519 (1950).

but it seems unlikely that forms of double- and triple-chain-length will transform reversibly one into the other, whether one is alpha and the other sub-alpha or both are sub-alpha as for the rather individualistic OSP which exhibits no alpha at all.

Only 2-oleyl glycerides show intermediate melting forms from the melt—both beta prime-2 and beta prime-3 for POS as compared with sub-beta prime-2 and beta prime-3 for POP and sub-beta-3 for SOS.

It has not been possible up to this time to develop a simple system to account for all the diverse polymorphic behavior of these glycerides.

Because of the considerable degree of individuality it should be possible to use the information now available to establish in many cases the identity of predominant oleyl-disaturated glycerides in such fats as lard, cacao butter and tallow, for example.

Acknowledgment.—Most of the experimental work was performed by Mr. C. B. Stewart and Mrs. R. M. Foltzer. The writer expresses appreciation to them and others of this Laboratory for essential help in assembling the information for this paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Mannich Reaction Involving Optically Active Substituted Mandelic Acids and Nitroalkanes[1,2]

BY GERALD F. GRILLOT AND RAYMOND I. BASHFORD, JR.[3]

The reaction of *d*- and *l*-*o*-nitromandelic acids with formaldehyde and piperidine gave Mannich bases as products whose rotations were higher than the rotation of the starting optically active mandelic acids. These results contradict the suggestion of Alexander and Underhill that enolization is a step in the mechanism that they suggested applied to the Mannich condensation of compounds having a methynyl group on a carboxyl group. The reaction of *d*-2-nitrobutane with formaldehyde and isopropylamine gave a Mannich base with but a slight rotation. The best explanation of this observation is that although the isopropylamine catalyzes the rapid racemization of much of the *d*-2-nitrobutane before the Mannich reaction occurs, some small amount does react in the unracemized state to give an optically active Mannich base.

On the basis of the fact that acetophenone will undergo the Mannich reaction, while the somewhat hindered α-methylbutyrophenone did not undergo this reaction, we are suggesting an S_N2 mechanism for the Mannich reaction rather than an ionization followed by a rapid union of the resulting carbanion with the alkylaminomethyl group.

This paper reports the results of a study of the stereochemical changes involved in the Mannich reaction when the reactive hydrogen of one of the reactants is attached to an asymmetric carbon atom. The cases examined are the condensation of *d*- and *l*-*o*-nitromandelic acids with formaldehyde and piperidine and of *d*-2-nitrobutane with formaldehyde and isopropylamine. The latter condensation using *d,l*-2-nitrobutane has previously been studied by Johnson.[4]

The condensation of *d*-*o*-nitromandelic acid $[\alpha]^{22}\text{D}$ +346° with formaldehyde and piperidine gave an optically active Mannich base with a rotation of $[\alpha]^{20}\text{D}$ +439°, while the *l*- acid, $[\alpha]^{20}\text{D}$ −320°, gave an isomer with a rotation of $[\alpha]^{20}\text{D}$ −449°. An equimolar mixture of these two Mannich bases gave a product that was identical with that obtained from *d,l*-*o*-nitromandelic acid.

If it is true that enolization involving an asymmetric center causes racemization, it is difficult to postulate an enolization step in the Mannich reaction involving *o*-nitromandelic acid with formaldehyde and piperidine. These results contradict the generalized statement made by Alexander and Underhill[5] that their mechanism (which involved an enolization) should hold for all compounds having a methynyl group.

It was hoped that rate studies on the reaction of *d*- and *l*-*o*-nitromandelic acid with formaldehyde and piperidine could be made by observing the change of rotation as the reaction proceeded. However, the reaction occurs so rapidly that this project had to be abandoned.

The condensation of *d*-2-nitrobutane, $[\alpha]^{20}\text{D}$ +5.07°, with formaldehyde and isopropylamine gave a Mannich base with an observed rotation of +0.03 ± 0.02°.

It was at first inferred that the Mannich reaction involving *d*-2-nitrobutane, formaldehyde and isopropylamine produced complete racemization However, the observed rotation 0.03 ± 0.02° is too large to assume experimental error from a zero reading. It was then called to our attention that very small amounts of piperidine produce a rapid mutarotation of nitrocamphor.[6] Lowry and Magson suspected that this was due to a change from the nitro to the aci-nitro isomer, but Bell and Sherred postulate that this involves a change to a diastereoisomer. Since isopropylamine should be about as basic as piperidine, we have reinterpreted our data to indicate that two simultaneous reactions are occurring. The first involves a very rapid racemization of the *d*-2-nitrobutane by the isopropylamine to give the *dl*-2-nitrobutane which then reacts with the isopropylaminomethanol to give the racemic Mannich base. A second and very much slower reaction involves the condensation of *d*-2-nitrobutane with isopropylaminomethanol to give an optically active Mannich base. The latter is responsible for the small rotation that we observed in the resulting product.

The yield study was made to determine optimum

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[1] Taken from the Ph.D. Dissertation of Raymond I. Bashford, Jr., Syracuse University, 1950.

[2] Presented before the Organic Division of the A.C.S., Chicago Meeting, September 6, 1950.

[3] Syracuse University Fellow 1948-1949; Allied Chemical and Dye Fellow, 1949-1950.

[4] H. Johnson, THIS JOURNAL, **68**, 12 (1946).

[5] E. Alexander and E. Underhill, *ibid.*, **71**, 4014 (1949).

[6] Lowry and Magson, *J. Chem. Soc.*, **93**, 107 (1908); Taylor and Baker, Sidgwick's "The Organic Chemistry of Nitrogen," Oxford Press, 1945, p. 234; Bell and Sherred, *J. Chem. Soc.*, 1202 (1940).