

tion. Finally, the pentachloride $\text{CCl}_2\text{-CCl}_2\text{-CHF}_2$, on dechlorination in the usual way in alcohol solution with zinc dust, readily yielded the olefin $\text{CCl}_2\text{=CCl-CHF}_2$, b.p. 113–115°. An accumulated sample gave a central cut, b.p. 114.8°, n_D^{20} 1.4456 (known¹⁸ b.p. 114.4°, n_D^{20} 1.4452).

Additive Bromination of CHCl=CCl-CHF_2 .—A 50-ml. sample of the olefin was placed in a flask equipped with a dropping funnel containing bromine, a reflux condenser, and illuminated by a 200 watt lamp at a distance of 1 inch. The bromine was added intermittently, as the resulting red color disappeared, for 16 hr., after which the product was washed with alkaline-sulfite solution, dried over anhydrous MgSO_4 and distilled through a 25-cm. Vigreux column under reduced pressure. About 90% of it came over from 85–88° at 24 mm.; and this, on redistillation, yielded pure $\text{CHCl-Br-CClBr-CHF}_2$, b.p. 87° at 24 mm., f.p. –45° (cooling curve), n_D^{20} 1.5078.

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{F}_2\text{Cl}_2\text{Br}_2$: F, 12.4. Found: F, 12.5, 12.6.

Chlorination of $\text{CHClBr-CClBr-CHF}_2$.—This reaction was carried out by bubbling chlorine through the liquid bromine adduct in a flask equipped with a reflux condenser and illuminated by a 200-watt lamp at a distance of 1 inch. After a 3-hr. induction period, the slow chlorination began, which displaced practically no bromine, and was apparently complete when all the sample had been converted into a white crystalline solid. This product decomposed on heating to 100°, but was shown to consist essentially of $\text{CCl}_2\text{-Br-CClBr-CHF}_2$ by the debromination of a 35-g. sample in alcohol solution with zinc dust in the usual way. The product was poured into water, extracted with CH_2Cl_2 , dried with anhydrous MgSO_4 and distilled through a 10-cm. Vigreux column. There was obtained 7.4 g. of $\text{CCl}_2\text{=CCl-CHF}_2$, b.p. 112–115°, central cut, b.p. 114°, n_D^{20} 1.4458. About 10% of the product was CHCl=CCl-CHF_2 , b.p. 89–92°, indicating that the crude dibromide must have been contaminated with some $\text{CHClBr-CClBr-CHF}_2$.

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The Polymorphism of *n*-Hexadecanol and *n*-Octadecanol

BY D. G. KOLP AND E. S. LUTTON

The polymorphism of the fatty alcohols, *n*-hexadecanol and *n*-octadecanol, has been studied by X-ray diffraction and thermal methods. Three forms corresponding to those indicated by dielectric constant data of Hoffman and Smyth have been found. The alpha form appears from the melt at the f.p. and exists as a metastable form in a narrow temperature range near the m.p. In this temperature range gradual transformation to the stable beta form occurs. Cooling the alpha form causes abrupt transformation to the sub alpha form, which also changes gradually to beta on aging. Only one m.p. has been found for each of the alcohols studied.

Introduction

The occurrence of polymorphism in *n*-hexadecanol and *n*-octadecanol has been demonstrated by thermal curves,^{1–3} X-ray diffraction^{4–7} and dielectric constant studies.^{8–10}

Whereas the thermal studies and X-ray diffraction work uncovered two forms (which do not seem to be the same two in all cases), dielectric constant data of Hoffman and Smyth¹⁰ clearly indicate the existence of three solid forms of *n*-octadecanol. (*n*-Hexadecanol was not considered experimentally by them but by Baker and Smyth⁸ who found two forms.) It is the purpose of this paper to clarify knowledge of the three forms of both *n*-hexadecanol and *n*-octadecanol by correlated diffraction and thermal data.

In this work, the names "alpha," "sub alpha" and "beta" have been adopted for the alcohol form first appearing from the melt, the form obtained on rapid chilling to room temperature, and the stable form obtained on aging, respectively. These names are in keeping with previous long chain alcohol nomenclature or are chosen by analogy with nomenclature used previously for certain other long chain compounds,

Experimental

Preparation of Compounds.—The *n*-hexadecanol and *n*-octadecanol used in this work were prepared by sodium re-

duction of natural fats, followed by distillation to separate the various homologous alcohols present. The resulting materials were crystallized from 10 volumes of petroleum ether. Crystallization was repeated to constant f.p.

Thermal Conditions for Obtaining Forms.—The following outline gives the thermal conditions under which each of the three forms was obtained.

A. Alpha Form.—(1) Melted; cooled to 2° below f.p.; X-rayed at this temperature. (2) Warmed sub alpha form to 2° below f.p.; X-rayed at this temperature.

B. Sub alpha Form.—(1) Chilled alpha form below transition temperature; X-rayed at room temperature.

C. Beta Form.—(1) Crystallized slowly from ethanol or petroleum ether; X-rayed at room temperature. (2) Stored alpha form 2 days at 2° below the f.p.; X-rayed at room temperature. (3) Stored sub-alpha form 1 day at 38° X-rayed at room temperature. (4) Stored beta 30 days at room temperature; X-rayed at room temperature.

Melting, Freezing and Transformation Points.—The m.p.'s reported below were obtained by raising the temperature of the sample (contained in a thin-walled glass capillary about 1 mm. in diameter), 0.5° per minute. M.p.'s were also determined by the thrust-in technique described by Lutton and Jackson.¹¹

Freezing-points were obtained on 3-g. samples allowed to cool in a doubly air-jacketed apparatus placed at room temperature.

The transformation points of the alcohols were determined from time-temperature cooling curves (details described later), run very slowly with small temperature gradient between sample and surroundings.

The melting, freezing and transformation points found are 49.7° (50.0¹²), 49.1° (49.3¹²) and 43.8° (45.0¹²), respectively, for *n*-hexadecanol and 58.6° (58.5¹²), 57.9° (57.9¹²) and 54.7° (53.6¹²), respectively, for *n*-octadecanol.

X-Ray Diffraction Powder Patterns.—X-Ray diffraction powder patterns were obtained on samples solidified in thin-walled glass capillaries under various conditions, and on solvent-crystallized samples ground with mortar and pestle and pressed into rod-like form. A standard General Electric XRD unit was employed in making the patterns. Sample-to-film distance of 5 cm. and a 0.025" pinhole collimator were used in recording patterns of the alpha forms. In obtaining patterns of the sub alpha and beta forms, 10-

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(12) J. C. Smith, *J. Chem. Soc.*, 802 (1931).

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cm. sample-to-film distance and a 0.005" slit collimator were used. The temperature of the sample was controlled, where necessary, within 0.5° by placing it in an electrically heated brass block.

The main X-ray spacings found for each of the three forms are given in Table I. Detailed X-ray data are given in the supplementary material.¹³

Time-Temperature Curves.—Thermal curves were obtained with a 1-g. sample in a jacketed tube of 0.5 cm. i. d. After pretreatment of the sample, the assembly was placed in a water-bath maintained at the desired constant temperature. Sample temperature was followed with a single-junction iron-constantan thermocouple (reference junction at 0°) and recorded automatically on a calibrated Brown potentiometer.

The curves obtained are shown in Fig. 1.

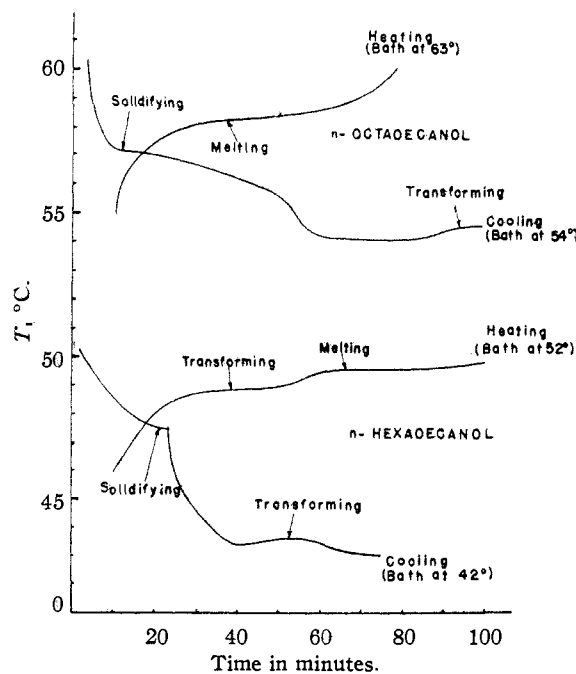


Fig. 1.

Discussion

Alpha Form.—For both *n*-hexadecanol and *n*-octadecanol the alpha form appears when the melt is cooled to the f.p., and this form is metastable in a region within a few degrees of the f.p. On heating, it melts at the level previously stated.

The X-ray diffraction characteristics of the alpha form of these fatty alcohols are very similar to those of the alpha phases of other long chain compounds.^{11,14,15}

The form here is called "alpha" both because of this similarity and also because the name is commonly applied to this fatty alcohol form in the literature.¹⁰

Transformation of Alpha to Sub Alpha.—On cooling below the transformation temperature, the alpha form transforms abruptly to the sub alpha form. The work reported here has indicated that this transition is reversible, for, in the case of both *n*-hexadecanol and *n*-octadecanol it has been

possible to transform alpha to sub alpha and then back to alpha as evidenced by powder patterns. Also the thermal curves of *n*-hexadecanol (Fig. 1) show transformation both on cooling alpha and on warming sub alpha.¹⁶ Transformation of *n*-octadecanol on warming, however, is not indicated by the thermal curves. Since the range between transition point (found on cooling) and m.p. is shorter (for the preparation used here) in *n*-octadecanol than in *n*-hexadecanol, and since the break in the *n*-hexadecanol heating curve is barely detectable, it is not surprising that the transition of sub alpha to alpha in *n*-octadecanol is too close to the melting point to be detectable by time-temperature curves. Another difficulty involved in detecting this transition by thermal curves is the gradual transformation, mentioned previously, of sub alpha to the stable beta form, which was found to be faster in the *n*-octadecanol sample than in the *n*-hexadecanol sample.

Sub Alpha Form.—The sub alpha form was produced only by transformation of the alpha form as discussed above. The form has been given the name "sub alpha" because in its characteristics and the conditions of its occurrence it bears a marked resemblance to the sub alpha form of monoglycerides.¹⁴ Thus in both cases sub alpha gives long spacings nearly equal to those of the respective alpha forms, and in both cases sub alpha is produced by chilling the alpha form below a specific reversible transformation temperature. The sub alpha form has been called "beta-1" by Hoffman and Smyth.¹⁰

The sub alpha forms of the fatty alcohols studied here consist of molecules lying perpendicular to the planes of their ends, as do the alpha forms. Thus, two of the three alcohol forms present perpendicular chains. Sub alpha has three main short spacings, in contrast to the alpha form which shows only one.

Transformation of Sub Alpha and Alpha to Beta.—On storage the sub alpha form and also the alpha form, in its narrow range of existence, change gradually and irreversibly to the stable beta form as indicated previously and as Hoffman and Smyth¹⁰ have reported.

Beta Form.—In addition to being produced by solid-solid transformation of the alpha and sub alpha forms, beta is obtained when *n*-hexadecanol and *n*-octadecanol are crystallized from volatile solvent (*e.g.*, petroleum ether or ethanol).

The name "beta" ("beta-2" in one case¹⁰) has been applied to this form whenever it has been specifically recognized^{5,10} and is therefore used here.

That the beta form is stable upon storage has been indicated in the tabulation of conditions under which the various forms arise and transform.

The long spacings of the beta form indicate (full extension of the chain molecules assumed) that the hydrocarbon chain axes are inclined to the planes formed by their ends. The short spacings, al-

(13) For material supplementary to this article, order Document 3329 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35-mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.

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(16) Figure 1 indicates that transformation of sub alpha to alpha (on heating) occurs at a higher temperature than the reverse transformation (on cooling). This must indicate that equilibrium conditions were not obtained in running the cooling curves, although the curves were run as slowly as possible. In the absence of further data, it can only be said that the equilibrium temperature lies between those found on heating and cooling.

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

Long spacing (C sin β), Å.	<i>n</i> -Hexadecanol						<i>n</i> -Octadecanol					
	Alpha		Sub alpha		Beta		Alpha		Sub alpha		Beta	
Literature ⁵	44.3		44.9		37.2		49.0		49.7		41.8	
			44.84		36.84				49.57		40.96	
Short spacings, Å.	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>
	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).

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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-oleylstearin (OSS) and 1-oleylpalmitin (OPP) and (2) the triacid compounds—2-oleylpalmitylstearin (POS), 2-palmityleylstearin (OPS) and 2-stearyleylpalmitin (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 OSP⁶ 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-monoolein, prepared by Dr. F. J. Baur using directed rearrangement⁷ and the corresponding fatty acid chlorides. The triglycer-

ides 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.	Theory	Mono-glyceride, %
1-Monoolein	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.^{3,4} 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, CuK α 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 preparation⁵ and along with this shows

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