

(7) C. M. Hain, D. T. Jones, R. L. Merker and W. A. Zisman, *ibid.*, **39**, 500 (1947).

adipate, di-(ethylhexyl) phthalate, 1,6-hexamethylene glycol di-(2-ethylhexanoate) and pentaerythritol tetracaproate, were found to possess the following properties: high viscosity index, low freezing point, high flash point and low volatility. In the present paper it will be shown that the 1,3-diolein and 1,3-distearin esters of fumaric, succinic and adipic acids possess some of the attributes just mentioned as well as other unique properties.

Experimental

Materials.—1,3-Distearin was prepared from purified stearic acid obtained by repeated crystallization from acetone of a commercial stearic acid, Hystrene S-97,⁸ which originally had a purity of about 97%. The purified acid was converted into a mixture of mono-, di- and tristearin under conditions which favored the formation of distearin. Briefly, 400 g. (1.41 moles) of stearic acid, 49.6 g. (0.538 mole) of glycerol in the form of the U. S. P. product and 0.72 g. (0.0032 mole) of stannous chloride dihydrate were mixed for 3 hours at 200° while under hydrogen at a pressure of 20 mm. Water was removed as it was formed. The reaction product, after washing with water to remove the uncombined glycerol, was subjected to repeated crystallizations from a solution of 70% isopropyl alcohol and 30% water followed by repeated crystallizations from *n*-hexane. The final 1,3-distearin product contained no monoglycerides and only a minor proportion of tristearin. The latter was found not to interfere with the subsequent preparation and purification of the dibasic acid esters.

The 1,3-diolein was obtained by repeatedly crystallizing from acetone a product originally containing about 85% of diolein, the other components being monoolein and triolein. The diolein product which was purified had been prepared in the course of other work and was one of the fractions obtained on molecular distillation of a mixture of mono-, di- and trioleins. This mixture was obtained in turn by allowing methyl oleate (purity, about 98%) and glycerol to react in the presence of a small amount of sodium hydroxide (0.1% based on the weight of methyl oleate) for about 15 minutes at 250° and then removing the soap and uncombined glycerol. The purified 1,3-diolein possessed the theoretical iodine value, a hydroxyl value of 86.0 (theoretical hydroxyl value, 90.3) and contained no monoglyceride according to the periodic acid method of analysis.

The fumaryl, succinyl and adipyl chlorides used in the preparations were obtained as Eastman grade from the Eastman Organic Chemicals Department of Eastman Kodak Co.⁸ and were used as received.

The various solvents and other reagents employed in the course of the work were given a special purification whenever this was deemed necessary. The pyridine was refluxed and then distilled over porous barium oxide to remove all traces of moisture. The chloroform was washed with water to remove ethanol and then dried to remove all of the water.

Methods of Preparation.—For reasons which will be discussed below, the diolein and distearin adipates⁹ were prepared by a procedure differing from that employed for the fumarates and succinates. The following example describes the typical preparation of the adipates: To 160 g. (0.256 mole) of moisture-free distearin kept under an atmosphere of dry nitrogen there was added 640 g. of chloroform, and the mixture was heated to dissolve the distearin, after which the solution was cooled to about 30°. Then 19.80 g. (0.250 mole) of pyridine was added. A solution consisting of 19.91 g. (0.1088 mole) of adipyl chloride and 50 g. of chloroform was added dropwise to the distearin solution while the latter was stirred constantly. The following day the temperature was increased to 50° and held at this level for 8 hours. On succeeding days the temperature was maintained at 50° until the total time at this temperature was 30 hours.

(8) This product is named as part of the exact experimental conditions. Naming it does not constitute a recommendation of the Department of Agriculture of this product over a similar product of any other manufacturer.

(9) For the sake of convenience the terms diolein adipate, distearin adipate, etc., will henceforth be used to indicate bis-(glycerol 1,3-di-oleate) adipate, bis-(glycerol 1,3-distearate) adipate, etc.

The following example describes the typical preparation of the fumarates and succinates: To 120 g. (0.192 mole) of moisture-free distearin kept under an atmosphere of dry nitrogen there was added 960 g. of chloroform, and the distearin was dissolved by heating the mixture and swirling the chloroform, after which the solution was cooled to approximately room temperature. Fumaryl chloride (14.68 g., 0.096 mole) was diluted with chloroform to a volume of 50 ml., placed in a buret, and protected from atmospheric moisture by a drying tube. A chloroform solution 50 ml. in volume and containing 28.5 g. (0.221 mole) of quinoline was placed in a similar buret and likewise protected from atmospheric moisture. Both burets were sealed to the flask containing the distearin solution. While the distearin solution was being continuously agitated with a mechanical stirrer, the solutions of fumaryl chloride and quinoline were added dropwise over a period of about 2 hours and in such a way that the total amount of quinoline (not the volume of quinoline-chloroform solution) added to the distearin solution was always equivalent to slightly more than the total amount of fumaryl chloride which had been added. After all of the fumaryl chloride solution was in the reaction flask, the remainder or excess of the quinoline solution was added. In the course of the following 4 days the reactants were kept at 50° for a total of 16 hours, the remainder of the time being at room temperature, 26°. The reaction product then was purified.

In each of the purifications the chloroform solution of the reaction product was washed first with a 0.25 *N* hydrochloric acid solution and then with water, after which the chloroform was removed by passage of hydrogen or nitrogen below atmospheric pressure and at about 100°. Further purification consisted of repeated crystallizations from *n*-hexane and from acetone, though in the case of diolein compounds these crystallizations served to solidify the impurities rather than the desired end products. The fumarates and succinates also were bleached with neutral, activated clay and activated carbon while in hexane solution.

Examination of Polymorphs.—X-Ray diffractions were obtained with a General Electric Diffraction Unit Model XRD,⁸ using filtered CuK α radiation and an exposure time of 4 hours. The pinhole method was used, and the patterns were recorded on flat film at a distance of 10 cm. The powdered specimen was packed to a thickness of about 1 mm. into a small glass ring which was directly affixed to the pinhole. Both long and short spacings were calculated from the same photograph.

Results and Discussion

The melting points, refractive indices and densities determined for the dibasic acid esters are recorded in Table I. The melting points listed for the distearin compounds are those for the highest melting polymorph. At least one additional and possibly more melting points exist for each compound, but up to this time it has not been possible to determine the other melting points with any degree of accuracy. The melting points listed, which are quite high for fatty compounds, might be compared with that of tristearin, m.p. 72.5°, and 1,3-distearin, m.p. 78°. The melting point of distearin succinate, 89.8°, is above that for carnauba wax, m.p. about 83.5°.

No melting points are listed for the diolein compounds because they either could not be determined with any degree of accuracy or because it has been impossible to solidify the compounds in a crystalline form. The diolein compounds possess the unique property of merely becoming more viscous on being cooled at a moderate rate. When stored at about -20°, some of the compounds appeared to change partly to a crystalline form while others appeared to be highly viscous liquids, even after several weeks at about -20°. When acetone solutions of the compounds are cooled to about

TABLE I
 CHARACTERISTICS OF DIGLYCERIDE ESTERS OF DIBASIC ACIDS

Com- pound	M.p., °C.	<i>n</i> _D	Density, g./ml., at			Molecular weight ^a		Hy- droxyl con- tent, ^b %	Free fatty acids, as oleic, %	Carbon and hydrogen, %				
			30°	50°	70.2°	Found	Theo- reti- cal			Theoretical		Found		
										C	H	C	H	
Diolein														
Fumarate	..	1.44900	0.9458	0.9346	0.9277	1091	1322	0.26	0.91	74.50	10.98	74.31	11.35	
Succinate	..	1.44709	.9384	.9281	.9206	1130	1324	.28	.25	74.38	11.12	74.29	11.05	
Adipate	..	1.44671	.9397	.9310	.9230	1312	1352	.19	.29	74.62	11.18	74.18	11.25	
Diolein	21.5	1.44408	
Distearin														
			94.6°	107.2°	123°	147.4°								
Fumarate	83.1	1.43851	0.9074	0.9008	0.8927	0.8795	1339	1330	0.41	0.30	74.05	11.52	74.31	11.93
Succinate	89.8	1.43861	.8682	.8641	.8583	.8419	1384	1332	.11	.37	73.93	11.65	74.12	11.50
Adipate	82.1	1.43844	.8910	.8831	.8731	.8615	1245	1360	.25	.83	74.17	11.71	74.31	11.74
Distearin	78.2	1.43583

^a By the Menzies-Wright procedures and apparatus.¹⁰ ^b By micro methods.

−80°, crystals do not form; instead two liquid phases form.

The molecular weights, hydroxyl contents and contents of free fatty acids listed in Table I provide only an indication of the purity of the different compounds. Not too much emphasis can be placed on a given value because the precision of the methods employed is not as high as might be desired. For example, the hydroxyl content, which was determined by a micro method, varied as much as six units on check samples.

Of the six compounds which were prepared the distearin and diolein adipates could be purified the most readily. The reaction between the adipyl chloride and diglycerides apparently proceeded smoothly with a low degree of side reaction. The crude reaction products were always white in color and no chloroform-insoluble products formed. On the other hand, reaction between the fumaryl and succinyl chlorides and the diglycerides under conditions similar to those employed with the adipyl chloride simultaneously produced a large amount of black, chloroform-insoluble material, which material was found to be the product of a reaction promoted by pyridine. The black material proved to be very difficult to remove from the desired end product.

The experiences of Wedekind, *et al.*,¹¹ are further confirmation that fumaryl and succinyl chlorides react in the presence of pyridine to form a compound or compounds other than an addition product with pyridine. These workers concluded that succinyl chloride in the presence of triethylamine forms cyclodecane-biscyclobutanedione. A solution of adipyl chloride and pyridine was claimed not to undergo such a reaction.

Because fumaryl and succinyl chlorides are unstable in the presence of organic bases, the reaction of these chlorides with the diglycerides was carried out in a relatively dilute chloroform solution, quinoline was used as the organic base because it has a molecular weight higher than that of pyridine, the acid chloride was added to the diglyceride solution at a very slow rate to decrease the concentration of uncombined acid chloride present at any given time, and the quinoline was added only as

needed. These precautions greatly reduced the formation of black, insoluble by-products but did not prevent it entirely.

As mentioned above, the distearin esters of the dibasic acids can exist in different polymorphic forms. Proof that each compound can have at least two forms is provided by the X-ray diffraction data recorded in Table II.

 TABLE II
 X-RAY DIFFRACTION DATA ON THE POLYMORPHIC FORM OBTAINED BY QUICK CHILLING AND ON THE HIGHEST MELTING POLYMORPHIC FORM OF DISTEARIN FUMARATE, SUCCINATE AND ADIPATE

Form	Distearin fumarate	Distearin succinate		Distearin adipate
		Long spacings, Å.		
Quick-chilled	58.3	56.1		56.6
Highest melting	49.8	50.5		51.6
Short spacings, Å.				
Quick-chilled	4.14VS ^a	4.14VS		4.14VS
Highest melting	7.67F	7.67F		5.28M
	5.61F	5.58F		4.79S
	4.56F	4.53F		4.50VS
	4.29VS	4.26VS		4.32F
	4.10S	4.09VS		3.91VS
	3.84VS	3.84VS		3.65M

^a Intensity of diffraction lines: VS, very strong; S, strong; M, medium; F, faint.

The quick-chilled form was obtained by plunging a capillary tube containing the melt into a Dry Ice-acetone mixture. After complete solidification the sample in each case was allowed to come to room temperature and the X-ray photographs were taken at room temperature. For the highest melting form each compound was crystallized from *n*-hexane and photographed at room temperature. As a check, each compound also was tempered for several hours at about 2° below its highest melting point and photographs were taken at room temperature. In each case the polymorphic form of the crystals obtained by fractional crystallization was identical with that of the tempered sample.

Because short spacings, such as are recorded in Table II, are a reflection of the cross-sectional arrangements of crystal chains, the short spacings recorded in the table might profitably be compared with those of tristearin. For the quick-chilled form of distearin fumarate, succinate and adipate a short spacing of 4.14 Å. was calculated from the

(10) A. W. C. Menzies, *THIS JOURNAL*, **43**, 2309 (1921); A. W. C. Menzies and S. L. Wright, Jr., *ibid.*, **43**, 2314 (1921).

(11) E. Wedekind, M. Miller and C. Weinland, *J. prakt. Chem.*, **109**, 911 (1925).

X-ray diffraction pattern. Significantly, the α or lowest melting polymorph of tristearin, and similar triglycerides, is characterized by a single strong line corresponding to about 4.15 Å. There is no such correlation between the β or highest melting form of tristearin and the highest melting form of the distearin compounds. The β -form of tristearin is characterized by a strong line corresponding to approximately 4.6 Å. The short spacings for the highest melting form of the distearin compounds correspond more nearly to those of the β' -form of tristearin, which is characterized by two strong lines corresponding to approximately 4.2 and 3.8 Å.

The long spacings for the α - and β -forms of tristearin are approximately 50.6 and 45.2 Å., respectively. These spacings are recognized as being associated with a double-chain-length structure; that is, the repeating units in the crystals have a length equal to about that of two stearic acid chains. The long spacings listed in Table II for the distearin fumarate, succinate and adipate range from 49.8 to 58.3 Å. It can be concluded that in the polymorphic forms represented in Table II the distearin compounds are crystallized in a double-chain-length structure.

When crystallized from solvents like *n*-hexane, the distearin compounds tend to form long, needle-like crystals. This tendency to form needle-like crystals appears to be enhanced by the presence of impurities. In the course of the experimental work some masses of crystals were obtained which resembled asbestos in appearance.

Insofar as infrared absorption spectra are concerned, each of the diolein and distearin esters of fumaric, succinic and adipic acids behaved like tristearin and other ordinary triglycerides containing no *trans* isomers. All of the characteristic absorption bands found for tristearin occur in the spectra of the dibasic acid-containing compounds; and the latter possess no unique bands.

One of the characteristics which differentiates the diglyceride esters of the dibasic acids from prac-

tically all of the ordinary triglycerides is their relatively high viscosity, a characteristic which should prove to be of practical value in several areas of utilization. In Table III are recorded the kine-

TABLE III
VISCOSITY OF SOME NATURAL OILS, 1,3-DIOLEIN AND THE FUMARATES, SUCCINATES AND ADIPATES OF 1,3-DIOLEIN AND 1,3-DISTEARIN

Compound	Kinematic viscosity, centistokes, at	
	38.8°	98.8°
Diolein fumarate	86.50	13.60
Diolein succinate	77.00	13.00
Diolein adipate	116.70	21.27
Distearin fumarate	Solid	20.64
Distearin succinate	Solid	17.87
Distearin adipate	Solid	18.93
1,3-Diolein	48.50	8.50
Coconut oil	29.79	6.06
Cottonseed oil	38.88	8.39
Castor oil	293.4	20.08

matic viscosities of the diglyceride esters of the dibasic acids at two temperatures, together with the viscosities of diolein and several common oils. At 38.8 and 98.8° the diolein esters of the dibasic acids are approximately twice as viscous as are cottonseed oil and coconut oil, though not as viscous as is castor oil. In conformance with the nature of the usual viscosity-temperature relationship for oils, the viscosity of the diolein esters increases quite rapidly as the temperature is decreased below 38.8°. At 28.2° the diolein adipate possesses a viscosity of 148.8 centistokes and the diolein succinate a viscosity of 128.0 centistokes.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Studies on the Synthesis of a Spiroepoxy Ketal¹

By K. R. HUFFMAN² AND D. S. TARBELL

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Treatment of 2-benzhydrylidene tetrahydrofuran with perbenzoic or perphthalic acid does not yield the expected spiroepoxy ketal. Action of *t*-butyl hypochlorite or *N*-bromosuccinimide on the benzhydrylidene tetrahydrofuran does not give the corresponding halohydrin, but leads to 2,2-diphenyl-3-ketotetrahydropyran by a rearrangement involving ring enlargement. Treatment of ethyl α -propionylpropionate with ethylene chlorohydrin and sodium hydride yielded, by ester interchange and alkylation on the carbonyl oxygen, a cyclic ketene acetal XVI whose structure was proved by degradation. α -Chloroacetyl- α -methyl- γ -butyrolactone has been synthesized; hydrolysis with mineral acid yields 2,3-dihydroxy-2,3-dimethyltetrahydrofuran by a rearrangement reaction. The structure of this compound was proved by periodate oxidation.

During studies on the structure of fumagillin,³ we have considered at various times the possibility that two of the non-carbonyl oxygens in alcohol-I, derived from fumagillin, were combined in a spiro-

ketal system. One such structure is the 1,4-dioxaspiro[2.4]heptane system (I), for whose presence in fumagillin some interesting arguments could be adduced. We have not found examples of structures analogous to I in the literature⁴; the present

(1) Aided by a grant from the National Institutes of Health.

(2) Abbott Laboratories Fellow, 1957-1958.

(3) J. M. Ross, D. S. Tarbell, W. E. Lovett and A. D. Cross, *THIS JOURNAL*, **78**, 4675 (1956), for example.

(4) A derivative containing a spiroepoxy ketal group is postulated as an intermediate in the formation of anhydro sugars by E. Zissis, L. C. Stewart and N. K. Richtmyer, *ibid.*, **79**, 2593 (1957).