4. Hoffpauir, C.L., Oil and Soap, *22*, 283–286 (1945).
5. Karon, M.L., and Hilleary, Barbara E., J. Am. Oil Chemists' Soc., *26*, 16–19 (1949).
6. "Official Methods of Analysis of the Assn. of Official Agricultural Chemists," 8th ed., Assn. of Official Agricultural Chemists, Washington, D.C., 1955.
7. "Official and Tentative Methods of the American Oil Chemists' Society," 2nd ed., American Oil Chemists' Soc., 1959.
8. Pickett, T.A., and Holley, K.T., "Peanut Roasting Studies," Tech. Bull. No. 1, Georgia Experiment Station, October, 1952.
9. Warner, M.G.R., Lawton, P.T., and Harris, G.O., "The Determination of the Moisture Content of Ground Nuts," Report No. 39, British Society for Research in Agricultural Engineering, National Institute of Agricultural Engineering, Bedfordshire, England.

[Received October 19, 1960]

Glycidyl Esters. II. Synthesis of Esters of Commercial and Pure Fatty Acids

GERHARD MAERKER, EDWARD J. SAGGESE, and WILLIAM S. PORT, Eastern Regional Research Laboratory,[1] Philadelphia, Pennsylvania

The reaction of salts of carboxylic acids with epichlorohydrin in the presence of quaternary ammonium halides to form glycidyl esters has been demonstrated to be applicable to a variety of acids derived from fats, including commercial mixtures.

The glycidyl esters of pelargonic, lauric, oleic, dimerized linoleic, ricinoleic, behenic, and sebacic acids as well as those of the fatty acids derived from tallow, wool wax, and soya oil have been prepared in 80–95% yields and purities.

THE INCLUSION of oxirane groups in materials derived from animal and vegetable fats has been studied widely, and several of the products of these studies are in commercial use. A common property of such epoxidized fatty materials is that the oxirane function is located internally along the hydrocarbon chain as, for instance, in 9,10-epoxystearic acid. On the other hand, the investigation of fat-derived materials with terminal epoxide groups has been neglected almost entirely. A program of preparation of glycidyl esters was undertaken for the purpose of partially filling this need.

A review of the literature revealed that several methods of preparation of glycidyl esters were available, but none appeared entirely suitable to the problem at hand. The direct esterification of glycidol with acid chlorides of carboxylic acids (4,5,16) requires not only several reaction steps to arrive at the desired product but also involves the use of relatively expensive chemicals. The reaction of monocarboxylic acids with epichlorohydrin (15), especially when catalyzed by compounds of the Friedel-Crafts type (7,13) or by basic organic nitrogen compounds (11,14), results in the formation of α-carboxylic esters of γ-chloropropylene glycol. These are then dehydrohalogenated in the presence of alkali to give the desired glycidyl ester (Equation A, Figure 1). Over-all yields are low.

Glycidyl esters can also be obtained directly from fatty acids and epichlorohydrin by the use of quaternary ammonium halide catalysts and a large excess of epichlorohydrin (10) (Equation B, Figure 1). The latter, besides acting as solvent, absorbs the hydrogen chloride evolved. Disadvantages of this method are that for each mole of ester formed two moles of epichlorohydrin are used up and that in many cases the products obtained are difficult to purify.

The uncatalyzed reaction of epichlorohydrin with salts of carboxylic acids, rather than with the free acids, has also been reported. Epichlorohydrin consumption is decreased to the stoichiometrically required amount, but the presence of even small amounts of moisture decreases the yields of glycidyl esters (1,8).

A number of glycidyl esters of fatty acids were prepared in high yields by Kester and co-workers (5,6) by the reaction of soaps of fatty acids and excess epichlorohydrin in the complete absence of moisture. Carried out at normal pressure, the reaction time was 5–11 hrs., but considerably less time was required at superatmospheric pressures. High pressures or traces of moisture caused the formation of considerable amounts of high-boiling and polymeric by-products. This method was described as inapplicable to the preparation of diglycidyl sebacate.

Recently the authors reported (9) the preparation of glycidyl stearate and diglycidyl azelate by reaction of sodium stearate and disodium azelate, respectively, with epichlorohydrin in the presence of benzyltrimethylammonium chloride (Equation C, Figure 1). This procedure, which may be carried out in moist or even partly aqueous media, requires only brief reaction periods, gives high conversions to glycidyl esters, yields easily purifiable reaction products, and may be adapted readily to bench-scale preparations. It is the purpose of the present paper to show the applicability of the new procedure to a variety of carboxylic acids of fatty origin.

Discussion

As reported earlier (9), both the carboxylic acids and their soaps react readily with epichlorohydrin in the presence of certain quaternary ammonium halides to give glycidyl esters. The soaps however give higher yields and purer products and were used exclusively in the present studies.

The required soaps were either prepared separately and isolated (nonaqueous method), or an aqueous solution of the neutralized acids was used directly (aqueous method). Experiments involving the isolation of soaps made from fatty acid stocks are illustrated in the experimental section and summarized in Table I. The procedure, which involved neutralization of an acetone solution of the acids, followed by filtration of the precipitated salts, was chosen for its convenience and ease of handling in the laboratory. In all cases somewhat less than the stoichiometrically required amount of base was used to avoid, as much as possible, the presence of free alkali in the soaps. As a result, some loss of fatty material was incurred

[1] Eastern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

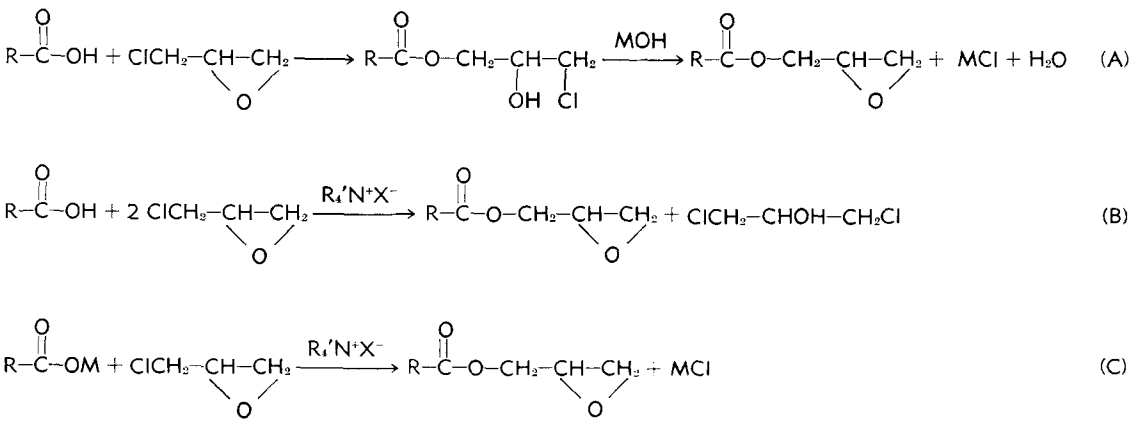

FIG. 1. Preparation of glycidyl esters.

because of the solubility of unneutralized acids and of the soaps in the aqueous acetone. As expected, the more highly unsaturated materials concentrated in the acetone filtrate as is shown by the loss of the iodine value of the isolated soap (Table I). On a percentage basis this effect was greatest in the case of the wool wax fatty acids, where a relatively small fraction of the acids is unsaturated. The concentration of unsaturation in the acetone filtrate was verified in the case of soya fatty acids, where the residue obtained from the evaporation of the acetone filtrate had an iodine value which was 40% higher than that of the main fraction and accounted for 63% of the missing unsaturation.

Two modifications of the same method were used to prepare all of the glycidyl esters described in this paper. In the majority of cases an essentially nonaqueous system was used although no effort was made to achieve an absolutely anhydrous system. The previously isolated and dried soaps were suspended in an excess of boiling epichlorohydrin and brought to reaction by addition of the catalyst. A somewhat different procedure was followed in the preparation of glycidyl pelargonate and diglycidyl sebacate, where an aqueous solution of the soap was slowly added to boiling epichlorohydrin containing catalyst, and the water so added was removed rapidly as the epichlorohydrin azeotrope. Results are summarized in Tables II and III.

The choice of the method, aqueous or nonaqueous, to be used in an individual synthesis was governed chiefly by the solubility of the particular soap in epichlorohydrin.

In most of the preparations the nonaqueous system was used since the presence of substantial amounts of water decreases the yields of desired products somewhat. The results in Table II show that in all of the preparations both yields and purities were in the 80–95% range. No effort was made to obtain maximum yields or to improve the purity of the crude products. It is probable that improvements in both the product yields and purities could be attained by changes in such reaction variables as reaction time, reaction temperature, moisture content, and catalyst concentration as well as by recovery of by-products. The latter are most likely α-carboxylic esters of γ-chloropropylene glycol predominantly (9) and, if recovered, could be converted to further amounts of glycidyl esters by well-established methods, such as treatment with alkali (3,12).

The sodium and potassium salts of dicarboxylic acids, such as azelaic acid and sebacic acids, and of shorter-chain aliphatic monocarboxylic acids appear to have relatively low solubility in epichlorohydrin. It has been reported previously (9) that the low solubility of disodium azelate causes its reaction with epichlorohydrin to be slow, giving rise to impure products in low yields. Use of a partly aqueous system was found to decrease reaction time greatly, at the same time leading to a more easily purifiable product. A partly aqueous system was similarly found to give good results in the preparation of di-

TABLE I

Conversion of Fatty Acids to Their Sodium Salts

Fatty Acid						NaOH % of stoichiometric requirement	Isolated Sodium Salt			
Name	Source	Weight (g.)	Equiv. weight[a]	Acid number	Iodine value		Weight (g.)	Acid number	Iodine value	
									Calc'd[b]	Found
Lauric acid	Neofat 11	120.2	200.0	280.6	<0.3	95	112.5	<0.5	<0.3	<0.3
Tallow fatty acids	Groco 41	146.0	274.5	204.4	49.0	95	147.4	8.2	45.4	42.2
Wool wax fatty acids	Laboratory sample	226.2	377.6	148.6[c]	15.5	95	182.5	<0.5	14.6	5.2
Soya fatty acids	Regular, Wilmar 611	170.1	282.9	198.3	121.4	98	163.0	2.6	112.6	103.3
Dimerized linoleic acid	Empol 1022	59.6	298.1	188.2	122.5	95	55.7	0.9	114.1	103.9
Oleic acid	Emersol 233, L.L. Elaine	167.4	278.4	201.5	88.0	98	168.3	2.2	81.6	80.1
Behenic acid	Laboratory sample	42.6	336.6	166.7	<0.3	95	41.7	6.7	<0.3	<0.3
Ricinoleic acid	Laboratory sample	156.5	298.1	188.2	83.3	95	146.8	1.0	77.6	79.7

[a] Determined by titration with alkali.

[b] $\text{I.V.} = \frac{\text{Equiv. weight of acid} \times \text{I.V. of acid}}{\text{Equiv. weight of salt}}$

[c] Saponification No. was 158.5.

TABLE II

Preparation of Glycidyl Esters from Fatty Acid Soaps, Nonaqueous Method

Parent acid	Crude Glycidyl Ester						
	Conversion %[a]	Purity %[b]	m.p.(°C) or n_D^{30}	Oxirane oxygen		Iodine value	
				Calculated %	Found %[b]	Calculated	Found
Lauric acid	83.6	88.1	1.4442	6.24	5.50	<0.3	<0.3
Tallow fatty acids	89.7	90.5	28.0–30.0	4.83	4.37	37.9	37.1
Wool wax fatty acids	94.6	93.0	45.0–50.0	3.69	3.43	4.8	4.6
Soya fatty acids	92.6	93.8	1.4622	4.71	4.42	92.9	91.1
Dimerized linoleic acid	92.6	86.9	1.4826	4.52	3.93	93.9	106.6
Oleic acid	85.8	91.0	1.4581	4.79	4.36	72.1	72.4
Behenic acid	80.9	89.4	62.0–64.0	4.07	3.64	<0.3	<0.3
Ricinoleic acid	82.1	82.6	1.4680	4.53	3.74	72.0	68.5

[a] Based on calculated equivalent weight of the prepared soap.
[b] Oxirane method of Durbetaki (2).
Ratio of reactants (equivalents), epichlorohydrin : soap : catalyst = 16 : 1 : 0.1.

glycidyl sebacate. The added water was permitted to be present only long enough to bring the reactants into intimate contact and to allow them to react. It was then removed as rapidly as possible by distillation of the water-epichlorohydrin azeotrope.

The aqueous method, although it is the more desirable for the reaction of soaps which have low solubility in epichlorohydrin, may also be applied to other soaps which are at least fairly soluble in boiling water. In such applications the minor yield losses involved in the aqueous method may be outweighed by the advantage of preparing the glycidyl ester directly from the acids or of using industrial aqueous soap stocks. Although the illustrations of the procedure, presented in the experimental section, indicate the use of potassium salts only, glycidyl esters have been prepared from sodium salts by this method with equal ease. Presumably other salts could be used as well.

The role which the catalyst plays in this reaction has not yet been defined. Compounds other than benzyltrimethylammonium chloride, for example tetraethylammonium bromide, have been used successfully and have given similar yields. On the other hand, tetramethylammonium chloride is unsuitable because of its low solubility in boiling epichlorohydrin.

The wide scope of this procedure in making glycidyl esters is shown by the variety of fatty acid starting-materials. It is evident from the experimental data that any unsaturation present in the reactant soaps is unaffected by the reaction.

The products are mostly oils or low-melting solids. Some of the former have quite low freezing points. For instance, the glycidyl ester of pelargonic acid freezes at about −35°C. while that of dimerized linoleic acid melts at −50°C. The solid glycidyl esters may be purified by crystallization, as illustrated for diglycidyl sebacate.

Experimental

Starting Materials

Commercial mixtures of fatty acids (Table I) were used as received. Laboratory samples of individual fatty acids were used as available without further purification. Commercial sebacic acid (Eastman Organic Chemicals, Practical Grade) was recrystallized twice from o-dichlorobenzene to obtain purified sebacic acid (A.N. 552, m.p. 132.5–133.7°C.).

Epichlorohydrin (Eastman Organic Chemicals) was used as received. Crystalline benzyltrimethylammonium chloride (Eastern Chemical Corporation), after drying at 110°C., was used without further purification.

Preparation of Sodium Salts of Fatty Acids

The method used was essentially that of Kester *et al.* (5). Physical constants and experimental variations are summarized in Table I.

Preparation of Glycidyl Esters of Fatty Acids: A. Nonaqueous Method

The following example illustrates the general method used for the preparation of the glycidyl esters listed in Table II. In all experiments the ratio of epichlorohydrin to sodium salt to benzyltrimethylammonium chloride was (in equivalents) 16:1:0.1. In one case, the preparation of glycidyl ricinoleate, the amount of epichlorohydrin was increased by 50% in order to improve the workability of the initial slurry.

Preparation of Glycidyl Laurate from Sodium Laurate. A suspension of sodium laurate (22.2 g., 0.1 mole) in epichlorohydrin (148.0 g., 1.6 mole) was agitated vigorously and heated to 110°C. Solid benzyltrimethylammonium chloride (1.86 g., 0.01 mole) was added in one batch, and the resulting mixture was heated at reflux (115°C.) for 25 min. The mixture was then cooled rapidly to 90°C., and water (100 ml.) was added. Intimate stirring was continued for 20 min., and the two liquid phases were separated. The epichlorohydrin solution was again washed with water (100 ml.) for 20 min., as above. The wash waters were discarded, and the organic solution was distilled at reduced pressure under a current of nitrogen until the residue in the still pot reached 70°C. at 1 mm. Last traces of epichlorohydrin were removed by azeotropic distillation under nitrogen with two portions of toluene (50 ml. each) until each time the material in the distilling flask reached 70°C. at 1 mm. The remaining yellow oil was crude glycidyl laurate [23.7 g.; oxirane oxygen, 5.50% (method of Durbetaki [2]). (Theory: 6.24%); n_D^{30} 1.4442].

TABLE III

Preparation of Glycidyl Esters from Carboxylic Acids, Aqueous Method

Acid	Water g./equiv. of acid	KOH % of stoichiometric requirement	Crude Glycidyl Ester				
			Conversion %[a]	Purity %	$n_D^{35.5}$	Oxirane oxygen	
						Calc'd. %	Found %[b]
Sebacic	362	99.0	78.3	70.9	1.4634	10.18	7.22
Pelargonic	590	98.7	92.7	82.7	1.4390	7.47	6.18

[a] Acid groups converted to glycidyl ester.
[b] Oxirane method of Durbetaki (2).

Preparation of Glycidyl Esters of Fatty Acids: B. Aqueous Method, Preparation of Diglycidyl Sebacate from Aqueous Dipotassium Sebacate

Epichlorohydrin (400 g., 4.3 mole) was heated to reflux in a 3-neck flask equipped with two addition funnels, stirrer, and Dean-Stark water trap topped by a reflux condenser. A solution of benzyltrimethylammonium chloride (11.6 g., 0.06 mole) in water (7 ml.) was added rapidly, followed by the addition, drop by drop, of a hot solution of sebacic acid (60.7 g., 0.3 mole) and potassium hydroxide (33.3 g., 0.594 mole) in water (210 ml.). During the addition the aqueous sebacate solution was kept near its boiling point by means of a heat lamp. Concurrently with the addition of the aqueous sebacate solution, epichlorohydrin (100 g., 1.1 mole) was allowed to enter the reaction mixture from the second addition funnel at a rate sufficient to keep the amount of epichlorohydrin in the reaction mixture approximately constant. Water and epichlorohydrin distilling out of the reaction mixture were collected in the trap and cooled to room temperature in a separatory funnel. The phases were separated, and the epichlorohydrin phase was returned to the proper addition funnel. (In later experiments, use of a modified trap permitted the continuous return of distilled epichlorohydrin to the reaction mixture.) Upon completion of the sebacate addition (44 min.), distillation of water and epichlorohydrin as well as epichlorohydrin recycling were continued for 26 min. Water recovered from the distillate totalled 212 ml. The reaction mixture was cooled and was washed twice with water (200 ml. each time) by vigorous agitation for 30 min. The combined wash water, after acidification, gave no precipitate, indicating complete consumption of sebacic acid. The epichlorohydrin solution was worked up in the usual manner by distillative removal of epichlorohydrin at reduced pressure under nitrogen. The semisolid still residue was crude diglycidyl sebacate (104.2 g.; oxirane oxygen, 7.22%; $n_D^{35.5}$ 1.4634). Conversion of carboxylic acid to glycidyl ester: 78.3%.

Crude diglycidyl sebacate (10 g., oxirane oxygen, 7.22%) in Skellysolve C (400 ml.) was heated to 78°C., the solution was decanted from the oily residue and allowed to cool to 25°C. The resulting mixture was reheated to 40°C., and the clear solution was decanted from a second oily residue. Cooling of the Skellysolve C solution at −20°C. and filtering gave crystalline purified diglycidyl sebacate [4.4 g.; oxirane oxygen, 9.44% (theory, 10.18%); m.p., 42.8–43.5°C.].

Preparation of Glycidyl Pelargonate from Aqueous Potassium Pelargonate

A solution of benzyltrimethylammonium chloride (5.6 g., 0.03 mole) in water (4 ml.) and a hot solution of pelargonic acid (47.5 g., 0.3 mole, A.N. 378) and potassium hydroxide (17.6 g., 0.296 mole) in water (177 ml.) were added to boiling epichlorohydrin (400 g., 4.3 mole), using the procedure outlined for the preparation of diglycidyl sebacate. The reaction product was worked up as described above, yielding crude glycidyl pelargonate [72.1 g.; oxirane oxygen, 6.18% (theory 7.47%); $n_D^{35.5}$ 1.4390]. Conversion of carboxylic acid to glycidyl ester: 92.7%.

REFERENCES

1. Dorough, G.L., U.S. Patent 2,524,432, October 3, 1950.
2. Durbetaki, A.J., Anal Chem., *28*, 2000 (1956).
3. Erickson, J.G., U.S. Patent 2,567,842, September 11, 1951.
4. Henkel and Cie., British Patent 735,001, August 10, 1955.
5. Kester, E.B., Gaiser, C.J., and Lazar, M.E., J. Org. Chem., *8*, 550 (1943).
6. Kester, E.B., and Preusser, H.M., U.S. Patent 2,448,602, September 7, 1948.
7. Knoevenagle, E., J. Chem. Soc., *1914*, AI, 163.
8. Köhler, R., and Pietsch, H., German Patent 944,995, June 28, 1956.
9. Maerker, Gerhard, Carmichael, J.F., and Port, W.S., J. Org. Chem., in press.
10. Mueller, A.C., U.S. Patent 2,772,296, November 27, 1956.
11. Shokal, E.C., and Mueller, A.C., U.S. Patent 2,895,947, July 21, 1959.
12. Starcher, P.S., McPeek, D.L., and Phillips, B., British Patent 794,209, April 30, 1958.
13. Stein, G., U.S. Patent 2,224,026, December 3, 1940.
14. Stein, G., German Patent 708,463, June 12, 1941.
15. Viard, M.J., French Patent 1,011,410, June 23, 1952.
16. Zetzsche, F., and Aeschlimann, F., Helv. Chim. Acta, *9*, 708 (1926).

[Received November 3, 1960]

Some Proposals Toward a New System of Oral Nomenclature for Long-Chain Fatty Acids[1,2]

L.J. MORRIS, The Hormel Institute, Austin, Minnesota

Proposals toward a new system of oral nomenclature for long-chain fatty acids and their derivatives are presented. The nomenclature suggested is, in general, merely a simplification of classical Geneva nomenclature, and it is hoped that its acceptance and utilization will result in a reduction in the use of meaningless, trivial names in oral presentations.

THE APPLICATION of new and ever more sensitive methods to studies of the fatty acid components of lipids is rapidly extending the range of known natural aliphatic acids. Novel acids of widely differing structures, occurring generally as minor and trace components of the lipids from animal or plant sources, are reported monthly, and the number of such new acids studied and described seems likely to increase progressively in the coming years.

When such acids are described in written communications, the use of the systematic nomenclature, under the relatively leisurely conditions of reading, allows ready appreciation of the structures being described. Systematic names however, because of their length and sometimes difficult pronunciation, are awkward to use in oral presentation. Resorting to trivial names may perhaps make it easier for the speaker but only adds to the confusion of the audience. The habit of christening new acids with meaningless trivial names is to be deplored, particularly when their structures are known. Trivial names of some kind must perforce be applied to acids whose structures are unknown at

[1] Presented at the 34th fall meeting, American Oil Chemists' Society, New York, October 16–19, 1960.
[2] Supported in part by the Hormel Foundation.