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.

the time of description, whether written or oral. These should not become permanent designations, and their use should be discontinued, in each case, as soon as the structure is known. The retention of such trivial names as permanent designations, in oral presentations in particular, is unlikely to be stopped until it is possible to avoid the cumbersome systematic nomenclature in some more logical way.

Some system of simplified but unambiguous oral nomenclature for fatty acids therefore seems desirable. The use of such a system should not only facilitate the recognition by the audience of the structure being described but should aid the speaker in his presentation.

The proposals advanced below are an attempt to provide the basis for such a system. Even if they prove unacceptable, they should stimulate an "agonizing reappraisal" of the whole question of nomenclature used in oral presentations. It has been attempted to give names which are as short as possible, which are readily pronounceable by a speaker and which will convey the structure in such a way as to be readily visualized by an audience.

The proposed nomenclature would, it is hoped, remove two of the causes of confusion engendered by the use of systematic nomenclature. One of these is that to some people the Greek-based prefixes, indicating chain length, require some mental juggling to convert them to numbers, particularly the less common ones such as "heneicosa" for C_{21}, "triaconta" for C_{30}, etc. The other common cause of confusion arises when there are several centers of usaturation in the molecule and possibly some substituent groups in addition. This results in a whole string of numbers from which many people may have difficulty in visualizing whether the unsaturated centers are methylene-interrupted, conjugated, or neither; or where substituents fit in in relation to them.

TO REMOVE these two causes of possible confusion, it is proposed, first, that chain length be designated as C_{10}, C_{20}, etc., and that, second, provided the unsaturation is serialized, *i.e.*, either methylene-interrupted or conjugated, only the number of the carbon where the series starts be indicated. Numbering will be from the carboxyl group throughout.

Specific proposals for the various classes of acids are as follows.

Saturated acids can be designated by their trivial names as hitherto or as C_{10} saturated, C_{12} saturated, etc. Palmitic and stearic acids will obviously be retained. Lauric, myristic, and arachidic might also be used, but otherwise the alternative designation is preferred. The confusion arising in discussion of short-chain acids because of the names caproic, caprylic, and capric would be removed by naming them C_6, C_8, and C_{10} saturated, respectively.

iso-Acids may be designated as C_9-8-methyl saturated, etc., and *anteiso*-acids as C_8-6-methyl saturated etc., where C_9, C_8, etc., indicate the length of the longest straight carbon chain and not the total number of carbon atoms. Other substituted saturated acids will be similarly named.

Monounsaturated acids and polyunsaturated acids with either methylene-interrupted or conjugated unsaturation will have a description consisting of three parts: a) an indication of chain length, C_{16}, C_{18}, etc., as with the saturated acids; b) the number of the carbon atom where the unsaturated system begins; and c) the unsaturated system.

If the double bonds of a polyenoic acid are methylene-interrupted, it is proposed that this type of name will be sufficient. Thus, for example, eicosa-5,8,11,14-tetraenoic, which is arachidonic acid, would be C_{20}-5-tetraene acid. If the unsaturation is conjugated however, this should be indicated, *e.g.*, octadeca-9,11,13,15-tetraenoic or parinaric acid would be C_{18}-9-conjugated tetraene acid.

The position, configuration (where required), and type of any substituent will be inserted immediately after the chain-length description, *e.g.*, 4-keto-octadeca-9,11,13-trienoic or licanic acid would be C_{18}-4-keto-9-conjugated triene acid, *cis*-15:16-epoxyoctadec-9,12-dienoic acid would be C_{18}-15-*cis*-epoxy-9-diene acid, and ω-(2-*n*-octyl-*cyclo*-prop-1-enyl)-octanoic or sterculic acid would be C_{18}-9:10-methylene-9-ene acid.

By composing the name for an acid of complicated structure in this way, I believe that maximum ease of assimilation will be achieved. With the chain length enumerated first the position of a substituent may be visualized immediately it is described and the unsaturated system may be readily fitted in.

It should be noted that the names proposed are those of the parent hydrocarbons, and any long-chain compound, related to the fatty acids, may be named as proposed by substitution of the word "acid" after the name by ester, alcohol, aldehyde, etc. This should remove any confusion engendered by the endings "ol" and "al" for alcohols and aldehydes in the systematic nomenclature.

Other unsaturated acids, having acetylenic unsaturation with or without additional ethylenic unsaturation, will be named on the same basis as above, provided the unsaturation is either methylene-interrupted or conjugated. Thus, for example, octadec-11-en-9-ynoic acid, which has two trivial names, ximenynic or santalbic acid, would be C_{18}-9-conjugated ynene, and octadec-13-en-9,11-diynoic or bolekic acid would be C_{18}-9-conjugated diynene acid.

IF THIS SYSTEM were used consistently for methylene-interrupted and conjugated polyunsaturated acids, then, in naming acids with ethylene-interrupted or nonserialized unsaturation, all double or triple bond positions could be indicated by number. This would immediately emphasize the fact that such acids have abnormal structures. For example, hexadeca-6,10,14-trienoic or hiragonic acid would be C_{16}-6,10,14-triene acid and docosa-4,10,13-16-tetraenoic acid would be C_{22}-4,10,13,16-tetraene acid.

Isanic or erythrogenic acid, namely, octadec-17-en-9,11-diyonic acid, would come under this classification unlike its isomer, bolekic acid, which has all-conjugated unsaturation. Thus it would be named C_{18}-9,11-diyn-17-ene acid, and the hydroxy acid which accompanies it in boleka oil, 8-hydroxyoctadeca-17-en-9,11-diynoic or isanolic acid, would be C_{18}-8-hydroxy-9,11-diyn-17-ene acid.

The configuration of ethylenic bonds in natural acids is predominantly *cis*, and it is proposed that, where this is so, the configuration need not be specified. When acids have *trans* ethylenic bonds and this is to be specified, it is suggested that the configurational description be added to the end of the name, where it can most readily be appreciated. Thus α-elaeostearic and punicic acids, the natural forms of octa-

deca-9,11,13-trienoic acid, would be C_{18}-9-conjugated triene acid *(cis, trans, trans)* and C_{18}-9-conjugated triene acid *(cis, trans, cis)*, respectively. These names are likely to be more readily understandable than octadeca-*cis*-9-,*trans*-11,*trans*-13-trienoic and octadeca-*cis*-9,*trans*-11,*cis*-13-trienoic acids, respectively.

It is again emphasized that these proposals are for oral use only and that no alteration in the use of the Geneva system of nomenclature in written papers is suggested. However it is hoped that they may be a first step toward resolution of the somewhat chaotic condition of nomenclature as applied to the oral description of fatty acids.

It is realized that these proposals may not be the final solution to the problem of oral nomenclature of fatty acids. It is hoped that any criticisms or suggestions for improvement will be made through this Journal since in the hands of the Nomenclature Committee of the American Oil Chemists' Society will be the final decision for recognition or for rejection of these proposals for use in the meetings of this Society.

[Received November 21, 1960]

Differentiation of 1- and 2-Monoglycerides by Near-Infrared Absorption Spectroscopy[1]

H. SUSI, S.G. MORRIS, and W.E. SCOTT, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

1- and 2-monoglycerides can be differentiated and mixtures analyzed by investigating the overtone of the OH stretching vibration, which occurs in the near-infrared spectral region close to 1.4 microns. The results are compared with data obtainable in the fundamental rock-salt region.

INFRARED spectroscopy of dilute solutions (1) and of crystalline films (2) has been shown to be of great value in the analysis and structure determination of mono-, di-, and triglycerides. One of the more difficult problems in glyceride analysis is differentiation and characterization of 1-monoglycerides and 2-monoglycerides. Chemical methods are tedious and time-consuming. Solution spectra obtained with infrared instruments equipped with conventional rock-salt optics differ in the 9-micron "fingerprint region," but the differences are relatively small and occur in a portion of the spectrum where many overlapping absorption bands are observed. Greater differences are observed if spectra of the solid compounds are obtained (2). Different thermal treatment of the 1-monoglycerides gives rise to different spectra, corresponding with the polymorphic forms, whereas 2-monoglycerides exist in only one form (2,3). The spectra of the most stable forms (β_L) differ considerably (2). However these procedures require great care. The solid state spectra moreover are not easily and directly utilizable for quantitative analytical determinations.

The purpose of this investigation was to establish the usefulness of near-infrared spectroscopy for differentiating between the two isomers and for the analysis of mixtures of 1- and 2-monoglycerides (in the absence of di- and triglycerides). Instruments with excellent photometric reproducibility and spectral resolution are now available for analytical spectrophotometry in the near-infrared spectral region. The main difference between the two isomers (OH groups in different intramolecular environment) appears to be of the kind which is well suited to investigation with near-infrared spectrophotometry where the greatest emphasis is on chemical groups and bonds involving hydrogen atoms.

Experimental

The 1-monoglycerides were prepared by the acylation of 1,2-acetone glycerol, followed by treatment with cold concentrated hydrochloric acid in ethyl ether; the 2-monoglycerides by the acylation of 1,3-benzylidene glycerol, followed by boric acid cleavage of the benzylidene-2-acylglycerol in dioxane.

The acetone glycerol was prepared according to Malkin and Shurbagy (4) except that the final distillation was over magnesium oxide instead of silver oxide. The 1,3-benzylidene-glycerol preparation was essentially that of Hibbert and Carter (5). The acylations were made with fatty acid chlorides in the presence of pyridine and chloroform solvents. To obtain the 2-monoglycerides from 1,3-benzylidene-2-acylglycerol, Martin's (6) method was used except that the alternate solvent, dioxane, was substituted for triethylborate.

Survey spectra in the conventional 2-15 micron region were obtained with a Perkin-Elmer Model 21 instrument equipped with rock-salt optics. Near-infrared absorption spectra from 1.0 to 2.5 microns were measured with a Cary Model 14 spectrophotometer. Cells of 1-cm. and 5-cm. path length were used. Sample concentrations ranged from 5 to 70 g./liter. Chloroform (Spectro-quality reagent, Matheson, Coleman, and Bell) was used as a solvent and as solvent compensator in the reference beam. The solvent was dried before use by bubbling through it a a stream of dry nitrogen. This method has proven highly successful in removing traces of H_2O from carbon tetrachloride. Solutions were prepared, and the absorption cells were filled in an atmosphere of dry nitrogen. Despite these precautions, small disturbances caused by H_2O absorption were observed. Fortunately these were found to be too small to interfere with the analytical measurements. Carbon tetrachloride is generally easier to obtain in a sufficiently anhydrous condition and is for this reason (among others, fewer absorption bands) usually preferred as a solvent for near-infrared work. Monoglycerides are unfortunately not sufficiently soluble in carbon tetrachloride; therefore chloroform was chosen for the present investigation.

[1] Presented at the 53rd fall meeting, American Oil Chemists' Society, New York, October 17–19, 1960.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.