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2,523,309

PREPARATION OF DIGLYCERIDES

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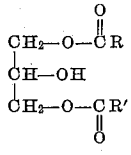
5 Claims. (Cl. 260—410.7)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented in any country, may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to me of any royalty thereon.

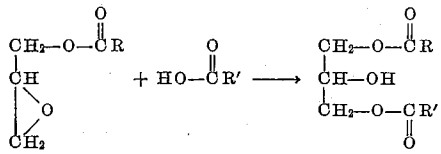
This invention relates to diglycerides having the structural formula



where R and R′ are the same or different aliphatic radicals containing at least 7 carbon atoms, and has among its objects the preparation of these esters in a substantially pure form by a simple and economical process.

Known methods for preparing compounds of the above type are not satisfactory because they produce mixtures of mono, di, and triglycerides, or, to obtain an individual compound it is necessary to use expensive reagents such as trityl ethers, etc. One known method involves heating a triglyceride with glycerine and a catalyst such as sulphuric acid. This technique produces a mixture of mono, di, and triglycerides which is exceedingly difficult to resolve. Further, if the acyl groups on the starting material are different from one another (mono-lauryl, distearyl glyceride, for example) then the product will contain a myriad of compounds differing in type of acyl radical, number of acyl radicals, position of acyl radicals, etc. Another known method involves reacting an alpha monoglyceride with a chloride of a fatty acid in the presence of pyridine as a hydrochloric acid acceptor. This process is likewise not clean-cut but produces a mixture of glycerides differing as to number and position of the respective acyl radicals.

It has now been found that diglycerides of the aforesaid type can be prepared in a simple and expeditious manner by reacting a glycidyl ester of an aliphatic carboxylic acid with an aliphatic carboxylic acid. The reaction which occurs can be represented by the following equation, wherein R and R′ have the significance above indicated:



(glycidyl ester) (acid) (formed diglyceride)

One advantage of my process is that a single

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compound is produced. In every case the product is the alpha, gamma diglyceride desired. There is no need to carry out laborious separations as with prior methods.

Another advantage of my process is that alpha, gamma diglycerides are produced exclusively. When glycerol or a monoglyceride is used as a reactant such a limited result cannot be achieved but the product may contain alpha, beta derivatives as well as alpha, gamma derivatives.

A further advantage of my process is its simplicity in that it is not necessary to employ any catalysts. A mere heating of the reagents, if desired in the presence of a solvent, is all that is required. The fatty acid which is used as a reactant directly is low in price in comparison to the acyl chlorides or trityl derivatives employed in previous methods.

Another advantage of my process is that it is particularly adapted to produce in one step a diglyceride in which the acyl radicals are different. By choice of the proper fatty acid and the proper glycidyl ester, any desired alpha, gamma diglyceride can be synthesized.

A further advantage of my process lies in the fact that the reactants need not be anhydrous. Contrary to most of the known syntheses, ordinary reagents may be used in my process without necessity for removal of the usual traces of water present in all commercial reagents.

The following examples illustrate the claimed process applied to particular materials under particular conditions. It is to be understood that these examples are submitted only by way of illustration and not limitation.

EXAMPLE I

Preparation of glycerol alpha, gamma lauro-stearate

20.4 g. (0.08 mol) of glycidyl laurate and 11.4 g. (0.04 mol) of stearic acid were mixed and heated for four hours at 128° to 130° C. At the end of this period, it was determined by titration of an aliquot sample of the reaction product that all but 2.6% of the stearic acid had reacted.

The reaction product was dissolved in hot absolute alcohol and on cooling 5.1 grams (25.4% yield) of alpha-lauryl, gamma stearyl ester of glycerol was obtained by filtering out the formed crystals. The product had a melting point of 62°–64° C. and a saponification equivalent weight of 271.5 (calculated 270.35). By recrystallization of the mother liquor, additional amounts of the product could be obtained.

EXAMPLE II

Preparation of glycerol alpha, gamma eruco-stearate

85 g. (0.251 mol) of erucic acid and 170 g.

(0.502 mol) of glycidyl stearate were added to 1 liter of chlorobenzene as the solvent contained in a 2-liter flask equipped with reflux condenser. The mixture was refluxed for 28 hours. At the end of this time, a titrated sample showed the reaction to be 99% complete.

The solvent was removed by distillation at about 20 mm. Hg pressure. The residue, 260 g., was dissolved in 780 ml. of hot hexane and crystallized by cooling to 23°–25° C. The product was washed with hexane and air-dried. A second crop was obtained by concentrating the mother liquor to half its volume and cooling. The two crops were combined and crystallized from hexane and then from absolute alcohol. The purified product, alpha erucyl, gamma stearyl glyceride weighed 65 g. (40% yield) and had a melting point of 56–57° C. Analysis: C, 76.1%; H, 12.1%; iodine value 36.2; saponification equivalent weight, 341. (Theoretical: C, 76%; H, 11.73%; iodine value, 37.3; saponification equivalent weight, 339.54).

The process herein disclosed is simple in that it merely involves contacting of the glycidyl ester and fatty acid under the influence of heat. In general, temperatures from about 50° C. to about 200° C., preferably from about 100° C. to about 200° C. are suitable. To promote contact between the reactants it is preferred to employ a solvent. In general any inert, hydrophobic organic solvent can be used such as benzene, chlorobenzene, toluene, xylenes, aliphatic hydrocarbons such as hexane, octane or mixtures of hydrocarbons such as petroleum ether, gasoline, naphtha, benzine, etc. When using a solvent it is preferred to reflux the reaction mixture to prevent loss of solvent. In such case the temperature of reaction will be approximately equal to the boiling point of the solvent. In general the glycidyl reactant and fatty acid may be employed in equimolecular proportions. However, it is preferred to employ the glycidyl reactant in excess. The reason for this is that thereby the reaction time is diminished and the excess glycidyl reactant can easily be recovered from the reaction mixture by distillation under reduced pressure. The glycidyl reactant so recovered can be used to prepare further quantities of the diglyceride.

The novel process is of wide versatility and can be used to prepare a wide variety of alpha, gamma diglycerides by selection of the proper reactants. As the glycidol reactant one may use any glycidyl ester of an aliphatic carboxylic acid containing at least 8 carbon atoms. Suitable reactants are, for example, glycidyl caprylate, glycidyl pelargonate, glycidyl caprate, glycidyl undecylate, glycidyl laurate, glycidyl tridecylate, glycidyl myristate, glycidyl pentadecylate, glycidyl palmitate, glycidyl margarate, glycidyl stearate, glycidyl nonadecylate, glycidyl arachidate, glycidyl oleate, glycidyl elaidate, glycidyl ricinoleate, glycidyl palmitoleate, glycidyl erucate, glycidyl brassidate, glycidyl linoleate, and so forth.

As the fatty acid reactant, one may use any aliphatic carboxylic acid containing at least 8 carbon atoms. Suitable acids are, for example, caprylic, pelargonic, capric, undecylic, lauric, tridecylic, myristic, pentadecylic, palmitic, stearic, margaric, nondecylic, arachidic, oleic, elaidic,

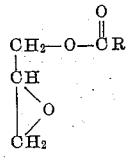
ricinoleic, palmitoleic, erucic, brassidic, linoleic acids, and so forth.

The alpha, gamma diglycerides produced in accordance with this invention can be used as intermediates in the preparation of wetting, deterging, emulsifying, and foaming agents, for example by sulphating the free hydroxyl group. They may also be employed as intermediates for preparation of plasticizers by esterification with polybasic acids such as phthalic, maleic, etc.

The compound glycerol alpha, gamma erucostearate, which may be also named alpha-erucyl, gamma-stearyl glyceride, is particularly adapted to be converted into a compound useful for emulsifying and dispersing purposes. To this end the glyceride is converted into its aminoethyl glycerophosphoric acid ester by the process as set forth in U. S. Patents 2,436,699 and 2,447,715 to W. G. Rose.

Having thus described the invention, what is claimed is:

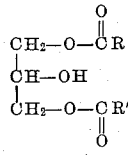
1. A process comprising heating to a temperature from about 50° C. to about 200° C. a reaction mixture of a glycidyl ester having the formula



and an acid having the formula



where R and R′ are aliphatic radicals containing at least 7 carbon atoms, to produce a diglyceride having the formula



2. The process of claim 1 wherein the reaction mixture contains an inert organic solvent and is refluxed during the heating.

3. The process of claim 2 wherein an excess of the glycidyl ester is used.

4. A process comprising heating to a temperature from about 50° C. to about 200° C. a reaction mixture of glycidyl stearate and erucic acid to produce glycerol alpha, gamma erucostearate.

5. The process of claim 4 wherein the reaction mixture contains an inert, organic solvent, an excess of glycidyl stearate is used, and the mixture is refluxed during heating.

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REFERENCES CITED

The following references are of record in the file of this patent:

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