

1

3,160,646

## PRODUCTION OF MONOGLYCERIDES

Werner Stein, Dusseldorf-Holthausen, and Josef Kretschmann, Dusseldorf, Germany, assignors to Henkel & Cie G.m.b.H., Dusseldorf-Holthausen, Germany, a German corporation

No Drawing. Filed Oct. 4, 1961, Ser. No. 142,783

Claims priority, application Germany Oct. 11, 1960

9 Claims. (Cl. 260-410.7)

This invention relates to new and useful improvements in the production of glycerides. The invention more particularly relates to a novel process for the production of glyceride mixtures having a high content of monoglycerides.

Monoglycerides constitute valuable commercial materials constituting excellent emulsifiers and are widely used for technical purposes and in the food industry.

Glycerides may be produced by the esterification of free fatty acids or the alcoholysis of fatty acid esters with glycerol. The glycerides so produced, however, are in the form of a mixture which contains, in addition to the monoglycerides, a relatively large content of di- and tri-glycerides. In the reaction mixture an equilibrium exists between glycerol, mono-, di- and tri-glycerides which can only be shifted in favor of the valuable monoglycerides by the presence of a large excess of glycerol. The shifting or the equilibrium in this manner, however, is impeded by the relative immiscibility of glycerol and tri-glycerols and/or glycerol and fatty acids.

Attempts have been made to overcome these difficulties by the use of solvents, such as phenol, cresol, or tertiary bases such as pyridine, chinoline, isochinoline, etc. With these solvents, it is possible to maintain a large excess of glycerol and to favorably shift the equilibrium so that the monoglyceride content will be as high as 75-78%. The use of the solvents, however, creates further difficulties, and even traces of the solvent which remain may be considered as contaminants and render the monoglycerides unsuitable for certain purposes, as for example in the food industry.

Other attempts to increase the monoglyceride content included adding up to 20% by weight of monoglyceride to the reaction mixture or using glycerol vapor as an entraining agent for distilling off monoglyceride from the reaction mixture. In the former case, monoglyceride contents of a maximum of 65-66% can only be obtained and in the latter case, very large quantities of glycerol were required and the heat expenditure in the process was considerable.

One object of this invention is a novel process for the production of glyceride mixtures having a high content of monoglycerides without the above-mentioned disadvantages.

This and still further objects will become apparent from the following description:

In accordance with the invention, it has been surprisingly discovered that glyceride mixtures with an extraordinarily high content of monoglycerides may be obtained in a simple commercially feasible manner without the use of solvents or catalysts if the glycerol and fatty acids and/or esters to be reacted are added at a carefully controlled rate with a controlled amount of glycerol to a reaction medium containing specific amounts of mono- and di-glycerides under carefully controlled conditions of temperature.

The reactants, used in accordance with the invention, consist of glycerol and the conventional fatty acids and/or fatty acid esters used in the production of glycerides. The glycerol must be present in a quantity with respect to the acids and/or esters so that there is at least two, as for example 2-6 mols of glycerol radicals present per mol

2

of fatty acid radicals. Preferably, the quantity should be such that there is about 3-5 mols of glycerol radicals per mol of fatty acid radicals. The glycerol and the fatty acids and/or fatty acid esters are introduced into a reaction medium containing glycerol and monoglycerides at a rate of not more than 0.5 part by weight per hour per part by weight of the initial reaction medium. The glycerol and the fatty acids and/or fatty acid esters, for example, could be introduced into the glycerol-glyceride reaction medium at a rate between about 0.15 and 0.5 and preferably 0.15-0.4 part by weight per hour per part of the initial reaction medium.

The reaction medium into which the glycerol and fatty acid and/or fatty acid esters is introduced at the controlled rate should contain at least 50 mol percent of glycerol, 10-35 mol percent of monoglycerides and not more than 15 mol percent as for example 5-15% of the higher glycerides, i.e. the di- and tri-glycerides.

The reaction should be effected at a temperature in excess of 260 degrees C., as for example between about 260-300 degrees C.

Preferably in accordance with the invention, the reaction media into which the glycerol and acid or ester is introduced at the controlled rate should have a glyceride content of 30-20 mol percent and a glycerol content of 60-75 percent. If the content of di- and tri-glycerides is high within the permissible maximum of 15 mol percent, it is desirable that the content of the glycerol be correspondingly greater.

The fatty acids from which the glycerides used in the reaction medium are produced may be of a random origin. Particularly applicable are saturated or unsaturated  $C_{10}$ - $C_{20}$  fatty acids of natural origin, such as, for example, occur in the fats of plants, land, and marine animals. Also suitable, however, are hydrogenation products of natural fatty acids as well as synthetic straight-or-branched chain fatty acids.

The fatty acids which are added with glycerol constitute the same group of acids. In place of the free fatty acids, or a mixture thereof, esters of these acids with glycerol or other mono-or-polyvalent alcohols may be used. The alcohol component of these esters should be alcohols having a boiling point below the boiling point of glycerol as for example  $C_{1-4}$  alcohols as for example methyl alcohol, ethyl alcohol, ethyleneglycol, propylene glycol, etc.

When initially starting the process in accordance with the invention, the monoglyceride used may be obtained from any source. Later the monoglycerides obtained according to the process itself may be used wherein also a part of the crude reaction product obtained in accordance with the invention may be recirculated so far as it has the necessary composition. The required mol ratio of fatty acid radicals to the glycerol radicals in the added glycerol and acid and/or esters is independent of the form in which these are charged and preferably lies between 1:3 and 1:5. So far as, for example, the fatty acid is charged in the form of di- or tri-glycerides, the glycerol introduced in this form must be also calculated since indeed it participates, like free glycerol, in the reaction.

The reaction is carried out at temperatures of at least 260 degrees C. and preferably of at least 270 degrees C., and it is desirable to preheat the glycerol and acid and/or ester introduced into the reaction medium. It is true, with rising temperature, the reaction velocity becomes greater, but simultaneously also rises the danger of decompositions, so that suitably one does not work at temperatures above 290 degrees-300 degrees C.

The minimum temperature necessary for the alcoholysis is somewhat dependent on the carbon number of the fatty acid radicals to be processed. In the production of  $C_{12}$ -monoglycerides technically useful reaction velocities are obtained at temperatures of less than 265 degrees C.; with

increasing carbon number of the fatty acid, this minimum temperature correspondingly increases so that, in the processing of C<sub>18</sub>-fatty acid, minimum temperatures of about 270 degrees C. are required. However, it is advisable to carry out the reaction at temperatures lying at least 5–10 degrees higher.

So far as glycerol distills off from the reaction mixture at the reaction temperature, it may be recirculated or supplemented through added fresh glycerol, so that the quantity of glycerol in the reaction mixture does not fall below the permissible minimum quantity. The maximum rate of introduction of the glycerol and acid and/or ester varies somewhat with the working temperature. It amounts at high temperatures of, for example 280 degrees C., at most about 0.4–0.5 weight part per hour preferably 0.3 weight part per hour but decreases at lower temperatures, for example at 260 degrees C. to about 0.2–0.15 weight part per hour. The process may be carried out continuously or semi-continuously. In semi-continuous operation, a quantity of reaction medium is used which only fills a part of the reaction vessel. As the added glycerol and acid and/or ester are converted to glycerides, the quantity of the reaction medium increases and the rate of introduction may be correspondingly increased. It is advisable to provide for as rapid and vigorous a mixing as possible, as for example, through the use of effective stirrers.

For continuous operation, an amount of converted material corresponding to the added glycerol and acid and/or ester is drawn off, continuously. It is merely necessary to observe that the time of stay of the material in the reaction vessel suffices for a conversion and that the reactants introduced into the reaction vessel are not too rapidly removed from the reaction vessel with the withdrawn product. This may be prevented by a suitable construction of the reaction vessels. For example, the reaction chamber may be subdivided into several individual reaction vessels, through which the reacting mixture flows. Therein the first vessel may take on the function of a mixer. However, it is also possible to mount in a single reaction vessel installations of the most varied type, through which the reacting mixture is positively guided. Finally, narrow long reaction vessels may be used, such as for example, pipe-lines, pipe coils, etc.

So far as the monoglycerides are formed from fatty acids or from fatty acid esters of such alcohols which are more volatile than glycerol, the volatile products formed in the reaction continuously distill off. Simultaneously, care must be taken that any jointly evaporated glycerol is condensed-out from the vapors and recirculated.

The formation of the monoglycerides may be accelerated through the use of conventional catalysts. For this purpose the known acid, basic, or metallic esterification or alcoholysis catalysts are applicable. To these belong, inter alia, metal oxides, metal hydroxides, or metal alcoholates, and the free metals which may be charged in the customary quantities, for example, about 0.1–5 weight percent, referred to the glycerol to be converted. However, it is a particular advantage of the process in accordance with the invention that the esterification and/or alcoholysis also takes place without catalysts with technically interesting velocities. Thus, a separation of the catalysts is unnecessary and a soap-free monoglyceride is directly obtained, which is particularly well suited for use in the food industry. If, however, operation is effected with catalysts, it is advisable to cool the still hot reaction product as rapidly as possible, or to inactivate the catalyst, before the cooling.

The crude alcoholysis mixture separates after the cooling into two layers: the lower layer consists essentially of glycerol, which may be recirculated, the upper layer contains besides the high-percentage monoglyceride which may be 80 percent by weight and more based on the glycerides, up to 30 percent and preferably 10–25 percent free glycerol. This may be separated in customary manner, for example through distillation, wherein, however,

disproportionation of the monoglyceride through too long heating should be avoided. Suitable for this purpose are the known thin-layer or molecular distillations. Besides, the glycerol may also be removed by washing with salt solutions or by washing with water. The washing with water has been described more in detail in the German prepublication of Patent DAS 1,066,573.

The present invention is further disclosed in the following examples which are illustrative but not limitative thereof:

The tests described in the examples were carried out under inert gas (N<sub>2</sub>, CO<sub>2</sub>) in a heatable flask provided with separate inlets for fatty acid and glycerol, outlet, stirrer, and thermometer. Volatile reaction products were removed through a perpendicularly standing air cooler, in which were condensed light quantities of jointly evaporated glycerol. The more volatile reaction products were condensed in a connected descending cooler and conducted into a receiver. The storage vessels for fatty acid and glycerol were heatable; the reactants were introduced into the reaction vessel preheated to a temperature of 200 degrees C.

#### Example 1

A mixture, obtained from a hydrogenated tallow fatty acid (Acid Number=202), of 57 weight parts monoglyceride, 17 weight parts diglyceride, 1 weight part triglyceride and 25 weight parts glycerol (34.3 mol percent monoglyceride, 57.6 mol percent glycerol) was heated with intensive stirring to 280 degrees C. Glycerol and the hydrogenated tallow fatty acid were added to the reaction mixture at rates of 17 and 13 parts by weight per hour respectively. Simultaneously a corresponding quantity of the reaction product was continuously drawn off through an overflow. The drawn off reaction product, after cooling, separated into a monoglyceride-containing upper phase and a lower phase essentially consisting of glycerol, which was recirculated into the process. After separation of the glycerol dissolved in the monoglyceride-containing phase, the monoglyceride content amounted to 79 weight percent; the Acid Number of the product was 0.7.

#### Example 2

The process described in Example 1 was carried out using, however, a reaction medium, which had been obtained from a C<sub>12</sub>- to C<sub>18</sub>-fraction of a cocinic acid (Acid Number=249) and contained 51 weight parts monoglyceride, 8 weight parts diglyceride, 1 weight part triglyceride and 40 weight parts glycerol (27.5 mol percent monoglyceride, 69.9 mol percent glycerol). The mixture was heated to 270 degrees C. and 10 weight parts fatty acid and 21 weight parts glycerol were added per hour. The product isolated from the raw product had a monoglyceride content of 84 weight percent and an Acid Number of 0.9.

#### Example 3

A mixture of 37 weight percent monolaurin, 7 weight parts dilaurin, 1 weight part trilaurin and 55 weight parts glycerol (18.2 mol percent monolaurin, 79.8 mol percent glycerol) was used as the starting material. The mixture was heated to a temperature of 270 degrees C. and 12 parts by weight lauric acid and 28 weight parts glycerol were added per hour. The product obtained after processing had a monolaurin content of 86 weight percent; the Acid Number was 0.7.

#### Example 4

A mixture of 57 weight parts mono-olein, 17 weight parts di-olein, 1 weight part triolein and 25 weight parts glycerol (34.1 mol percent mono-olein, 57.9 mol percent glycerol) was heated to 280 degrees C. and olive oil and glycerol were added at an hourly rate of 14 and 16 parts by weight respectively. The product obtained after the processing of the crude reaction product had a monoglyceride content of 78 weight percent.

## Example 5

To the mixture of lauric acid glycerides mentioned in Example 3, 13 weight parts lauric-acid-methyl-ester and 27 weight parts glycerol per hour were added at a temperature of 270 degrees C. The methanol liberated in the re-esterification distilled off through the air cooler and was condensed in the descending water cooler. The technical monoglyceride obtained after the processing had a monolaurin content of 87 weight percent.

What is claimed is:

1. In the process for the production of glycerides in which a member selected from the group consisting of fatty acids, fatty acid esters and mixtures thereof is reacted with glycerol, the improvement for the production of a glyceride mixture with a high content of monoglycerides which comprises maintaining a reaction medium containing at least 50-mol percent of glycerol, 10-35 mol percent of monoglycerides, and not more than 15 mol percent of higher glycerides at a temperature between about 260-300° C. while adding said reactants thereto at a rate of not in excess of 0.5 part by weight per hour per part by weight of said reaction medium, said added reactants containing at least 2 mols of glycerol radicals per mol of fatty acid radicals, and recovering the glyceride mixture formed.

2. Improvement according to claim 1 in which said reaction medium contains about 50-80 mol percent of glycerol.

3. Improvement according to claim 1 in which the reactants are added to the reaction medium at a rate of about 0.15-0.5 part by weight per hour per part of said reaction medium.

4. Improvement according to claim 1 in which said reaction medium contains about 20-30 mol percent of monoglycerides and 60-75 mol percent of glycerol.

5. Improvement according to claim 1 in which the reactants are added to the reaction medium at a rate not in excess of about 0.4 part by weight per hour per part by weight of the reaction medium.

6. Improvement according to claim 1 in which the reactants are continuously added to the reaction medium and which includes substantially continuously withdrawing a corresponding quantity of the reaction product formed.

7. Improvement according to claim 1 in which the quantity of said reaction medium is substantially continuously increased by products formed during the reaction and in which the reactants are added at said rate calculated on the increased amount of reaction medium.

8. Improvement according to claim 1, wherein said ester is selected from the group consisting of methyl and glycerol esters of fatty acids.

9. Improvement according to claim 1, wherein said ester is of an alcohol having up to four carbon atoms.

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,383,581	Arrowsmith et al. -----	Aug. 28, 1945
2,478,354	Allen et al. -----	Aug. 9, 1949
2,634,278	Kuhrt -----	Apr. 7, 1953
2,732,387	Brokaw -----	Jan. 24, 1956
2,744,124	Alsop -----	May 1, 1956