Food Emulsifiers: Surface Activity, Edibility, Manufacture, Composition, and Application

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ABSTRACT

Food emulsifiers are indispensable ingredients in most processed foods containing fats and oils. Terms like surface activity and edibility have a special relevance to emulsifiers and are described. Food emulsifiers may be grouped according to different aspects. In this paper they are described from the viewpoint of their origin, and special attention is given to monoglyceride derivatives, such as lactylated monoglycerides, to glycerol-free fatty acid derivatives, as well as to monodiglycerides and distilled monoglycerides. The mesomorphic behavior of aqueous emulsifier systems is mentioned, and certain production aspects of food emulsifiers, including the distillation of monoglycerides, are given.

INTRODUCTION

In the context of this Conference, the subject of food emulsifiers may sound like a minor point in comparison with many of the other products we have been hearing about during the past few days, at least where amounts produced and turnovers obtained are concerned.

However, food emulsifiers are present, although in minor quantities, in most fat and oil containing processed foods, and it might consequently be worthwhile to take a closer look at this group of compounds, the more so as they are performing functions which make them indispensable in such food products.

FOOD EMULSIFIER CHARACTERISTICS

What are the special characteristics of food emulsifiers? As the term suggests, it is a group of products having at least two properties: 1) surface activity and 2) edibility.

Surface active agents are, chemically, schizophrenic molecules, having polar and nonpolar parts spatially separated from each other in a balanced way.

The monoglyceride molecule shown in Figure 1 can, due to its balanced hydrophilic/lipophilic structure, place itself at the boundary between an oil and a water phase, thereby contributing to the suppression of the interfacial tension.

The term HLB, meaning hydrophilic/lipophilic balance, has been created to quantify the balanced polarity of surface active molecules, but such figures have proved less valuable in the food industry because of the very complicated nature of most food systems. Other properties are of greater importance in food systems even though the major reason for the effect of food emulsifiers depends chiefly on the balanced structure of the molecule. Those properties, which are typical for food emulsifiers, are, for instance, the capacity to create and stabilize foams, crystal modification with starch as well as gluten, and the ability to bind water in semicrystalline phases.

Food emulsifiers must, of course, be edible; and, being food additives, they are among the most studied food ingredients. Seen from a toxicologist's standpoint, they have been studied more completely than most so-called natural food components. Thus, an Acceptable Daily Intact (ADI) value has been allocated to most food emulsifiers by FAO/WHO's Codex Alimentarius Committee based on intensive toxicological studies, including short and long term feeding tests, and studies on metabolism. The ADI value (Table I) refers to the amount of the product you may eat each day of your whole lifetime without the development of toxic effects and provides a basis for local food law making. Unfortunately, the food laws of the various countries in the world differ considerably due to differences in local circumstances such as climate, eating habits, religion, etc.; but also, inside a limited area like Europe, and even between the nine EEC countries, the food laws differ widely. Since different food laws may act as a barrier to trade between these countries, the EEC Commission has initiated harmonization in this field, and 1½ years ago a new EEC directive on emulsifiers and stabilizers was published.

The EEC directive lists emulsifiers in two sections (Table II). Annex I substances all bear E numbers and shall be authorized for use by all member states. Annex II substances may be authorized for use by any member state for a period of 5 years starting from 1974.

At the time when the finishing touches were being put on this directive, the major European producers of food emulsifiers formed the European Food Emulsifier Manu-

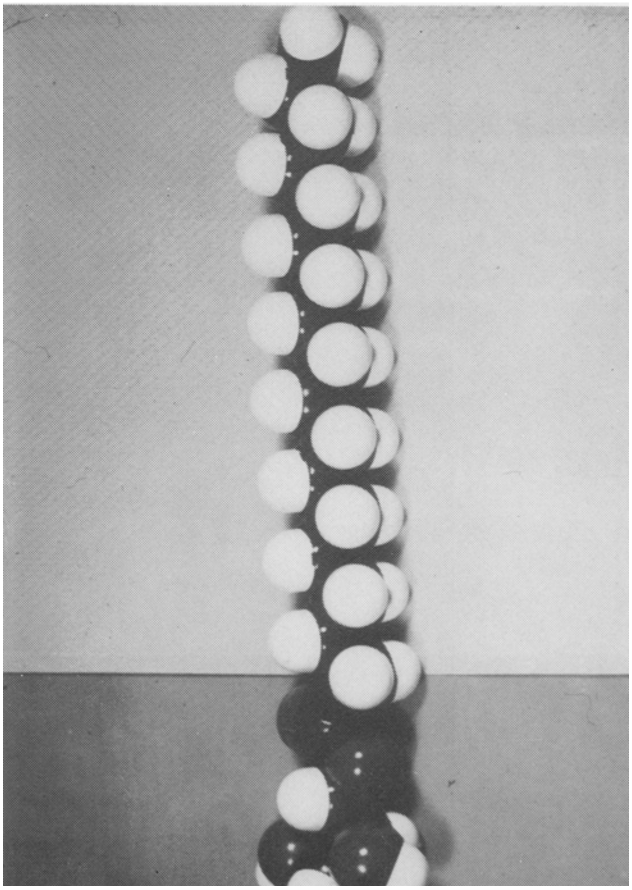

FIG. 1. Monoglyceride molecule at an oil-water interface.

TABLE I

Acceptable Daily Intake (ADI) for Man for Selected Food Emulsifiers[a]

Food emulsifier	ADI (mg/kg body wt/day)
Acetic, citric, and lactic acid esters of mono- and diglycerides	not limited
Diacetyl tartaric acid esters of mono- and diglycerides	0-50
Mono- and diglycerides	not limited
Polyglycerol esters of fatty acids	0-25
Polyglycerol esters of interesterified ricinoleic acid	0- 7.5
Polysorbates	0-25
Polyoxyethylene (8) and (40) stearates	0-25
Propylene glycol esters of fatty acids[b]	0-25
Sorbitan esters of fatty acids	0-25
Stearoyl lactylate, Ca and Na salts	0-20
Sucrose esters of fatty acids and sucroglycerides	0- 2.5

[a] Based on 15th and 17th Reports of the Joint FAO/WHO Expert Committee on Food Additives.

[b] As propylene glycol.

TABLE II

EEC Council Directive of June 18, 1974

Draft EEC number	Food emulsifier type
	Annex I (condensed)
E 322	Lecithins
E 470	Salts of fatty acids
E 471	Mono- and diglycerides
E 472 a-e	Acetic, lactic, citric, tartaric, and diacetyl tartaric acid esters of mono- and diglycerides
E 473-74	Sucrose esters and sucroglycerides
E 475	Polyglycerol esters
E 477	Propylene glycol esters
E 480-82	Stearoyl-2-lactylic acid and salts
E 483	Stearyl tartrate
	Annex II (condensed)
	Polyglycerol ester of condensed castor oil acids
	Sorbitan esters
	Polysorbates
	Polyoxyethylene (8) and (40) stearates
	Glycerol esters of heat oxidized soy oil acids
	Lactylated glycerol and propylene glycol esters
	Dioctyl sodium sulphosuccinate
	NH_4-phosphatides

TABLE III

Contents of EFEMA[a] Monographs on Food Emulsifiers

1. Name and Numerical References
   1.1 Name and synonyms (languages of EEC countries)
   1.2 Numerical references (EEC, FAO/WHO, National)
2. Description and Properties
   2.1 Chemical description and outline process
   2.2 Appearance
   2.3 Solubility
3. Analysis
   3.1 Methods relating to EFEMA specifications
   3.2 Other methods
   3.3 Determination in foodstuffs
4. Specifications (EFEMA, FAO/WHO, National)
5. Safety in Use
   5.1 Metabolism
   5.2 Toxicology (including evaluation)
6. Application in food
7. Nonfood applications
8. References

[a] EFEMA = European Food Emulsifier Manufacturers' Association.

facturers' Association (EFEMA). One of EFEMA's main aims is to assist in the devising of appropriate legislation in the field of food emulsifiers.

As part of this work, EFEMA is preparing a series of monographs covering the emulsifiers to be permitted inside the Community. Each monograph will be in accordance with the list of contents shown in Table III. The monographs are expected to be published later this year.

ORIGIN OF FOOD EMULSIFIERS

Food emulsifiers are almost exclusively partial esters of fatty acid and polyols, and/or water soluble organic acids. There are various ways of grouping these substances; one is to look at food emulsifiers from the viewpoint of their origin. Figure 2 shows the most important raw materials for the production of food emulsifiers. The fundamental reaction is photosynthesis, which, directly in plants or indirectly in animals, produces vegetable and animal oils as well as the carbohydrates and others which serve as basis materials for the raw material production. In this connection, we may also consider crude oil and naphtha (an important fraction of mineral oil) as a several hundred

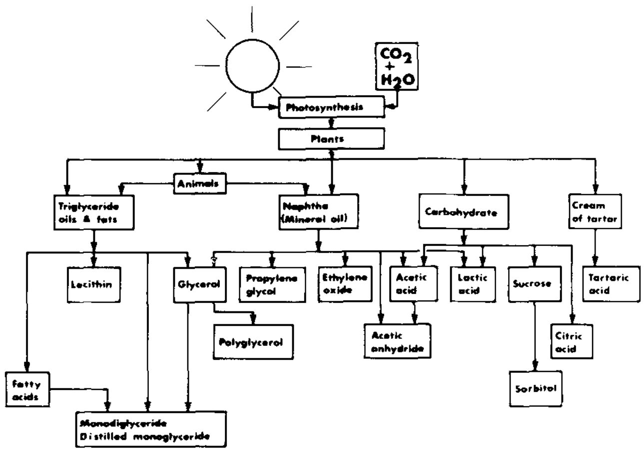

FIG. 2. The origin of raw materials for food emulsifiers.

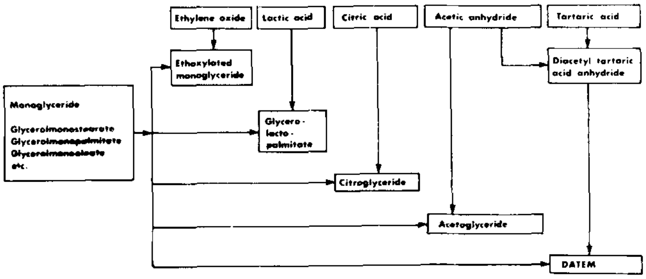

FIG. 3. The origin of some monoglyceride derived food emulsifiers.

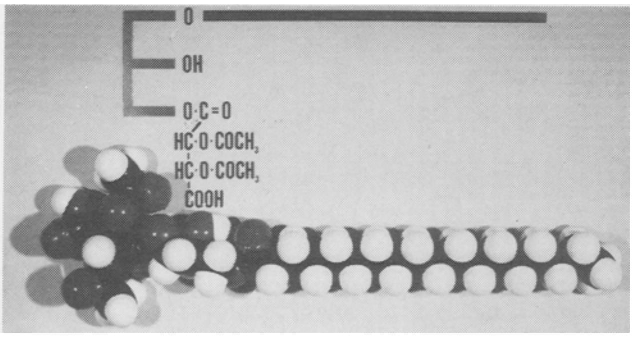

FIG. 4. Diacetyl tartaric acid ester of 1-glycerol monostearate.

million years old store of animal and vegetable residues.

Several substances can be made from naphtha or from today's plant or animal products, plus glycerol and acetic acid. As the products, which originate from crude oil, normally have a very high degree of purity, they are very suitable raw materials for the production of food emulsifiers. Each of the two products, fatty acids and monoglycerides, also shown in Figure 2 are raw materials for a whole range of food emulsifiers.

MONOGLYCERIDE DERIVATIVES

Monoglycerides, by combination with some of the raw materials of Figure 2, can produce other food emulsifiers (Fig. 3).

Ethoxylated monoglycerides are produced by the ethoxylation of monodiglycerides under alkaline catalysis, and the resulting product is a very hydrophilic molecule being used especially in the bread industry as a dough conditioner.

Another hydrophilic substance is produced by the reaction between diacetyl tartaric acid anhydride and monoglycerides, resulting in the product illustrated in Figure 4. In comparison to the monoglyceride molecule (Fig. 1), a diacetyl tartaric ester of monoglycerides has a considerably greater hydrophilic part and is thus a typical oil-in-water emulsifier. Due to its free carboxylic group, it has a pronounced ability to bind to gluten in wheat doughs, thus improving the gluten's ability to hold gas bubbles. This property is used extensively, especially in the European bread industry.

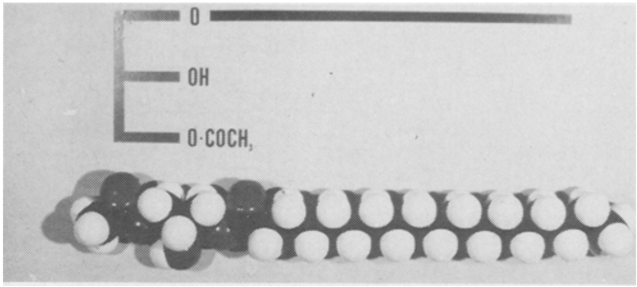

FIG. 5. Acetic acid monoester of glycerol monostearate.

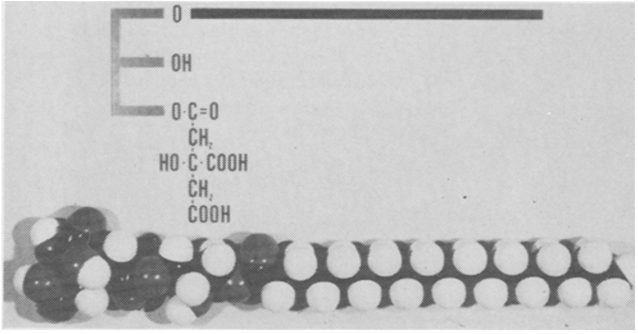

FIG. 6. Citric acid ester of glycerol monostearate.

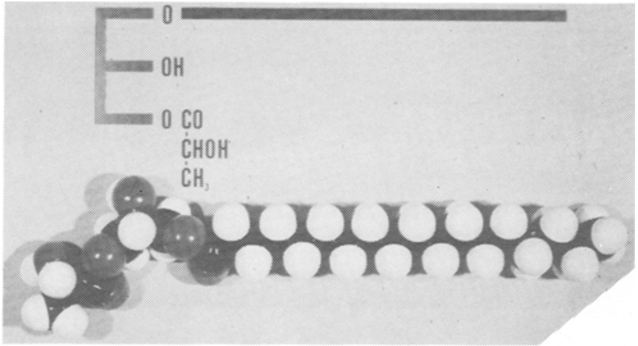

FIG. 7. Lactic acid ester of glycerol monostearate.

Another acetic acid derivative is the acetoglyceride (Fig. 5), which may be produced by acetylation of monoglycerides using acetic anhydride or by the reesterification of mono- and diglycerides with triacetin. This product belongs to the group of α-tending emulsifiers, so called because of their stability in the α-crystal form. Since this crystal form is a flexible one, products like acetylated monoglycerides have found use as coating materials for fruits like nuts and raisins and also for meat products like sausages. Another property of these α-tending emulsifying agents is their ability to improve agglomeration and thus the whippability and foam stabilization of various food emulsions, such as whipped toppings and other dessert products.

The citric acid ester of monoglycerides (Fig. 6) is produced by the esterification of citric acid with monoglycerides and is used in the meat industry as an emulsifier for sausages and also in the margarine industry as an anti-spattering agent.

As an example of the complexity of an apparently very

TABLE IV

Column Chromatography of a Lactylated Monoglyceride[a]

Fraction number	Solvent	Type of compound eluted	Percent eluted
1	Benzene	No OH-groups	2.0
2	Ethyl ether:benzene 1:9	1) 1 OH-group (except lactic acid) 2) Fatty acids	34.0
3	Ethyl ether	2 OH-groups	46.4
4	Ethyl ether:methanol 1:1	1) 3 OH-groups 2) Lactic acid	17.6

[a] Packing material: Mallinckrodt Silicic Acid, 100 mesh (Mallinckrodt, St. Louis, MO).

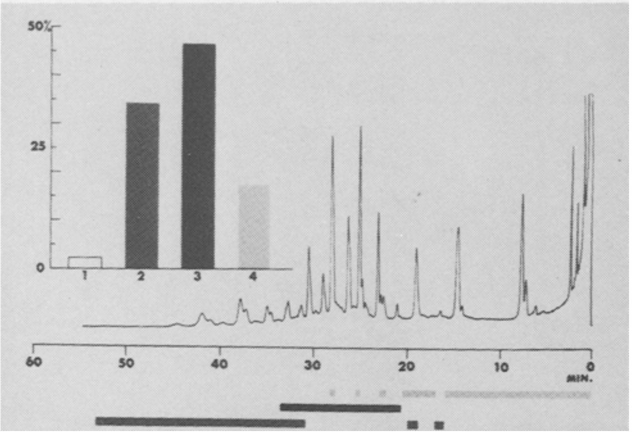

FIG. 8. Analysis of a lactylated monoglyceride. Column chromatogram of product (upper left). Gas-liquid chromatogram of trimethylsilyl-derivative (center). Localization of CC-fractions on gas chromatogram (bottom).

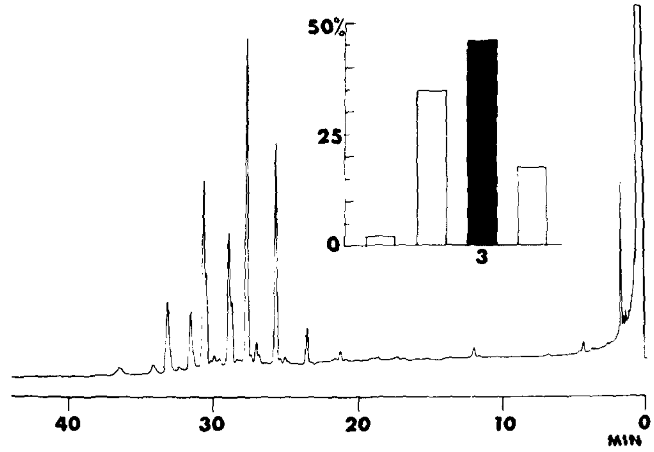

FIG. 10. Analysis of a lactylated monoglyceride. Column chromatography of fraction 3, compounds with two hydroxyl groups (upper right). Gas-liquid chromatogram of trimethylsilyl-derivative (center).

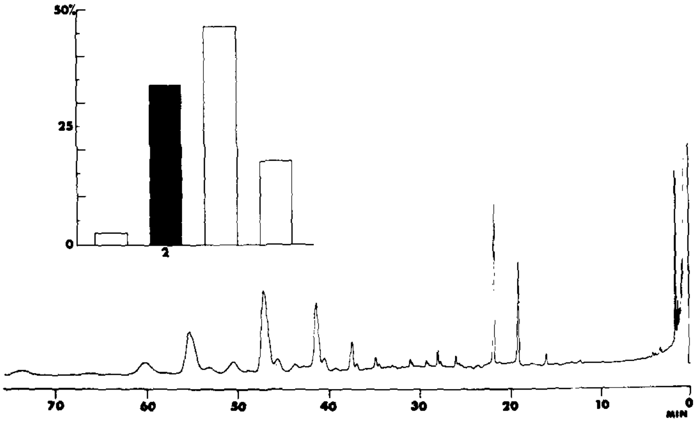

FIG. 9. Analysis of a lactylated monoglyceride. Column chromatography of fraction 2, compounds with one hydroxyl group (except free lactic acid) and fatty acids (upper left). Gas-liquid chromatogram of trimethylsilyl-derivative (center).

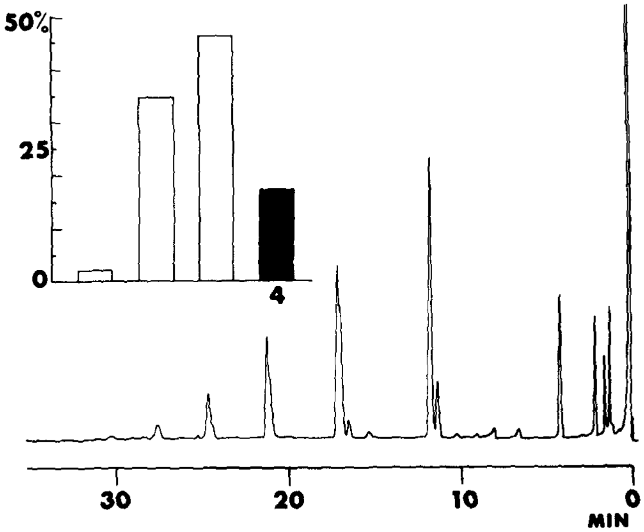

FIG. 11. Analysis of a lactylated monoglyceride. Column chromatography of fraction 4, compounds with three hydroxyl groups and lactic acid (upper left). Gas-liquid chromatogram of trimethylsilyl-derivative (center).

simple emulsifier, I should like to comment a little more in detail on the composition of glyceryl lactylpalmitate/stearate, the lactic acid ester of a monoglyceride. It is a common emulsifier for cake, shortenings, and cake mixes, as well as for toppings, where, due to its α-tending properties, it serves as an agglomerating agent.

Glyceryllactylpalmitate may be produced in standard batch reaction vessels simply by esterifying fatty acid monoglycerides with lactic acid or the equivalent amounts of fatty acid, glycerol, or lactic acids. If the product is the result of a reaction of molar parts of the three ingredients, Figure 7 might give a fair representation of the compound produced. If, however, a column chromatographic analysis of the product is performed using the conditions of Table IV, four different fractions are easily recovered, as shown in Figure 8, which also shows a gas chromatogram of the trimethylsilyl derivatives of the total product. If each of the three main fractions is analyzed by the same gas-liquid chromatographic technique, gas chromatograms as shown in Figures 9, 10, and 11 are obtained.

Fraction 4 (Fig. 11), for instance, gives information on the composition of the water soluble part of the reaction product, namely, the homologous series of the glycerol esters of lactic acid, which may be removed during production of lactylated monoglyceride emulsifiers, but which analytically is interesting because of the clarity with which

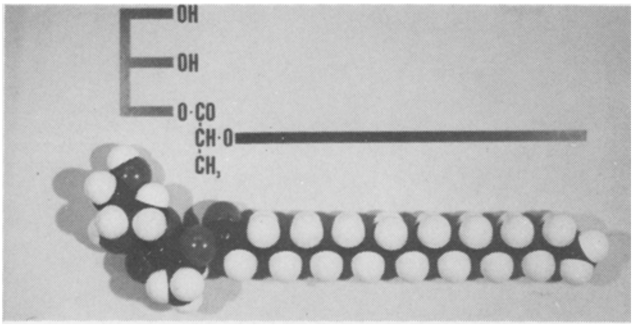

FIG. 12. Glyceryllactylpalmitate.

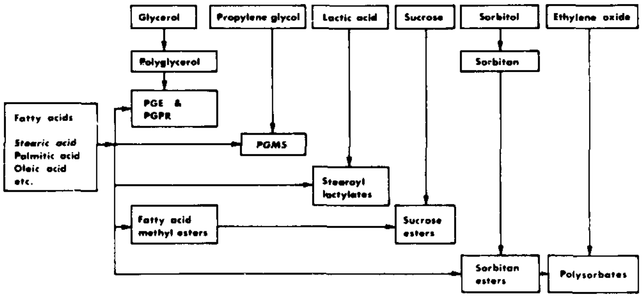

FIG. 13. The origin of some fatty acid derived food emulsifiers.

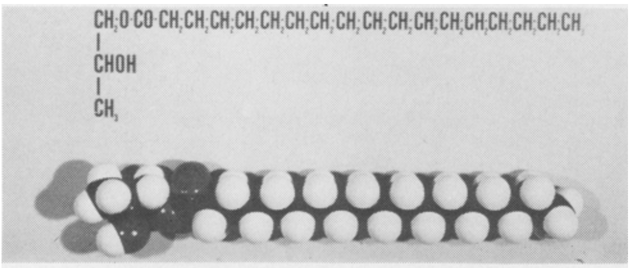

FIG. 14. 1-Propylene glycol monostearate.

it illustrates the complexity of this emulsifier. If all the fraction 4 peaks are studied through combined gas chromatography–mass spectrometry, it can be shown that these peaks represent the homologous series of glycerol lactates from mono to at least hexa lactates. By this technique, not only the gross formula but also more detailed information on the composition of the many isomers is revealed (1).

The usefulness of this technique can be further illustrated by studying the two isomeric fatty acid esters of 1-glyceryl-lactate, one with a terminal glycerol group (Fig. 12) and one with a terminal lactic acid group (Fig. 7).

With the usual chemical analysis methods, these two compounds will behave identically, but, based on their mass spectra, these two isomers–although different only in the order of the three molecular parts lactic acid, glycerol, and fatty acid–are highly different.

Since, of course, it is important for the manufacturer to know which of the components in the product are bearers of the effect, and since this study showed that more than 200 different molecular species including isomers were present in a commercial lactylated monoglyceride, it is easily understood that the production of a competitive lactylated monoglyceride requires more than just mixing the three components under esterification conditions.

FATTY ACID ESTERS OF ALCOHOLS OTHER THAN GLYCEROL

The emulsifiers discussed so far could all be considered derivatives of monoglycerides. Another range of food

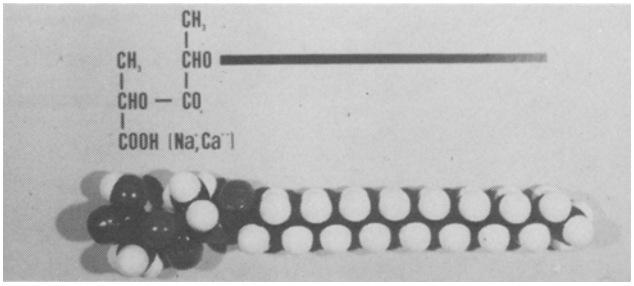

FIG. 15. Stearoyl-2-lactylates.

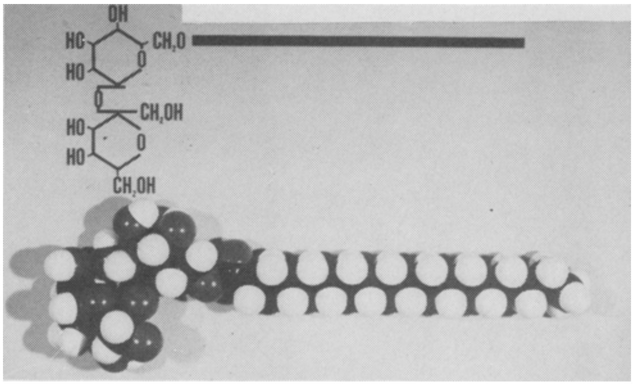

FIG. 16. Sucrose monostearate.

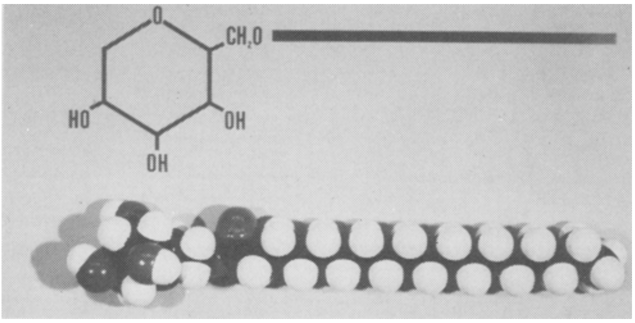

FIG. 17. Sorbitan monostearate.

emulsifiers can be considered derivatives of fatty acids (Fig. 13).

Propylene glycol monostearate (Fig. 14) may be produced by the esterification of propylene glycol with fatty acid and has properties comparable to acetoglycerides and glyceryllactylpalmitate.

Stearoyllactylates (Fig. 15) are produced during the reaction of fatty acids, lactic acid, and a suitable sodium or calcium source, and are used primarily in the baking industry as dough conditioning agents.

Sucrose esters (Fig. 16) are reaction products of sucrose and methyl esters of fatty acid. Earlier, this reaction was performed in a solvent like dimethylformamide; but, because of the toxicity of this solvent and the difficulty of removing it from the reaction product, other methods have been introduced, like reaction in a propylene glycol medium and most recently reaction in a medium containing water only as a solvent. Unfortunately, these last methods require the presence of considerable amounts of surface active agents to establish a micro-emulsion; partly due to difficulties with the removal of these auxiliary agents from the reaction mass and partly to restrictive food laws, sugar esters are among the least used food emulsifiers today. If sucrose esters are mixed with monodiglycerides, or if the fatty acid methyl esters in the reaction are exchanged with triglycerides, an emulsifier group called sucroglycerides is

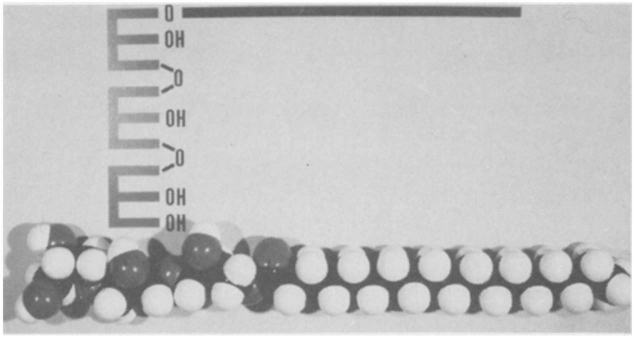

FIG. 18. Triglycerol-1-monostearate.

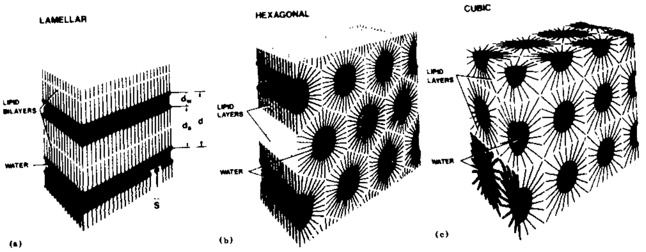

FIG. 19. Liquid crystalline structures (schematic): (a) lamellar, (b) hexagonal (reversed), and (c) cubic ("viscous isotropic").

produced, but it should be remembered that they are only mixtures of certain sucrose fatty acid esters with certain mixtures of mono-, di-, and triglycerides.

Sorbitan esters of fatty acids (Fig. 17) are produced by esterification of fatty acids with dehydrated sorbitol and are effective antiblooming agents in confectionery products containing cocoa butter substitutes. If such products are ethoxylated, a hydrophilic range of sorbitan esters is produced, called polysorbates.

Another range of hydrophilic emulsifiers is the polyglycerol esters. Polyglycerol is produced by esterification of glycerol under alkaline catalysis at elevated temperature. A triglycerol monostearate is shown in Figure 18. Polyglycerol esters are utilized in cakes and cake mixes as emulsifying agents.

MESOMORPHIC BEHAVIOR

One of the characteristic features of many food emulsifiers, including sorbitan and polyglycerol esters and distilled monoglycerides, is their ability to form lyotropic mesophases. This is seen when the emulsifiers, which are normally insoluble in water, are dispersed in water and heated. At a certain temperature close to the melting point, the hydrocarbon chains of the molecules become liquid, and at the same time the water will penetrate between the polar groups, resulting in the formation of liquid crystalline structures, which can be of lamellar, hexagonal, or cubic types (Fig. 19).

The polar groups of the emulsifiers are oriented towards the water, which in the lamellar phase is present in films, alternating with the lipid bilayers. In the hexagonal and cubic lyotropic mesophases, the molecules are arranged in cylinders and spheres, respectively. The structure of such mesophases can be studied by X-ray diffraction, and structural parameters such as thickness of the water layer and the lipid bilayer can be determined. In Table V, the mesomorphic behavior of several food emulsifiers is shown, and it should be noted that several of these compounds produce different mesophases at different temperatures.

The mesomorphic behavior of distilled monoglycerides in water is demonstrated in a binary phase diagram (Fig. 20).

At temperatures slightly above the melting point of the saturated monoglyceride, a lamellar mesophase is formed. At higher temperatures, a cubic viscous isotropic mesophase is produced, and anyone who has worked with distilled monoglycerides knows that it is most important to avoid the formation of this phase because of its stickiness and the difficulty of removing it, especially from long product pipes having been steam "cleaned." While it is thus important on the production side to have a knowledge of the mesomorphic phases of monoglycerides and other emulsifiers, it is even more important for the application. Table VI shows the function of a distilled, saturated monoglyceride in a sponge cake recipe. In all preparations, exactly the same amount of monoglyceride is used, i.e., 0.4% on total batter weight. The specific volume of cake batter as well as of the finished cake is very dependent on the mesomorphic state of the monoglycerides used, and only the lamellar dispersion and the α-crystalline gel phases provide satisfactory cake and batter volumes.

MONOGLYCERIDES AND DISTILLED MONOGLYCERIDES

If a triglyceride is reacted with glycerol at a high temperature, e.g., at 200 C under alkaline catalysis, the resulting product is a mixture of mono-, di-, and triglycerides as well as traces of unreacted glycerol. Provided that the reaction temperature is high enough, the composition of the reaction product will depend only on the relative dosage of fat/glycerol, and the composition may be calculated from a Feuge and Bailey equilibrium diagram (Fig. 21). For instance, a normal commercial monoglyceride may be obtained as a result of the reaction between ca. 1 mol triglyceride and 2 mol glycerol. At lower temperatures, however, a product like this is no longer in an equilibrium state; and, as a consequence, the monoglyceride content tends to decrease as a function of temperature, time, and catalyst traces (Fig. 22). It is thus important to avoid extended heating of

TABLE V

Mesomorphic Behavior of Food Emulsifiers in Water

Type of emulsifier	Temperature for mesophase formation in water (C)	Types of mesophases formed	HLB range[a]
Saturated monoglyceride (90% monoester)	55	Lamellar $\xrightarrow{68\text{ C}}$ cubic	3.5-4
Unsaturated monoglyceride (90% monoester)	20	Cubic $\xrightarrow{55\text{ C}}$ reversed hexagonal	3.5-4
Sorbitan monostearate	55	Lamellar	4-7
Polyglycerol monostearate	60	Lamellar	6-9
Diacetylated tartaric acid esters of monoglycerides	48	Lamellar (pH 5)	8-10
Polysorbate	40	Hexagonal (middle) or micelles	12-15
Sodium stearoyl-2-lactylates	45	Lamellar (pH 5)	15-20

[a] HLB = hydrophilic/lipophilic balance.

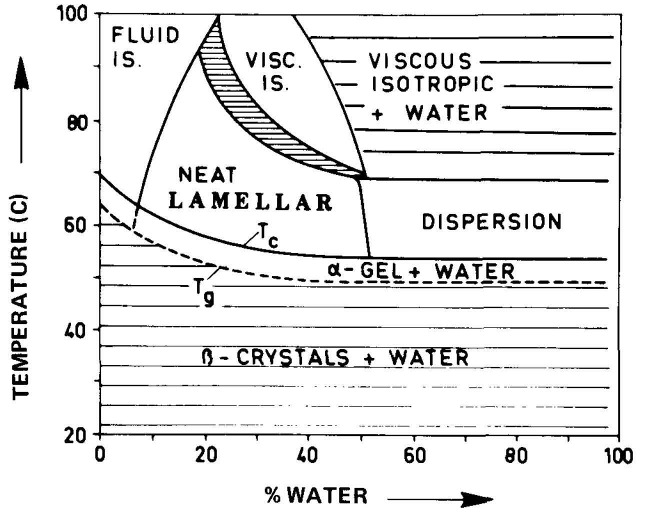

FIG. 20. Phase diagram of an aqueous system of a saturated distilled monoglyceride (fatty acid composition as fully hydrogenated lard).

monoglycerides.

Monoglycerides exist in two isomeric forms, the 2-form and the 1-form. Only the latter responds to periodic oxidation, which is the basic reaction in the normally applied chemical determination of monoglyceride contents. The relative amount of the two isomers is a result of an equilibrium which is temperature dependent. At 200 C, the equilibrium content of 1-monoglyceride is 82%, but at 20 C it is 95%. Since the distilling temperature is rather high, low 1-mono-contents might be obtained even though the total monoglyceride content is in the order of 95% in commercially distilled products (Table VII).

Distilled monoglycerides are produced batchwise or continuously, and production takes place in two steps. The first one results in a monodiglyceride mixture, which can either be finished and brought into the trade, for instance, in the form of spray crystallized powder or flakes. In the second step, the monodiglycerides are further concentrated through molecular distillation.

Figure 23 shows a schematic representation of the flows involved in such a process. It is characteristic for this process that a considerable amount of the equilibrium mixture, i.e., di- and triglycerides as well as the excess glycerol, is carried back into the process and is used again as a raw material. Besides the main product, the distilled monoglyceride, two flows are important: the residue removal, which in a controlled way serves to remove decomposition products, catalyst residue, and coloring substances, which otherwise would accumulate in the system; and the direct loss to the atmosphere, the cooling water, etc. The economy of the process depends, among

TABLE VI

Effect of Various Mesomorphic Phases of Distilled, Saturated Monoglycerides in Sponge Cake

Type of mesophase	Water contents of preparations (%)	Specific volume of cake batter (ml/kg)	Specific volume of cake (ml/kg)
Neat (lamellar)	40	1,140	3,400
Viscous isotropic (cubic)	40	1,112	3,320
Viscous isotropic + water	90	1,560	5,060
Dispersion (lamellar)	90	2,970	6,900
Gel (α-crystalline)	90	2,700	6,000
Coagel (β-crystalline)	90	1,020	2,400

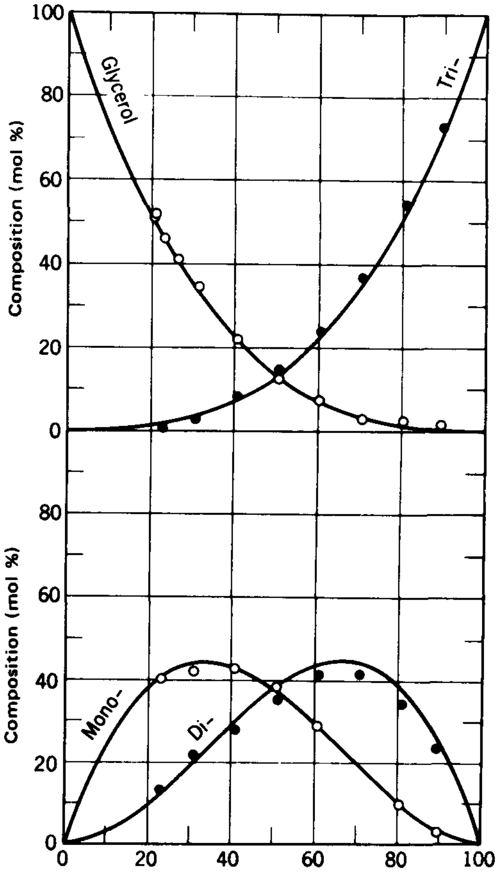

FIG. 21. Composition at equilibrium of single-phase reaction mixtures of highly hydrogenated cottonseed oil with an excess of glycerol. Curves represent composition calculated on the basis of random distribution; plotted points represent experimentally determined compositions (3).

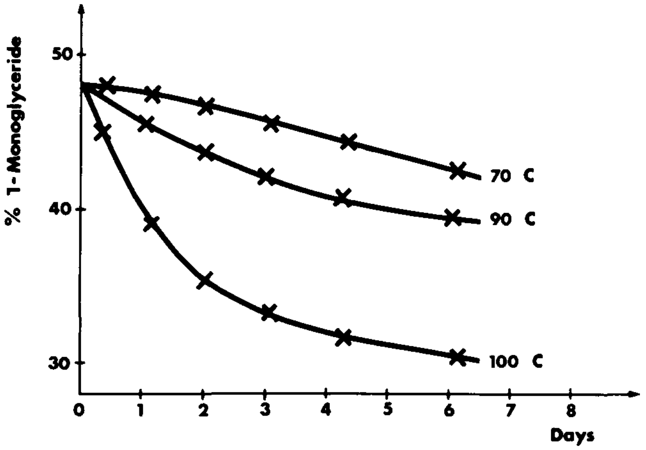

FIG. 22. Reduction in monoglyceride content in a commercial monodiglyceride as a function of time and temperature.

TABLE VII

Composition of Commercially Distilled Monoglyceride

Monoglycerides	94.2%
Diglycerides	3.6%
Triglycerides	0.7%
Fatty acids	0.8%
Glycerol	0.7%

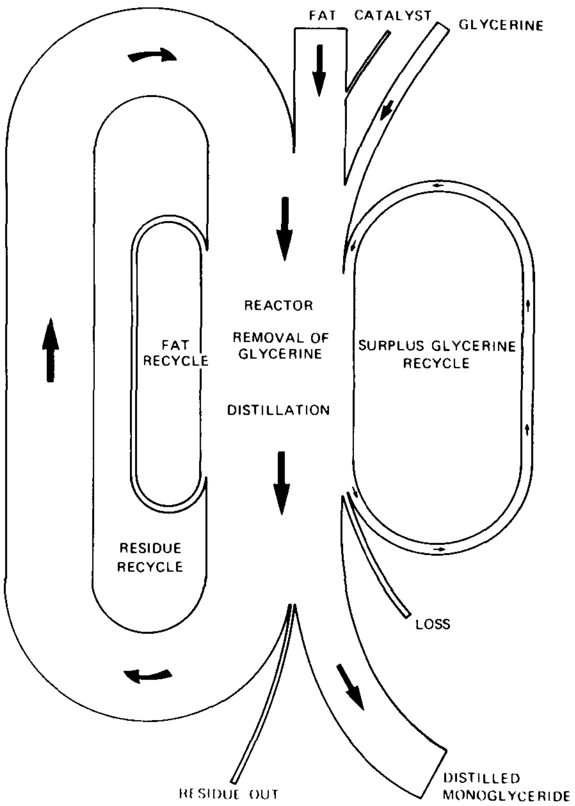

FIG. 23. Schematic diagram illustrating the production of distilled monoglycerides.

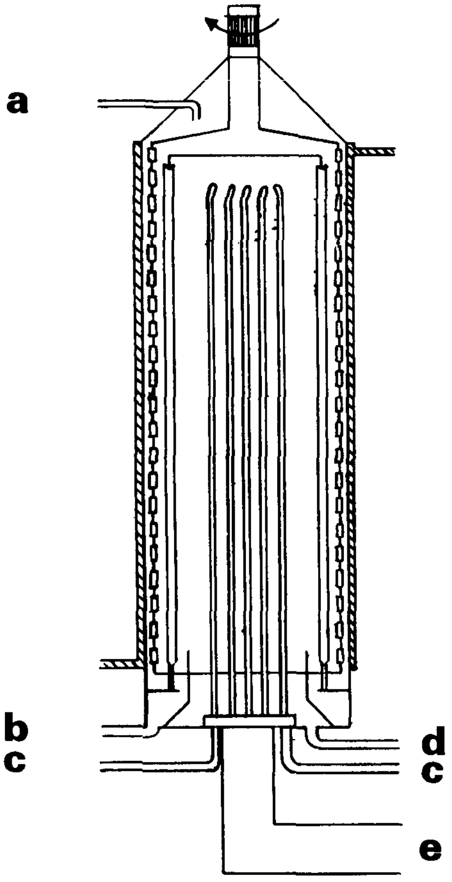

FIG. 24. Molecular still: (a) glycerolysis product inlet, (b) residue removal, (c) cooling medium in and out, (d) distillate removal, and (e) to vacuum pumps.

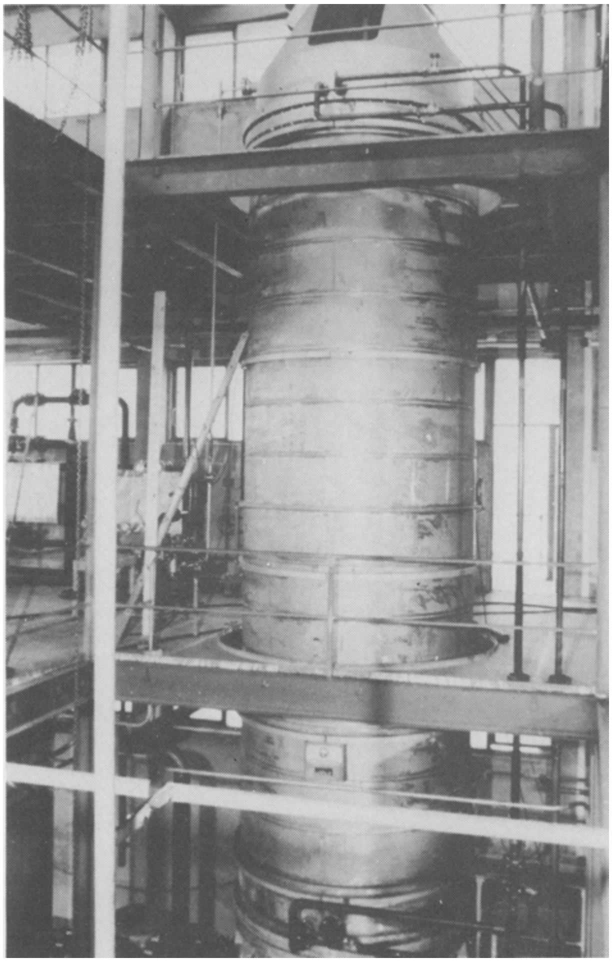

FIG. 25. Commercial molecular still.

other factors, of course, upon the minimization of these two flows.

The heart of a plant for the production of distilled monoglycerides is the molecular still. It is necessary to work under extremely low pressure, i.e., down to 1/1,000 mm mercury. At higher pressures, undesired decomposition products are obtained.

In Europe, stills of the wiped falling film type are frequently used (Fig. 24). The material which is to be distilled runs in through the upper left tube and is evenly distributed by a rotating disc on the inner side of the distillation column as a thin film which is brought into turbulent downwards flow by means of rotating wiper aggregates.

The column is heated from the outside, and the monoglycerides evaporate at the low pressure. They move in the vapor phase the short distance towards the middle of the column until they collide with the condenser, whereby on cooling they again become liquid, and the liquid monoglycerides run off the condenser. Then the distilled product is removed at the bottom through the tube d. The residue is removed through tube b, and the vacuum is maintained through tube e.

A molecular still unit for the production of distilled monoglycerides in our production plant is shown in Figure 25. In 1964, this plant was the first to be constructed in Europe.

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