indicated O–H of hydroperoxide (Table II). In the near-IR region several bands were attributed to the –O–O–H group, (Table III). These bands indicated that there was some autoxidation of the product during the time elapsed (over 3 months) between synthesis and the IR spectra determination. It also explained the higher iodine index of the product compared to the theoretical value, which was estimated nearly 5 months after the synthesis.

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Stearyl Monoglyceridyl Citrate as an Emulsifier Enhancer[1]

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Abstract

Stearyl monoglyceridyl citrate, a fatty acid ester, is a semisolid compound with a slightly acidic flavor. In its liquid state it is completely miscible with vegetable and animal fats and oils. Although the compound exhibits surfactant activity and reduces interfacial tensions, its major function is emulsifier enhancement and emulsion stabilization when used in shortening systems along with accepted emulsifiers.

Very acceptable liquid and plastic shortenings can be prepared through the addition of stearyl monoglyceridyl citrate and primary emulsifiers. Effective levels of stearyl monoglyceridyl citrate in shortenings enhance performance and permit use of lower levels of primary emulsifiers. Shelf-life stabilities, smoke points, plasticity, and compatibility with primary emulsifiers in finished shortenings are good.

Additions to margarines and whip toppings and performance in baked goods, as well as food additives status, are discussed.

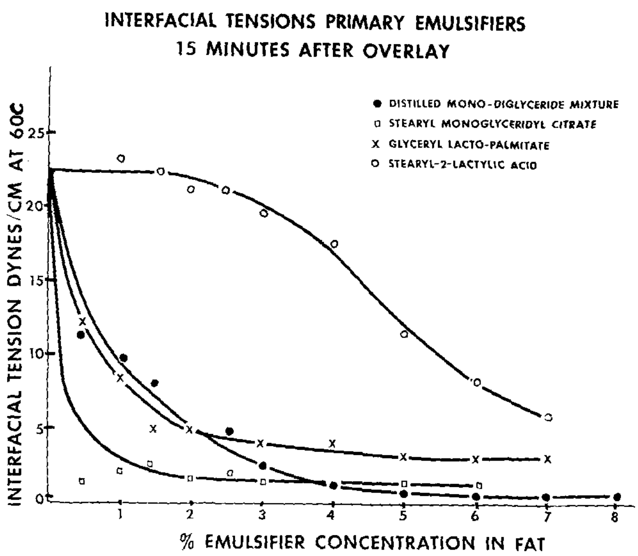

FIG. 1.

Introduction

STEARYL monoglyceridyl citrate is the reaction product of stearyl alcohol, monoglycerides (glyceryl esters of fatty acids derived from cottonseed oil), and citric acid. This fatty acid ester is a somewhat sticky, waxy semi-solid and has a slightly acidic, astringent taste. The compound has acid value 40–52, saponification number 215–255, and a citric acid content of 15–18%. The compound melts at ca. 130F, and in the liquid state is miscible at all levels with vegetable and animal fats and oils; it is insoluble and does not disperse in water.

The physical characteristics and the general configuration of stearyl monoglyceridyl citrate indicate hydrophilic and lipophilic tendencies. Interfacial tension determinations, using cottonseed oil as the emulsifier carrier, confirmed the expected surface or interfacial tension-depressant effects. Figure 1 shows that stearyl monoglyceridyl citrate had a greater interfacial tension-depressant effect at levels under 2% in the fat phase than did the distilled mono-diglyceride mixture (monoglycerides and diglycerides of fatty acids derived from cottonseed oil), glyceryl lacto-palmitate (glycerol ester of palmitic and lactic acids)

TABLE I
Interfacial Tensions of Emulsifier Combinations in Cottonseed Oil (15 min after overlay)

System	Interfacial tension
	dynes/cm, 60C
Cottonseed oil control	21.4
0.10% Stearyl monoglyceridyl citrate	8.5
0.10% Glyceryl lacto-palmitate	21.2
0.10% Stearyl monoglyceridyl citrate + 0.10% Glyceryl lacto-palmitate	8.1
0.10% Distilled mono-diglyceride mixture	20.4
0.10% Stearyl monoglyceridyl citrate + 0.10% Distilled mono-diglyceride mixture	4.8
0.10% Stearyl-2 lactylic acid	23.4
0.10% Stearyl monoglyceridyl citrate + 0.10% Stearyl-2 lactylic acid	5.8
0.10% Sorbitan monostearate	4.5
0.05% Stearyl monoglyceridyl citrate + 0.05% Sorbitan monostearate	4.1
0.10% Polyoxyethylene (20) sorbitan monostearate	3.7
0.05% Stearyl monoglyceridyl citrate + 0.05% Polyoxyethylene (20) sorbitan monostearate	4.5

[1] Presented at the AOCS meeting in New Orleans, 1962.

TABLE II
Bake Tests with High-Sugar (138%) White Cakes

Shortening composition	Batter sp gr	Layer weight	Layer volume	Cake specific volume	Comments
Plastic Shortenings		g	cc	cc	
Commercial nonemulsifier shortening	0.99	396	950	2.4	Curdled batter; poor grain and texture; tough crumb; cakes fell
95% Commercial nonemulsifier shortening 4% Glyceryl lacto-palmitate 1% Stearyl monoglyceridyl citrate	0.90	366	1,100	3.0	Good grain and texture
Commercial emulsifier shortening	0.91	370	1,000	2.7	Good grain and texture
Liquid Shortenings					
Cottonseed oil (control)	1.13	406	815	2.0	Tough crumb; poor texture; cakes fell
95% Cottonseed oil 5% Glyceryl lacto-palmitate	0.83	389	900	2.2	Tough crumb; poor texture; cakes fell
95% Cottonseed oil 4% Glyceryl lacto-palmitate 1% Stearyl monoglyceridyl citrate	0.90	407	960	2.4	Excellent grain and texture

or stearyl-2 lactylic acid (acyl-2 lactylic acid). In view of this activity, stearyl monoglyceridyl citrate appeared to be a superior emulsifying agent.

Experimental Procedures and Discussion

Because past experience showed no correlation between interfacial tensions and use data, preliminary bake tests were made. These tests showed that emulsifier activity was present, but not as significant as that of the recognized emulsifiers (1–4) and definitely not as active as indicated by the interfacial tension results.

Interfacial tension tests were made with combinations of stearyl monoglyceridyl citrate and established emulsifiers (Table I). These data show that 0.10% stearyl monoglyceridyl citrate in combination with 0.10% glyceryl lacto-palmitate, distilled mono-diglyceride mixture or stearyl-2 lactylic acid, materially reduced interfacial tension. Combinations of 0.05% with sorbitan monostearate or polyoxyethylene (20) sorbitan monostearate indicated no apparent benefit, at these levels, from the addition of stearyl monoglyceridyl citrate.

Bake Tests. Bake tests with a high-sugar (138%) white cake recipe were made, using combinations of emulsifiers in the shortenings. The results show enhancement of the primary emulsifier activity by the addition of stearyl monoglyceridyl citrate (Table II). A level of 1% stearyl monoglyceridyl citrate with only 4% glyceryl lacto-palmitate produced finished cakes with greater specific volumes, and with grain and structure equivalent to those made with commercially available plastic shortenings. This is significant in view of the general use of levels of 6–10% of mono-diglyceride mixtures or glyceryl lacto-palmitate in shortenings.

Plastic shortenings were used as the emulsifier carrier. The shortenings were prepared by melting the calculated amounts of additives, with about 5% of the base shortening stock, on a hot-water bath. The melted premix was blended into another 5% of

TABLE III
Accelerated Product Stability Tests with Stearyl Monoglyceridyl Citrate

	Active oxygen measure	Peroxide value
	hr	mmole
Stearyl monoglyceridyl citrate	13.5	51
Refined deodorized cottonseed oil	4.75	64
99% Refined deodorized cottonseed oil 1% Stearyl monoglyceridyl citrate	10.0	50
98% Refined deodorized cottonseed oil 2% Stearyl monoglyceridyl citrate	10.5	49
95% Refined deodorized cottonseed oil 4% Glyceryl lacto-palmitate 1% Stearyl monoglyceridyl citrate	10.5	48

the base shortening stock on a hot-water bath. The melted premix was blended into another 5% of the plastic shortening, using a spatula. The semisolid concentrate was then added to the balance of the plastic shortening, using a Hobart mixer at low speed. The experimental shortening was tempered 24 hr at 80F before use in the baking tests.

Because of the interest in liquid shortenings, stearyl monoglyceridyl citrate was studied as an emulsion stabilizer in conjunction with primary emulsifiers for this use. Very acceptable liquid shortenings were prepared, having crystalline suspensions that showed a remarkable tendency to remain in suspension. Cottonseed oil was heated to 130F in a three-neck flask immersed in a hot-water bath. Using slow agitation, the calculated quantities of primary emulsifiers, stearyl monoglyceridyl citrate, and 0.10% of a distilled mono-diglyceride mixture were added. The mono-diglyceride mixture was added to aid in maintaining the crystalline suspensions. When the additives melted, the flask was transferred to a cold-water bath and agitation was continued until the temperature of the mixture dropped to ca. 70F. The contents were transferred to an electrolytic-type beaker immersed in an ice-water bath. The mixture was con-

TABLE IV
Influence of Emulsifiers and Stearyl Monoglyceridyl Citrate on Shortening Smoke Points

	Smoke point
Cottonseed Oil	°F
No additive	450
1% Stearyl monoglyceridyl citrate	374
4% Stearyl monoglyceridyl citrate	350
4% Glyceryl lacto-palmitate + 1% Stearyl monoglyceridyl citrate	302
2% Stearyl-2 lactylic acid	355
2% Stearyl-2 lactylic acid + 2% Stearyl monoglyceridyl citrate	350
Plastic Shortening	
No additive	495
1% Stearyl monoglyceridyl citrate	475
4% Stearyl monoglyceridyl citrate	450
4% Glyceryl lacto-palmitate + 1% Stearyl monoglyceridyl citrate	384
2% Stearyl-2 lactylic acid	424
2% Stearyl-2 lactylic acid + 2% Stearyl monoglyceridyl citrate	428
Commercial high-emulsifier plastic shortening	355

TABLE V
Emulsifier Activity In Margarines

Emulsifier addition	Cream-mix appearance	Spatter result
Control (no emulsifier)	Weeping, grainy, surface crust	Excessive
Commercial margarine	No weeping or crust, smooth	Heavy
0.10% Stearyl monoglyceridyl citrate	No weeping or crust, smooth	Heavy
0.05% Lecithin + 0.05% Stearyl monoglyceridyl citrate	Slight weeping, slight crust, smooth	Very slight
0.05% Lecithin + 0.05% Mono-diglyceride mixture + 0.05% Stearyl monoglyceridyl citrate	No weeping or crust, smooth	Very slight

TABLE VI
Emulsifier Effect on Whip Toppings Stored at 45F

Emulsifier addition	Appearance of topping	Comments
Control (no emulsifier)	Glossy, weak peaks, not smooth	Excessive weeping; emulsion collapsed
0.20% Polyoxyethylene (20) sorbitan monostearate + 0.10% Stearyl monoglyceridyl citrate	Glossy firm peaks	No apparent weeping
0.20% Mono-diglyceride mixture + 0.10% Stearyl monoglyceridyl citrate	Slightly glossy, firm peaks	Slight weeping; slight fatty flavor
0.20% Glyceryl lacto-palmitate + 0.10% Stearyl monoglyceridyl citrate	Glossy, firm, tight emulsion	No apparent weeping

tinuously stirred with a wiping action to sweep crystal formations away from the beaker surface. As the mass dropped below 50F, a haze and an increase in viscosity occurred. The contents, at this point, were transferred to a container and the liquid shortening was stored 24 hr at 75–80F, before evaluation in bake tests.

Bake tests using the 138% sugar white cake recipe and a 130% sugar yellow cake recipe were made. Although stearyl monoglyceridyl citrate was not as efficient as primary emulsifiers, it exhibited some emulsifying action at a 4% level in the liquid shortening. The finished white cake, however, had a poor, coarse texture. The next series of bakes involved various levels of glyceryl lacto-palmitate to determine its performance in white cakes. Although a 3–5% level in the shortening produced a reduction in the batter sp gr, the finished cakes fell and were poor from a grain and texture standpoint (Table II). Blends of the two components were studied, and a combination of 1% stearyl monoglyceridyl citrate with 4% glyceryl lacto-palmitate, based on liquid oil weight, produced a highly acceptable white cake when judged by specific volume, grain, and structure. This final shortening contained the same total quantity of additives, yet was superior in action to the 5% level of glyceryl lacto-palmitate.

In the tests with yellow cakes, the liquid shortening containing 4% stearyl monoglyceridyl citrate produced an acceptable finished cake from a volume and texture standpoint. This improvement in performance in comparison to the white cake result is probably due to the emulsifier action of the whole egg. Superior results were achieved using a liquid shortening containing 1% stearyl monoglyceridyl citrate with 4% glyceryl lacto-palmitate.

The use of low levels of stearyl monoglyceridyl citrate results in liquid shortenings that are highly acceptable for cake production. Also, lower levels of primary emulsifier are possible because of the emulsifier-enhancing action of the stearyl monoglyceridyl citrate addition.

Evaluations in Shortenings. Resistance to rancidity and compatibility in shortenings is of prime importance in fats and oils. Active oxygen measure determinations (AOM) were performed on stearyl monoglyceridyl citrate and on the refined deodorized cottonseed oil used in the preparation of the liquid shortenings. Table III shows that the test compound was approximately three times as resistant to development of a peroxide value. Table III also indicates the hours required on the AOM to induce a peroxide value of ca. 50 in the various experimental liquid shortenings. Stearyl monoglyceridyl citrate at a 1 or 2% level in cottonseed oil, or at a 1% level with 4% glyceryl lacto-palmitate, did not reduce the stability time of the cottonseed oil.

Plastic shortening studies showed a similar pattern in AOM data. The use of 1–2% stearyl monoglyceridyl citrate had no apparent effect on the plasticity of the finished tempered shortenings. Bake tests performed on samples of experimental liquid and plastic shortenings stored for 6 months at 75F produced acceptable finished cakes, indicating that there was no incompatibility between the additives.

Smoke point-depressant characteristics are necessary in the evaluation of emulsifier candidates. A number of combinations in liquid and plastic shortenings was studied (Table IV), and as would be suspected, stearyl monoglyceridyl citrate depressed the smoke point of shortenings. However, at the optimum use levels of 1–2%, the smoke point was not depressed below that of commercially acceptable plastic shortenings (355F).

Margarines and Whip Toppings. In view of the successful performance in baking operations, stearyl monoglyceridyl citrate was screened as an emulsion stabilizer in other food areas.

Margarines were prepared in the laboratory by dissolving the emulsifier systems in margarine oils. The blend was mixed with the aqueous-milk phase and the entire mass was hand homogenized, then cooled in an ice-water bath until semisolid. The finished margarines were studied and compared with emphasis on creaming with sugar and water blends, and on spatter reduction during frying. Table V shows that stearyl monoglyceridyl citrate at a level of 0.10% had an emulsifying action on creaming, but no antispatter action. A level of 0.05% stearyl monoglyceridyl citrate with 0.05% each of lecithin and a monodiglyceride mixture was superior to all other blends, and to a commercial margarine in spatter reduction and production of superior creams.

Stearyl monoglyceridyl citrate exerts a somewhat variable action with primary emulsifiers in whip toppings. Generally, stearyl monoglyceridyl citrate additions resulted in tighter emulsions with slight variations in weeping characteristics (Table VI). These conditions very likely can be altered by changing the ratio of the emulsion stabilizer to the primary emulsifier.

In evaluating successful new candidates, one of the prime questions is food additive status. The March 17, 1962, *Federal Register* (5) gave stearyl monoglyceridyl citrate approval as an emulsion stabilizer in the following manner: "The additive is used or intended for use as an emulsion stabilizer in or with shortenings containing emulsifiers."

With every indication that stearyl monoglyceridyl citrate will perform as an emulsion stabilizer under varying conditions, further work is in progress in many other food applications.

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