Conjoined Crystals. I. Composition and Physical Properties[1]

N. H. KUHRT, R. A. BROXHOLM, and W. P. BLUM, Distillation Products Industries, Division of Eastman Kodak Company, Rochester, New York

Abstract

Conjoined Crystals is the name given to a new food emulsifier whose special properties are associated with its content of glycerol monoester in a stabilized α-crystalline form (6). It consists of the mixture of crystals formed by cooling a melt containing approximately equal molecular proportions of certain long chain fatty acid monoesters of glycerol and of 1,2-propanediol. A practical composition contains a blend of glycerol monostearate and 1,2-propanediol monostearate.

Conjoined Crystals disperse readily in water and retain this ability for periods of over a year, a property which appears to be closely associated with their effectiveness in baking and in other applications. This water dispersibility contrasts with the behavior of the usual modification of glycerol monostearate which is difficult to disperse in water.

Infrared analysis indicated that the major part of the glycerol monoester in the mixed crystals is in the α-crystalline modification. Studies by X-ray diffraction supported this conclusion. Thus, we have consistently associated ready water dispersibility and the α-form with the enhanced emulsifying ability.

Introduction

During the course of studies on the emulsifying action of saturated monoglycerides, glycerol monostearate was prepared in powdered form by spraying the melted material. When freshly prepared, the monoester was readily dispersible in water, unlike the usual form of glycerol monostearate, and the dispersions foamed when shaken. This ready dispersibility promised to be a useful property since it would minimize incorporation problems in baking, and a number of applications were envisaged.

Unfortunately, the preparation lost this ready dispersibility in a short time and became difficult to disperse in water like the usual commercial forms of glycerol monostearate.

Studies were therefore made on the effect of combining a number of related monoesters with the glycerol monostearate, with the objective of retaining this water dispersibility for longer periods of time. The most effective mixture found contained approximately equal molar proportions of glycerol monostearate and propylene glycol monostearate, and was representative of the class of monoester mixtures we have called Conjoined Crystals (6). The present report (Part I) covers its properties and some of those of the other combinations investigated. The baking and other applications are covered in Part II.

Infrared (IR) studies, confirmed by X-ray diffraction, indicated that the major proportion of the glycerol monoester in Conjoined Crystals is in the α-crystalline form. Loss of water dispersibility on standing was accompanied by change to the β-crystalline form. An IR method was developed for determining the percentage of the β-form in such blends and used to determine the stability of the α-form on storage.

Melting point studies indicated that Conjoined Crystals exist as a "solid solution" (mixed crystals).

During the work, IR and X-ray diffraction data were obtained on the polymorphic forms of glycerol monostearate which are reported here. Earlier reports on this subject were made by Chapman (4,5) and Lutton et al. (7,8). IR and X-ray diffraction data on the polymorphic forms of propylene glycol monostearate are reported for the first time to our knowledge.

Experimental Procedures

Monoester Preparation. Glycerol monostearate was prepared from glycerol and fractionally distilled methyl stearate using 0.1% strontium hydroxide catalyst, reacting for 1 hr at 250C. The glycerol monostearate was purified by molecular distillation, followed by two crystallizations from an ethanol-Skellysolve F solvent mixture. Purity was 99.2% 1-monoglyceride by the periodic acid method (1); fatty acid moiety contained 99.2% stearic and 0.8% palmitic acids by GLC (2). The melting point for the α-polymorphic form was 73.5C, and for the β-polymorphic form, 81.5C.

Glycerol monopalmitate was similarly prepared from glycerol and palmitic acid (Armour Industrial Chemical Co., Neofat 16), followed by molecular distillation and crystallization. Purity was 98.0% 1-monoglyceride; composition was 89.0% palmitic, 8.8% stearic and 2.0% myristic acids by GLC. Melting points were 66C and 77.5C for the α and β-forms.

Propylene glycol monostearate was prepared from 1,2-propanediol and pure stearic acid using 0.1% calcium oxide as catalyst, reacting for 10 hr at 175C. Molecular distillation of the reaction product gave a fraction with a purity of 99.6% monoester as determined by hydroxyl value (3). The fatty acid moiety contained 99.4% stearic and 0.6% palmitic acids by GLC. The β-form of the propylene glycol monostearate had a melting point of 56.5C. The α-polymorphic form of pure propylene glycol monostearate is difficult to obtain and its preparation is discussed below. Melted and resolidified, purified propylene glycol monostearate was mostly in the crystalline β′-form and melted at 46.5C.

Propylene glycol monopalmitate was made from recrystallized palmitic acid (Armour, Neofat 16) and 1,2-propanediol using 0.1% p-toluene sulfonic acid as catalyst, reacting for 8 hr at 120C. Molecular distillation of the reaction product gave a material having 88% monoester by hydroxyl value and a composition of 94.3% palmitic and 5.3% stearic acids by GLC. The melting point for the α-polymorphic form was 36.5C; for the β′-form 39.5C; and for the β-form 42.5C.

1,3-Propanediol monostearate was made from stearic acid and 1,3-propanediol using 0.1% p-toluene sulfonic acid as a catalyst, reacting for 20 hr at 135C. Molecular distillation of the reaction mixture gave a product which by hydroxyl value was 95.6% monoester; by GLC contained 93.0% stearic, 3.6% palmitic and 3.0% arachidic acids, with a melting point of 53C.

---

[1] Communication No. 293.

TABLE I

IR Wavelengths for Forms of Glycerol Monostearate

Sub-α		α		β′		β	
Band μ	Strength	Band μ	Strength	Band μ	Strength	Band μ	Strength
9.48	VS	9.53	VS	9.48	VS	9.41 ⎫	VS
						9.55 ⎭	VS
9.90	M			9.90	M		
10.13	S	10.16	M	10.04 ⎫	S	10.08	S
				10.12 ⎭	S		
				10.27	W		
10.67	M	10.70	M	10.65	S	10.60	S
				10.89	M	10.95	M
11.28	M			11.35	S	11.25	VW
11.35	M	11.40 to 11.75	M	11.60	M	11.40	W
11.72	M					11.75	M
				12.07	M	12.05	M
12.34	W	12.35	W	12.34	W	12.35	W
12.79	W	12.78	W	12.78	W	12.78	W
13.15	M	13.16	W	13.16	M	13.15	W
13.72 ⎫	VS	13.88	VS	13.72 ⎫	VS	13.88	VS
13.90 ⎭	VS			13.90 ⎭	VS		

VW—Very weak; W—weak; M—medium; S—strong; VS—very strong.

Ethylene glycol monostearate was prepared from recrystallized stearic acid and ethylene glycol with 0.06% p-toluene sulfonic acid as catalyst, reacting for 9 hr at 120C. Molecular distillation of the reaction mixture gave a product with a purity of 100% monoester with a fatty acid moiety of 91.5% stearic and 7.7% palmitic acids and having a melting point of 59C.

Glycerol monoesters, mainly glycerol monostearate, were prepared by the molecular distillation of the monoesters from either hydrogenated soybean oil (stearic to palmitic acid ratio, approximately 90:10) or hydrogenated lard (ratio, approximately 70:30). The products contained at least 93% 1-monoglyceride with melting points for the α-polymorphic form of 73 and 70.5C, respectively, and for the β-form of 77 and 73.5C.

Glycerol monoester was made from palmitic acid (Armour, Neofat 16) and glycerol, reacted with strontium hydroxide as a catalyst, and molecularly distilled to give a product having a purity of 93% monoglycerides. Fatty acid composition by GLC was 91.2% palmitic, 3.7% myristic, and 3.3% stearic acids. The melting point for the α-polymorphic form was 66C; and for the β-polymorphic form was 75C.

Propylene glycol monoester was prepared from a commercial stearic acid (Humko Products Division, National Dairy Corp., Hystrene S-97) and propylene glycol using 0.2% d-10-camphor sulfonic acid catalyst, reacting for 2 hr at 165C. Molecular distillation of the reaction product gave a product with a purity of 93% monoester; composition of 84.8% stearic, 11.6% palmitic and 2% arachidic acids; and a melting point for the α-crystalline form of 43.5C.

TABLE II

IR Wavelengths for Forms of Propylene Glycol Monostearate

α		β′		β	
Band μ	Strength	Band μ	Strength	Band μ	Strength
		9.05	S	9.08 ⎫	S
				9.22 ⎭	S
		9.30	S		
9.45	VS				
				9.65	M
		9.87	S	9.87	M
10.06	S	10.07	S	10.03	M
				10.37	VS
10.53	S	10.55	S		
10.73	M	10.72	S	10.81	M
11.17	W	11.25	VW	11.23	VW
11.38	VW	11.40	W	11.41	M
11.77	M	11.79	S	11.73 ⎫	M
				11.82 ⎭	M
12.10	VW				
12.34	VW	12.34	W	12.36	M
12.79	W	12.78	W	12.75	VW
13.15	W	13.16	M	13.17	M
13.87	VS	13.74 ⎫	VS	13.70 ⎫	VS
		13.91 ⎭	VS	13.91 ⎭	VS

VW—Very weak; W—weak; M—medium; S—strong; VS—very strong.

Preparation of Powdered Emulsifiers. Powdered emulsifiers were prepared by melting and spray cooling with a DeVilbiss paint spray gun, Type CM501.

Polymorphic Forms of Glycerol and Propylene Glycol Monostearates

Glycerol Monostearate. The polymorphic forms were made according to the procedure of Lutton (7).

sub-α—By melting the monoglyceride on one sodium chloride crystal of an IR cell and immediately placing a cold sodium chloride crystal on top of the melt to solidify the monoglyceride rapidly below the α/sub-α transition temperature, or by a slow cooling of the monoglyceride in a heated cell to a temperature below the α/sub-α transition temperature.

α—By melting and cooling the glycerol monostearate to a temperature above the α/sub-α transition temperature.

β′—By a very rapid crystallization from a 300:1 ratio of ethyl ether to monoglyceride using a dry ice-acetone bath, a rapid filtration through a dry ice chilled Büchner funnel with the residual ether removed cold under vacuum.

β—By either a slow solvent crystallization or by waiting for the α to β-crystalline shift to occur.

Propylene Glycol Monostearate. The polymorphic forms and the allocations of crystal structure were made on the basis of melting points and infrared and X-ray diffraction studies.

α—Prepared in a melted and cooled sample when small amounts of impurities such as propylene glycol monopalmitate or propylene glycol distearate are present.

β′—By a very rapid crystallization from a 200:1 ratio of ethyl ether to propylene glycol monostearate free of impurities, using a dry ice-acetone bath, a rapid filtration and the residual ether removed cold under vacuum.

β—By a very slow crystallization from acetone.

The α-crystalline form shows good stability. The β′-polymorphic form shifts to the β-form after several years of storage.

Studies of the Polymorphic Forms of Glycerol and Propylene Glycol Monostearates

By Infrared Analysis. IR absorption curves were prepared using a Perkin-Elmer Model 21 IR spectrophotometer. With the exception of the α and sub-α forms of pure glycerol monostearate, all the polymorphic forms were examined as Nujol mulls. Because of the instability of the α and sub-α forms of pure

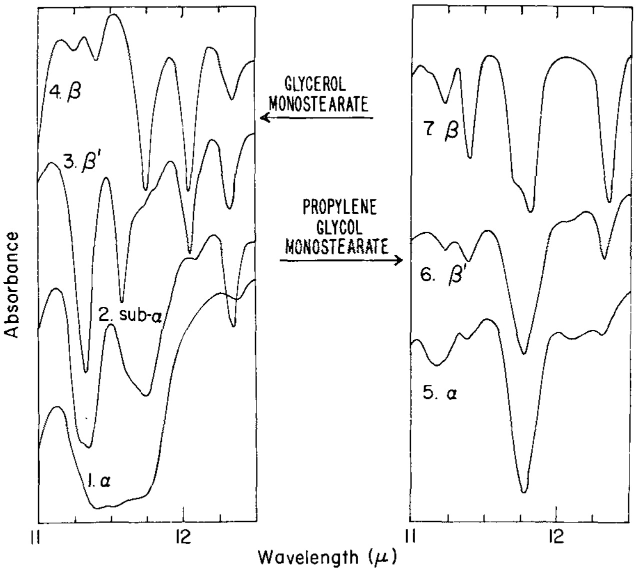

FIG. 1. Partial IR spectra of crystalline forms of glycerol monostearate: 1, α; 2, sub-α; 3, β'; 4, β. Partial IR spectra of crystalline forms of propylene glycol monostearate: 5, α; 6, β'; 7, β.

glycerol monostearate, measurements were made in the IR cell in which they were prepared.

Table I lists the principal bands with relative strengths of absorbance for the four polymorphic forms of glycerol monostearate, as indicated by our measurements. Table II notes similarly the principal bands and relative strengths of absorbance observed for the three polymorphic forms of propylene glycol monostearate.

Figure 1 shows the IR absorption curves from 11 to 12.5 μ for the sub-α, α, β' and β-polymorphic forms of glycerol monstearate and α, β' and β-polymorphic forms of propylene glycol monostearate.

Determination of the Percentage of Glycerol Monostearate in β-Crystalline Form

An IR procedure was devised for determining the percentage of the β-crystalline form of glycerol monostearate in mixtures of glycerol and propylene glycol monostearates (Fig. 2).

Calculations are based on the ratios of the absorbances at 11.77 and 12.05 μ. Base lines are drawn from 11.10 to 12.20 μ and from 11.95 to 12.20 μ and the absorbances at 11.77 and 12.05 μ are determined from these base lines. The formula is:

Per cent β-form of glycerol monostearate = 100 (A/B)/C, where
A = absorbance at 12.05 μ
B = absorbance at 11.77 μ, and
C = mole fraction of glycerol monostearate.

Curve 1, Figure 2 is typical of a freshly prepared sample of Conjoined Crystals composed of glycerol monostearate and propylene glycol monostearate. Curve 2 was obtained for a sample which had been stored for two years. Curve 3 was obtained for a sample which was obtained by mixing equal molar proportions of a powdered glycerol monostearate which was 100% in the β-form with powdered propylene glycol monostearate.

Identification of the β'-Crystalline Form of Propylene Glycol Monostearate in Conjoined Crystals

IR spectrophotometry of many samples of Conjoined Crystals has shown that within a few weeks a very weak peak at 13.73 μ develops. The sub-α and β'-forms of glycerol monostearate, and the β' and β-forms of propylene glycol monostearate have absorbance in this region of 13.73 μ. Any change from the α to the sub-α-form of the monoglyceride should occur immediately at room temperature (7). Other peaks characteristic of the β'-form of glycerol monostearate and the β-form of propylene glycol monostearate were not present. Therefore, we concluded that some change of the α-form to the β'-form of propylene glycol monostearate occurred. Supporting this conclusion, a mixture of the α-form of glycerol monostearate and the β'-form of propylene glycol monostearate gave a similar absorption curve.

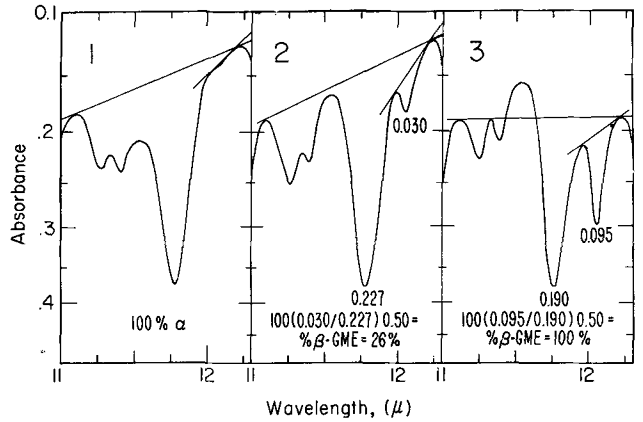

FIG. 2. IR curves illustrating the determination of the percentage of β-crystalline form of glycerol monostearate in a sample of Conjoined Crystals, 50:50 blend on molar basis: 1, 0% of glycerol monostearate in β-form; 2, 26% of glycerol monostearate in β-form; 3, 100% of glycerol monostearate in β-form.

X-ray Diffraction Studies. X-ray diffractometer tracings were prepared in the Eastman Kodak Co. Industrial Laboratory, using North American Phillips X-ray equipment. The powder sample was packed in a one-inch diam cup and rotated in the specimen holder. Diffractometer tracings were made over the range of 4–50 degrees, 2 θ, using copper K alpharadiation at 40 kv and 20 ma.

The principal lines and relative intensities from the diffraction patterns of glycerol and propylene glycol monostearates in their various polymorphic forms are noted in Table III.

The patterns of the α, β', and β-polymorphic forms of glycerol monostearate agree well with those described in the literature (7,8). The patterns of the three polymorphic forms of propylene glycol monostearate have not been previously reported.

Diffraction patterns of the β-polymorphic forms of the two monoesters have little similarity and can easily be differentiated.

As a method of identification of the polymorphic forms of glycerol monostearate or propylene glycol monostearate, X-ray diffraction is as effective as IR analysis, with the exception that both the α-forms of glycerol monostearate and propylene glycol monostearate give similar X-ray diffractometer tracings.

X-ray diffraction is also less effective than IR analysis in detecting small changes in the amount of the β-form of glycerol monostearate in Conjoined Crystals preparations. However, X-ray diffraction can detect a change from the α to the β'-form of propylene glycol monostearate in such preparations better than IR analysis.

We concluded from the X-ray diffraction and IR

TABLE III

X-ray Diffraction Data of Glycerol Monostearate and Propylene Glycol Monostearate

α-GMS		α-PMS		β'-GMS		β'-PMS		β-GMS		β-PMS	
d	RI	d	RI	d	RI	d	RI	d	RI	d	RI
18.0	VW	......	......	16.5	M	......	......	17.0	S	15.4	W
13.5	VW	13.5	M	12.8	W	12.0	W	12.5	S	10.3	M
9.1	VW	8.6	W	8.4	W	9.6	VW	8.4	S	9.0	W
......	......	......	......	4.98	VW	8.0	W	6.3	W	6.0	W
4.2	VS	4.2	VS	4.2	VS	6.1	VW	5.7	VW	5 6	W
......	......	......	......	3.85	M	4.2	VS	5.0	W	5.2	W
......	......	......	......	3.73	S	3.68	S	4.8	VW	5.0	VW
......	......	......	......	3.57	W	2.52	W	4.58	S	4.7	W
......	......	......	......	3.42	VW	2.37	W	4.43	S	4.2	VS
......	......	......	......	3.13	VW	2.29	W	4.24	W	3 55	S
......	......	......	......	2.52	W	2.21	W	4.15	W	3.51	VS
......	......	......	......	2.38	W	2.13	VW	3.88	VS	3.30	VW
......	......	......	......	2.26	VW	2.06	VW	3.80	W	3.00	W
......	......	......	......	2.08	W	......	......	3.72	W	2.50	W
......	......	......	......	2.06	VW	......	......	3.53	W	2.39	W
......	......	......	......	......	......	......	......	3.45	VW	2.24	M
......	......	......	......	......	......	......	......	3.35	W	2.14	W
......	......	......	......	......	......	......	......	3.15	M	2.07	W
......	......	......	......	......	......	......	......	2.98	VW	1.99	W
......	......	......	......	......	......	......	......	2.80	VW	1.93	W
......	......	......	......	......	......	......	......	2.66	VW	......	......
......	......	......	......	......	......	......	......	2.54	VW	......	......
......	......	......	......	......	......	......	......	2.45	M	......	......
......	......	......	......	......	......	......	......	2.38	W	......	......
......	......	......	......	......	......	......	......	2.27	W	......	......
......	......	......	......	......	......	......	......	2.17	M	......	......
......	......	......	......	......	......	......	......	2.08	W	......	......
......	......	......	......	......	......	......	......	2.00	W	......	......

d = Interplaner spacing in Angstroms.

RI = Relative Intensity. (Intensities are influenced by packing procedure used in loading cup. They are estimations based on height of the diffraction peak.)

VS—very strong; VW—very weak; M—medium; S—strong; W—weak.

measurements that there is no evidence of interaction or complex formation in Conjoined Crystals preparations.

X-ray diffraction patterns were sensitive enough to detect the beginning of a change from the α to the β'-form of propylene glycol monostearate which occurred in one day. The patterns also showed that only the α-form of glycerol monostearate and the α and β'-forms of propylene glycol monostearate were present. The formation of small amounts of the β'-form of glycerol monostearate was detected both by IR analysis and by X-ray diffraction patterns.

The β-form of propylene glycol monostearate was not found in these compositions by either IR or X-ray diffraction analysis.

Melting Point-Composition Curves. Figure 3 is a melting point-composition curve for glycerol monopalmitate and propylene glycol monostearate. This is an isomorphous system (solid solution). Higher melting points were noted after 3 and 18 days for compositions containing up to 60 molar per cent of propylene glycol monostearate. IR analysis showed this increase in melting point to be associated with a change in the glycerol monopalmitate from the α to the β-crystalline form.

Figure 4 is the melting point-composition curve for glycerol monostearate and propylene glycol monostearate. This system is also isomorphous. Mixtures containing molar percentages of 0, 10, 20, and 30 of propylene glycol monostearate showed an increase in melting point, on aging for 6 days and 20 days. IR analysis indicated that this was associated with a change in the glycerol monostearate from the α to the β-crystalline form. Mixtures containing molar percentages of propylene glycol monostearate greater than 30 showed no increase in melting point on aging for these periods. IR analysis indicated little or no change in the glycerol monostearate to the β-crystalline form.

Effect of Changes in Composition on Properties. The rate of change to the β-crystalline form of glycerol monoesters in mixtures of glycerol monoesters and glycol monoesters from various sources of stearic and palmitic acids (Table IV) is shown in Table V. The

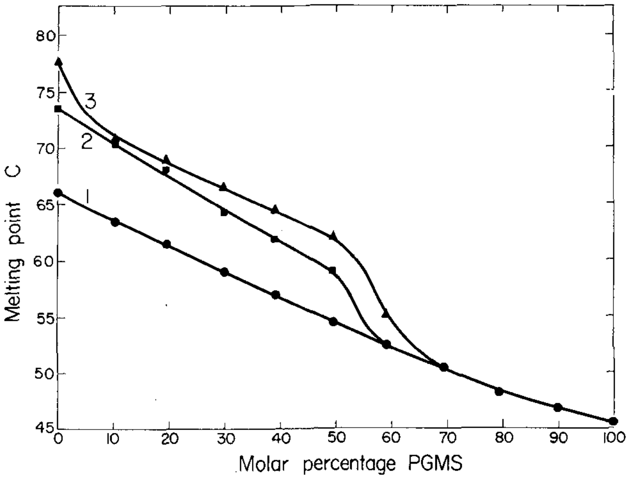

FIG. 3. Melting point diagram of glycerol monopalmitate and propylene glycol monostearate: 1, aged 0 days; 2, aged 3 days; 3, aged 18 days.

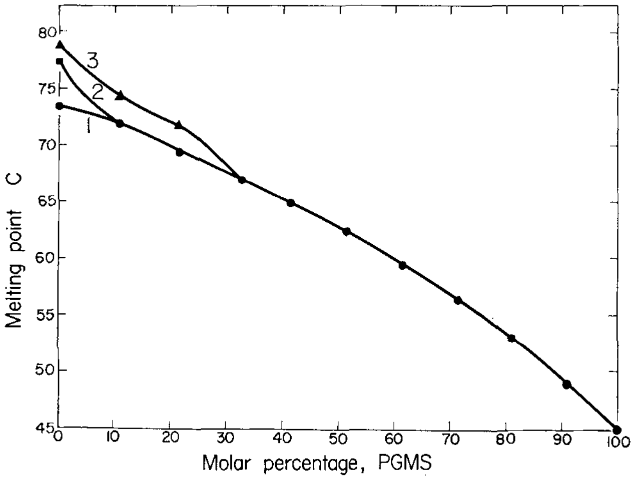

FIG. 4. Melting point diagram of glycerol monostearate and propylene glycol monostearate: 1, aged 0 days; 2, aged 6 days; 3, aged 20 days.

TABLE IV
Compositions, Mole %, for Use with Tables V and VI

Example	Glycerol esters			Glycol esters [a]		
	From	Mono-ester	Di-ester	From	Mono-ester	Di-ester
1	Stearic acid	49.2	0.5	Stearic acid	50.2	0.1
2	Palmitic acid	45.8	1.8	Stearic acid	50.3	2.0
3	Palmitic acid	44.0	1.7	Palmitic acid	50.3	4.0
4	Hydrogenated lard	50.6	2.0	Palmitic acid	43.6	3.8
5	Hydrogenated lard	43.5	1.0	Stearic acid	53.7	2.0
6	Hydrogenated soybean oil	46.3	1.7	Stearic acid	50.1	2.2
7	Hydrogenated lard	38.6	0.9	Stearic acid	58.3	2.2
8	Hydrogenated soybean oil	38.2	1.4	Stearic acid	55.8	4.6
9	Hydrogenated lard, mono-diglyceride mixture	39.8	15.1	Stearic acid	41.5	3.6
10	Hydrogenated lard, mono-diglyceride mixture	34.0	11.9	Stearic acid	51.0	3.1
11	Hydrogenated lard	47.8	1.8	Stearic acid	49.2	1.3
12	Hydrogenated lard	50.3	0	Stearic acid	49.7	0

[a] In *Examples* 1–10 the glycol was 1,2-propanediol; in Example 11 it was 1,3-propanediol; in Example 12 it was ethylene glycol.

corresponding changes from water dispersibility to water repellency and loss of frothing ability are shown in Table VI.

A simple test was used to determine water dispersion and frothing of spray chilled products. A 0.2 g sample was added to 50 ml of water in a 150 ml beaker. By stirring, it was determined whether the product was dispersible in water or had become repellent to water. A stream of air was passed through the dispersion, and the frothing was judged to be excellent if over the top of the beaker; good if the froth reached the top of the beaker; and fair if the froth reached halfway to the top of the beaker. A more quantitative test was also used and will be reported in Part II.

A Conjoined Crystals preparation from glycerol monostearate and propylene glycol monostearate developed only 25% of β-crystalline form of the glycerol monoester after storage for 21 months (Example 1, Table V). During this period, the preparation readily dispersed in water and retained its ability to froth (Example 1, Table VI).

When approximately equimolar mixtures of glycerol monopalmitate and propylene glycol monostearate were tested, the glycerol monopalmitate shifted rapidly to the β-crystalline form, and the preparation became water repellent and quickly lost the ability to froth (Example 2).

In a Conjoined Crystals preparation containing ca. equimolar blends of glycerol monopalmitate and propylene glycol monopalmitate (Example 3), the glycerol monopalmitate shifted more rapidly to the β-crystalline form than in the case of the corresponding monostearates. However, the blend was readily water dispersible and showed good retention of its frothing ability.

The blend of glycerol monoesters from hydrogenated lard with propylene glycol monopalmitate (Example 4) showed a relatively rapid shift to the β-crystalline form of the glycerol monoester. The blend retained its water dispersibility, but quickly lost the ability to froth.

In Examples 5 through 10, the propylene glycol monostearate was prepared from a commercial grade of stearic acid (Hystrene S-97). In Examples 5 and 7, in which the fatty acid moiety of the glycerol monoester was from hydrogenated lard (ratio of stearic to palmitic acid, ca. 70:30) there was a slow change to the β-crystalline form. This was especially true in Eaxmple 7, in which the mole ratio of the propylene glycol monostearate was increased to 58.

TABLE V
Beta Crystalline Form of Glycerol Monoester, %

Example	Months at room temperature														
	1	2	3	4	5	6	7	8	9	10	11	12	17	19	21
1	10				10					15				20	25
2	70														
3	48		60												
4	56							68							
5	22	54					62								
6	12		16				19			18				27	
7	16	28	33				55								
8	2				7					9			15		
9	43		58			60									
10	7					14		27							
11	80				100										
12	20	30				58									

TABLE VI
Water Repellency and Frothing

Example	Water repellency		Frothing in water					
	Slight Age	Considerable Age	Excellent		Good		Fair	
			Age	% β	Age	% β	Age	% β
1	> 21 months		21 months	25				
2		7 days	7 days	51			10 days	62
3	> 8 months		4 months	60	8 months			
4	> 5 months		12 days	38	22 days	54	1 month	56
5	1 month	6 wk	1 month	22	6 wk	27	7 wk	26
6	19 months		10 months	18	19 months	27		
7	> 1 month		2 months	28	3 months	33		
8	> 17 months		17 months	15				
9		3 days					0 days	5
10	> 6 months		8 days	7	2 wk	7	2 months	10
11	10 days	18 days	18 days	78			24 days	
12	1 month	2 months	27 days	20	36 days	24	2 months	30

Water repellency and loss of frothing ability in water developed after 6 and 7 weeks' storage, respectively.

In Examples 6 and 8, in which the glycerol monoester was prepared from hydrogenated soybean oil (ratio of stearic to palmitic acid ca. 90:10), a slower shift to the β-crystalline form occurred. The blend retained its water dispersibility and continued to froth even after 1½ years' storage.

In Examples 9 and 10, the source of glycerol monoester was a commercial mono and diglyceride product. These preparations showed poor α-crystalline stability, water dispersibility, and frothing ability when the mole per cents of the glycerol and propylene glycol monoesters were nearly the same (Example 9), but these properties were improved by using a 50% molar excess of propylene glycol monostearate over glycerol monostearate (Example 10).

1,3-Propanediol monostearate was ineffective in stabilizing the glycerol monoester of hydrogenated lard in the α-crystalline form, possibly because of its dissimilar crystalline modification (Example 11).

Glycerol monoesters from hydrogenated lard blended with ethylene glycol monostearate showed good stabilization of the glycerol monoester in the α-crystalline form and retention of frothing ability (Example 12).

It was concluded from these experiments that a composition of Conjoined Crystals, as judged by retention of the α-crystalline form during storage, and by retention of frothing ability, is obtained by melting and solidifying a blend of glycerol monostearate and 1,2-propanediol monostearate in approximately equal molecular proportions. With glycerol monoesters from hydrogenated soybean oil and hydrogenated lard, in which glycerol monostearate is mixed with other monoesters, such as glycerol monopalmitate, a blend containing a higher ratio of propylene glycol monoester to glycerol monoester gave better stability.

ACKNOWLEDGMENT

X-ray diffraction data by R. L. Dehm and R. R. Parmerter, Industrial Laboratory, Eastman Kodak Co.

REFERENCES

1. AOCS Official and Tentative Method Cd 11-57, 2nd ed., Rev. to 1958.
2. *Ibid.* Ce 1-62, 2nd ed., Rev. to 1962.
3. *Ibid.* Cd 13-60, 2nd ed., Rev. to 1961.
4. Chapman, D., J. Chem. Soc., 55 (1956).
5. Chapman, D., 1956. Colloquium Spectroscopicum Internationale. VI, Pergamon Press Ltd., London, 609 p.
6. Kuhrt, N. H., and R. A. Broxholm, U.S. Patent 3,034,898.
7. Lutton, E. S., and F. L. Jackson, J. Am. Chem. Soc., *70*, 2445 (1948).
8. Lutton, E. S., JAOCS, *27*, 276 (1950).

[Received October 29, 1962—Accepted May 16, 1963]

Conjoined Crystals. II. Applications[1]

N. H. KUHRT and R. A. BROXHOLM, Distillation Products Industries, Rochester, New York

Abstract

Mixed crystals of glycerol monostearate and 1,2-propanediol monostearate (propylene glycol monostearate) (a useful composition of Conjoined Crystals, see Part I) disperse readily in water, retaining this property for long periods of time. The effect of composition on retention of the α-crystalline form of the glycerol monoester in such dispersions is discussed.

The water dispersions foam when shaken or when air is blown through the dispersion, a property which appears to be associated with the superior activity of the mixed crystals as a food emulsifier. A test method for measuring foam retention is described.

The crystals, or their water dispersions, are useful in the preparation of low-calorie, fruit "fluffs," such as whipped applesauce. Sponge cakes with fine grain, improved volume, and texture were prepared with the water dispersions. The crystals are effective emulsifiers in cake mixes and bread. These tests are described.

Introduction

IN PART I, the preparation and physical properties of a number of compositions of Conjoined Crystals were described. In Part II, we report on the properties of water dispersions and the application of the crystals and/or the water dispersions in fruit purees or "fluffs," sponge cakes, cake mixes and bread (3).

Experimental Procedures and Data

Monoester Preparation

Propylene glycol monoesters were made from commerical arachidic acid (75% arachidic, 25% stearic) and propylene glycol using 0.1% p-toluene sulfonic acid as a catalyst, reacting at 125C for 3 hr, and molecularly distilling to give a monoester having a purity of 92% as determined by the official AOCS method (2).

Glycerol monoesters were prepared from partially hydrogenated soybean oil having an iodine value (I.V.) of 15 by reacting the hydrogenated fat with glycerol and 0.1% strontium hydroxide catalyst for one hour at 245C and distilling in a molecular still to give a monester having a purity of 91% (1) and a melting point of 63–64.5C.

Propylene glycol monoesters were prepared from partially hydrogenated soybean oil having an I.V. of 15 by reacting the fatty acids, obtained from the hydrogenated fat by alkaline hydrolysis, with propylene glycol and 0.2% d-10-camphor sulfonic acid as a catalyst at a temperature of 165C for one hour and molecularly distilling to give a monoester having a purity of 94% with a melting point of 36.5–37.5C.

The preparation of glycerol monostearate, glycerol monopalmitate, 1,2-propanediol monostearate, 1,3-propanediol monostearate, and ethylene glycol monostearate were reported in Part I. Glycerol monoesters, mainly glycerol monostearate, were prepared by the molecular distillation of the monoesters from either hydrogenated soybean oil (stearic to palmitic acid ratio, approximately 90:10) or hydrogenated lard (ratio, approximately 70:30).

The powdered emulsifier used in the "Applications" section was prepared by spray cooling, as described in Part I, and contained a molar ratio of 45:55 of the glycerol monoesters from hydrogenated soybean oil and the propylene glycol monoesters prepared from a commerical stearic acid (Humko Products Division, National Dairy Corp., Hystrene S-97, stearic acid to palmitic acid ratio, approximately 90:10).

Water Dispersions

Water dispersions were made by two methods. In

---

[1] Communication no. 294 from the Research Laboratories of Distillation Products Industries, Division of Eastman Kodak Co.