Polyglycerol Esters Composition: Theoretical Random Distribution versus HPLC Analysis

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ABSTRACT

Product composition of polyglycerol esters, prepared from a direct alkaline polymerization of glycerol followed by esterification with stearic or oleic acids, has been studied. The internal product composition, as analyzed by high performance liquid chromatography (HPLC), shows clearly that in contradiction to what has been published recently, the fatty acid radicals are *not* distributed at random among all available hydroxyl groups, and thus, any theoretical calculation on the product composition could not be correct. The product composition of the crude material indicates clearly that the internal positions (secondary hydroxyls) of the glycerol polymer are esterified with greater difficulty than the primary hydroxyl groups.

INTRODUCTION

Polyglycerol esters have been known for many years and their preparation has been described in detail (1,2). Yet, the product composition was never fully analyzed and most of the information on the crude product comes from indirect tests such as viscosity, refractive index, color, acid number, hydroxyl and ester values.

Polyglycerol esters are being offered by several companies as food additive amendments to the FDA regulations and for the issuance of tests for GRAS (Generally Recognized As Safe) substances (3,4). Recently, they have been gaining more interest because their properties and applications prove to have significant advantages over other food emulsifiers.

To familiarize the readers with the polyglycerol esters, a review article has recently been published (5) describing the general methods of manufacture as well as some of the properties and uses of those materials. The author states that, in the commercial manufacture of partial esters, the reaction proceeds by chance and thus the homogeneous system of the esterification reaction gives a mixture in which the fatty acid radicals are distributed at random among all available hydroxyl groups. The calculated composition, at equilibrium of a single-phase reaction mixture of several possible reactions, has been presented in several histograms indicating that, indeed, those are the real, obtained and analyzed, compositions of the products. The purpose of this paper is to show that the product composition is not distributed at random and that all available positions of the polyglycerol are not of the same reactivity toward esterification. The information on the product distribution is important, mainly because of the regulations limiting the chain length of polyglycerol and the amounts permitted as food additives (6).

EXPERIMENTAL

Materials

Glycerol 1-monooleate (puriss) and glycerol 1,3-dioleate (puriss) were obtained from Sigma Chemicals. Glycerol monostearate and mixtures of glycerol mono- and distearates were commercially available products from Grindsted Products and Atlas Europol A.p.S.; sunflower oil was commercially available.

Polyglycerol esters were synthesized in our laboratory (1,5,7) and for comparison, were purchased from Capitol City Products, Columbus, OH (Caprols) and Durkee Food Division SCM Corp., Cleveland, OH (Santones). The eluents were *n*-hexane (Uvasol) and isopropanol (A.R.) purchased from E. Merck, Darmstadt, West Germany.

Procedure

The analyses were performed on a Spectra Physics Model SP-8000 HPLC chromatograph equipped with SP770 variable wavelength UV-detector at 220 nm. The separations were achieved on 25 cm × 4.6 mm id S.S. columns prepacked with 10 μm LiChrosorb Diol purchased from Alltech Associates, Inc. (8).

A gradient elution with *n*-hexane and isopropanol was done as described in our previous report (8) at a flow rate of 1 mL/min and a pressure of about 150 psi. The chromatograms were analyzed using an SP-8000 data system built in the instrument to achieve peak areas and retention times. The samples were dissolved in isopropanol (up to 15% w/w) and 10 μL of solution was injected by automatic loop injector. For further details on the technique of analysis, see ref. 8.

RESULTS

It is important to notice that before injecting the samples into the HPLC we have separated the free polyglycerol layer (phase) from the polyglycerol ester phase by a simple decantation (the 2 phases are completely immiscible). The product was titrated with KOH using the standard procedure to evaluate the acid number in order to learn whether the reaction was finished and the fatty acid was fully consumed. The amount of the polyglycerol was determined by weight.

The product composition of several so-called "polyglycerol monooleates" such as glycerol monooleate (1.G. 1.0); triglycerol monooleate (3.G. 1.0); hexaglycerol monooleate (6.G. 1.0); octaglycerol monooleate (8.G. 1.0); and decaglycerol monooleate (10.G. 1.0), was studied in our previous report (8) and it has been shown that each product is a complex mixture of several isomers. This report discusses the results obtained by high performance liquid chromatography (HPLC) and compares the results to previous publications dealing with the random distribution of the direct esterification of polyglycerol.

Table I summarizes the results obtained from our measurements on triglycerol esters in comparison to the theoretical calculation made by McIntyre (5), assuming all the polyglycerol positions are similar and the triglycerol was a pure triglycerol linear polymer.

For example, for triglycerol monooleate (3.G. 1.0), only 7.7 wt % of free polyglycerol has been found in the product in comparison to 15.5 wt % as calculated from the random distribution. The polymer (40.7 wt %) was esterified by one mole equivalent of fatty acid (monoesterified, called 3.G.1.0), according to the calculated distribution in comparison to 41.0 wt % as actually found by the HPLC. The product (40.7 wt %) was polyglycerol

TABLE I

Composition at Equilibrium of Reaction Mixtures of Triglycerol and 1, 2 and 4 Mole Equivalents of Stearic Acid as Calculated from Random Distribution and as Found from HPLC Analysis

Number of hydroxyl groups esterified	Triglycerol/fatty acid (1:1)		Triglycerol/fatty acid (1:2)		Triglycerol/fatty acid (1:4)	
	Calculated from random distribution (%)	Analyzed by HPLC (%)	Calculated from random distribution (%)	Analyzed by HPLC (%)	Calculated from random distribution (%)	Analyzed by HPLC (%)
0	15.5	7.7	2.4	1.8	0	0
1	41.0	40.7	17.0	39.8	0.2	12.9
2	31.2	40.7	34.6	45.5	3.1	38.5
3	10.5		31.0		16.8	
4	1.6	10.9	13.0	12.8	42.4	48.6
5	0.1		2.1		40.8	

TABLE II

Composition at Equilibrium of Reaction Mixtures of Hexaglycerol and Decaglycerol with One Mole Equivalent of Stearic Acid as Calculated from Random Distribution and as Found from HPLC Analysis

Number of hydroxyl groups esterified	Hexaglycerol/fatty acid (1:1)		Decaglycerol/fatty acid (1:1)	
	Calculated from random distribution (%)	Analyzed by HPLC (%)	Calculated from random distribution (%)	Analyzed by HPLC (%)
0	21.8	13.9	26.0	18.5
1	39.3	29.6	38.4	20.9
2	26.8	39.8	24.2	36.7
3	9.7		8.8	
4	2.1	16.6	2.1	23.9
5	0.3		0.3	
6	0.04		–	

esterified in 2 positions (two hydroxyl groups esterified 3.G.2.0) according to HPLC, whereas only 31.2 wt % of the product was composed of 3.G.2.0 from the theoretical calculations. No differentiation could be made by HPLC between higher esterified groups. Thus, all the higher isomers, including 3.G.3.0, 3.G.4.0 and 3.G.5.0, were combined together and calculated as a single component. A value of 10.9 wt % of the product was composed of such higher isomers (3, 4 and 5 hydroxyl groups esterified) in our results, in comparison to 10.5, 1.65 and 0.1 wt % according to the calculations.

The so-called crude "triglycerol dioleate" (prepared from 1 mol of triglycerol polymer with 2 mol of oleic acid) has been shown to have entirely different composition in comparison to the calculated values. Two and 4/10 wt % free polyglycerol was assumed to exist according to calculations in comparison to 1.8 wt % as found practically. Thirty-nine and 8/10 wt % of the product was 1 hydroxyl group esterified, as found by HPLC, whereas it should consist of only 17.0 wt % according to calculations. The 45.5 wt % was 2 hydroxyl groups esterified in comparison to 34.6 wt % as calculated. Only 12.8 wt % of the product was 3 and more hydroxyl groups esterified in comparison to almost 46 wt % as theoretically calculated. Similar discrepancies were also found for the so-called "triglycerol tetraoleate." In all cases, it was clear that the first hydroxyl group was easy to esterify and, thus, we have always found a higher percentage of monoesterified groups compared to the calculated random distribution. When the oleic acid was in significant excess (3.G.2.0 and 3.G.4.0), the monosubstituted hydroxyl group was a higher percentage compared to the calculated value.

Similar product distribution can be found for higher polyglycerol chains (see Table II).

DISCUSSION

The results from the HPLC analysis of the product distribution of several polyglycerol esters indicate clearly that, during direct esterification, there is no random distribution of fatty acids on available hydroxyl groups. Several reasons could be given for the deviation from the random distribution: (a) the primary hydroxyl groups (at the end of the polymeric chain) are more reactive than the secondary groups due to stearic hindrance problems. (b) The primary hydroxyl group, which is the first to be esterified by a long-chain fatty acid, is practically blocking the secondary hydroxyl group, which is the first to be esterified by a long-chain fatty acid, is blocking the secondary hydroxyl group and reducing its reactivity toward the entrance of additional fatty acid radicals. Thus, the second available acid will prefer to esterify another primary group which is free of such hindrance. (c) Each polyglycerol that has been esterified once becomes a potential emulsifier and is more soluble in the upper layer, consisting of the fatty acids and the product, and thus, it has higher chance to react with another free fatty acid which is available at the upper phase. (d) Different chain lengths of polyglycerol will have significantly different chances to react with the fatty acids because, in short-chain polymers (triglycerol, for

example), a high percentage of the hydroxyl groups was neutralized after one esterification (20% of the available hydroxyl groups for triglycerol), whereas only a small percentage of the hydroxyl group is occupied in long-chain polymers (8% of the hydroxyl groups for decaglycerol).

Many other reasons for not having random distribution among the hydroxyl groups can be listed, stressing the need for full analysis of the product. Therefore, it is advisable to elaborate better techniques for evaluation of the product composition of any food emulsifier in order to meet the food regulations and to better understand its function and applications.

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