**· Technical**

# Preparation and Properties of Some Polyglycerol Esters of Short and Medium Chain Length Fatty Acids[1]

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## ABSTRACT

Mono- and diesters of the short and medium chain acids were prepared with polyglycerols and compared with their corresponding mono- and diglycerides. The physical and chemical properties of such partial esters of polyglycerols, particularly with respect to their oil, water and solvent solubility are given. Polyglycerol esters become more hydrophilic as the molecular weight of the polyol increases. Polyglycerol esters become less hydrophilic as the length of the aliphatic chain of the acid used in esterification is increased. Polyglycerol esters of such short and medium chain fatty acids show promise in applications where surface activity and emulsification, solubilization of oil and water systems is desired.

## INTRODUCTION

Polyglycerols and polyglycerol esters of 16 and 18 carbon-containing fatty acids are well known. They are, in fact, manufactured and sold for a wide variety of uses at the present time. Some of these applications are indicated in a recent communication by Babayan (1).

Bodansky et al. (2) and Babayan et al. (3) have examined the nutritional aspects of the esters prepared from commercial fats and polyglycerols containing from 2 to 30 glycerol moieties. When these compounds were fed to rats, no deleterious effects were noted in appearance, weight gains or cellular structure of the internal organs. Polyglycerols were not deposited in the body fat.

The nutritional value of the mono-, diesters formed by condensation of medium chain fatty acids (caproic, caprylic and capric) and polyglycerols is unknown. In contrast, the medium chain triglycerides have been shown to have unique nutritional properties. Authorities in this field discussed their findings at a special symposium at the University of Pennsylvania (4). It was shown that these oils are readily absorbed via the portal system instead of the lymphatic route of most fats, and they are particularly effective in the treatment of malabsorption syndromes and allied clinical disorders. In this work it has been found there is a rapid, supplemental carrying effect or sparing action for protein and calcium ions which possibly may be explained by the greater surface activity, that is, the hydrophilic properties of medium chain monoglycerides. Greenberger and Skillman (5) have recently updated the literature on the medium chain triglycerides, emphasizing and refocusing attention on the unique character of this class of tailor made fats and oils and their special applications.

The potential uses of short and medium chain esters is not limited to clinical applications. Since the caloric value of partial esters of polyglycerols is between that of carbohydrates and fats, they may find use in the formulation of dietary foods and supplements. The hydrophilic nature of these compounds should make them useful in altering properties of protein solutions and suspensions, in stabilizing agents, moisturizers and softeners, and in many other areas where the high water affinity of the partial esters can be useful.

The purpose of the present study on the mono-, diesters of polyglycerols has been to obtain information on the degree of hydrophilic activity of these compounds. The short and medium chain esters were prepared and partially characterized. Also, the water absorption, solubility and emulsifying properties of the esters were determined by simple tests. For comparative purposes, the corresponding glycerol esters were prepared and similarly evaluated.

## EXPERIMENTAL PROCEDURES

Commercially available polyglycerols of better than 90% purity were obtained from the Drew Chemical Corporation. The pelargonic acid of 95% purity was obtained from Emery Industries, Inc., and the other chemicals from

TABLE I

Properties of Polyol Esters

| Polyol esters | Acid value | Density, g/cm$^3$ | Hydroxyl value |  |
|---|---|---|---|---|
|  |  |  | Calculated | Found |
| Glycerol |  |  |  |  |
| Acetate | 0.10 | 1.205 | 835 | 741 |
| Butyrate | 0.10 | 1.110 | 691 | 606 |
| Caproate | 0.10 | 1.045 | 589 | 525 |
| Benzoate | 0.02 | 1.223 | 572 | 514 |
| Caprylate | 0.05 | 1.008 | 514 | 415 |
| Pelargonate | 0.08 | 0.990 | 482 | 362 |
| Caprate | 0.12 | 0.979 | 456 | 320 |
| Laurate | 0.36 | — | 409 | 215 |
| Triglycerol |  |  |  |  |
| Acetate | 0.25 | 1.255 | 793 | 792 |
| Butyrate | 0.26 | 1.200 | 722 | 743 |
| Caproate | 0.31 | 1.158 | 663 | 718 |
| Benzoate | 0.30 | 1.261 | 652 | 612 |
| Caprylate | 0.48 | 1.112 | 612 | 603 |
| Pelargonate | 0.40 | 1.100 | 589 | 613 |
| Caprate | 0.40 | 1.081 | 569 | 560 |
| Laurate | 0.14 | 1.059 | 532 | 508 |
| Hexaglycerol |  |  |  |  |
| Acetate | 0.39 | 1.266 | 779 | 764 |
| Butyrate | 0.15 | 1.245 | 737 | 752 |
| Caproate | 0.13 | 1.212 | 701 | 701 |
| Benzoate | 0.39 | 1.275 | 693 | 629 |
| Caprylate | 0.18 | 1.184 | 667 | 680 |
| Pelargonate | 0.30 | 1.176 | 652 | 647 |
| Caprate | 0.28 | 1.157 | 636 | 623 |
| Laurate | 0.20 | 1.139 | 610 | 604 |
| Decaglycerol |  |  |  |  |
| Acetate | 0.21 | 1.288 | 771 | 729 |
| Butyrate | 0.16 | 1.263 | 745 | 702 |
| Caproate | 0.19 | 1.236 | 720 | 673 |
| Benzoate | 0.38 | 1.297 | 715 | 659 |
| Caprylate | 0.39 | 1.219 | 697 | 659 |
| Pelargonate | 0.22 | 1.216 | 687 | 642 |
| Caprate | 0.30 | 1.204 | 676 | 631 |
| Laurate | 0.45 | 1.189 | 656 | 615 |

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[1] Presented at the AOCS Meeting, New York, October 1968.

TABLE II

Solubility of Polyol Esters

| | Glycerol | | | Triglycerol | | | Hexaglycerol | | | Decaglycerol | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Polyol ester, % added | 1% | 10% | 100% | 1% | 10% | 100% | 1% | 10% | 100% | 1% | 10% | 100% |
| Water | | | | | | | | | | | | |
| Acetate | S[a] | S | S | S | S | S | S | S | S | S | S | S |
| Butyrate | S | S | D | D | D | S | S | S | S | S | S | S |
| Caproate | D | D | D | D | D | S | D | D | S | S | S | S |
| Benzoate | D | I | I | D | D | I | D | S | I | D | S | S |
| Calrylate | S | I | I | D | D | S | D | S | S | S | S | S |
| Pelargonate | D | I | I | D | D | D | S | S | S | S | S | S |
| Caprate | D | D | D | D | D | D | S | D | D | S | S | S |
| Laurate | D | I | I | D | D | D | D | D | D | S | D | D |
| Ethanol | All esters were miscible with 95% ethanol. | | | | | | | | | | | |
| Isopropanol | | | | | | | | | | | | |
| Acetate | S | S | S | S | S | S | S | D | | D | D | |
| Butyrate | S | S | S | S | S | S | S | D | | D | D | |
| Caproate | S | S | S | S | S | S | S | S | | S | S | |
| Benzoate | S | S | S | S | S | S | S | S | | S | S | |
| Caprylate | S | S | S | S | S | S | S | D | | D | D | |
| Pelargonate | S | S | S | S | S | S | S | D | | D | D | |
| Caprate | S | S | S | S | S | S | S | S | | S | D | |
| Laurate | S | S | S | S | S | S | S | D | | S | D | |
| Cottonseed oil | | | | | | | | | | | | |
| Acetate | D | D | | I | I | | I | I | | I | I | |
| Butyrate | D | D | | I | I | | I | I | | I | I | |
| Caproate | S | D | | I | I | | D | D | | I | I | |
| Benzoate | S | D | | D | D | | D | D | | I | I | |
| Caprylate | S | S | | D | D | | D | D | | I | I | |
| Pelargonate | S | S | | S | D | | D | D | | I | I | |
| Caprate | S | S | | S | D | | D | D | | I | I | |
| Laurate | S | S | | S | D | | D | I | | I | I | |

[a] **Abbreviation:** S, soluble; D, dispersible; I, insoluble.

laboratory supply houses. The gas chromatographic analysis of the acids fractionated in our laboratories indicated a purity of better than 93%. Each ester was formed by heating the free acid with the molar equivalent of the polyol at a temperature where water formation was rapid and steady. Esterification temperatures ranged from 300 F at the start to 400 F towards the end of the reaction. When volatile acids were used in the reaction, it was necessary to add slightly more than the equivalent weight to replace that lost by volatilization. The reaction, carried out under a carbon dioxide atmosphere, was considered complete when the acid value was less than two. The product was deodorized under vacuum of less than 5 mm Hg for 1-2 hrs at temperatures from 230 to 300 F depending upon the ester. The deodorization removed low molecular weight odoriferous by-products, unreacted polyol and the free acids to lower the acid value to less than 0.5.

## RESULTS AND DISCUSSION

It would be impossible to synthesize and characterize all of the short and medium chain esters of all possible polyglycerols. Triglycerol, hexaglycerol and decaglycerol were selected as being representative of this class of compounds; glycerol was also chosen because of its similarity to these compounds and it is more familiar and therefore useful for comparative purposes. Even carbon aliphatic carboxylic acids from acetic to lauric, the nine carbon containing pelargonic acid, and benzoic acid, an aromatic ring containing carboxylic acid, were each reacted with the homologous series of polyglycerols.

TABLE III

Absorption of Water by Monoesters, %

| Compound | Glycerol | Triglycerol | Hexaglycerol | Decaglycerol |
|---|---|---|---|---|
| Acetate | inf | inf | inf | inf |
| Butyrate | 42 | inf | inf | inf |
| Caproate | 9 | 230 | 620 | 900 |
| Benzoate | 10 | 85 | 290 | 320 |
| Caprylate | 4 | 1800 | 850 | inf |
| Pelargonate | 16 | 500 | inf | inf |
| Caprate | 14 | 250 | 800 | inf |
| Laurate | — | 30 | 70 | 100 |

All of the partial esters of the polyglycerols were liquids at room temperature; the glycerol mono-, diesters of capric, pelargonic and lauric acids were crystalline whereas the lower esters were liquid. They varied in color from about Gardner 1 to 8. The decaglycerol esters were heavy and so thick that they were barely pourable at room temperature. The viscosity of the triglycerol esters was the least of the polyglycerols but still greater than that of the glycerol mono-, diesters.

Some of the properties of the esters are shown in Table I. The hydroxyl values found for the glycerol series were, as a whole, low as compared to the calculated. The calculated values represent 100% monoglyceride whereas the reaction of equimolar mixtures of glycerine and acid does not produce such an ideal product. If the laws of random distribution are applied to this reaction we would expect about 45 mole per cent monoglyceride and 30 mole per cent free glycerol at completion. This would correspond to a free glycerol content from 10-20% by weight for the laurate and acetate esters respectively. Removal of free glycerol lowers the hydroxyl value dramatically, since the theoretical hydroxyl value of glycerol is 1800.

The triglycerol esters were stripped less rigorously than the glycerol esters as evidenced by higher acid values. The observed hydroxyl values are, however, reasonably close to the values calculated from the monoesters. The hexaglycerol esters likewise had hydroxyl values which were in line with the theoretical values for the monoester.

In all cases the observed values for the decaglycerol monoesters was considerably below that of the calculated value. In this series the high viscosity of products necessitated the use of higher stripping temperatures to

TABLE IV

Stability of Oil-Water Suspensions in the Presence of Polyglycerol Esters

| | Glycerol | | | Triglycerol | | | Hexaglycerol | | | Decaglycerol | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | PN | IPM | MO | PN | IPM | MO | PN | IPM | MO | PN | IPM | MO |
| Acetate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Butyrate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Caproate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Benzoate | — | — | — | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 0 |
| Caprylate | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| Pelargonate | 2 | 0 | 0 | 4 | 2 | 4 | 1 | 1 | 0 | 4 | 1 | 2 |
| Caprate | — | — | — | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 2 |
| Laurate | 4 | 4 | 2 | 4 | 4 | 4 | 2 | 2 | 3 | 4 | 3 | 2 |

remove the free acid and polyol. This perhaps resulted in the loss of some of the shorter chain polymers in the decaglycerol with the resultant lowering of the hydroxyl value. It is also conceivable that there was some polymerization during the stripping.

The observed densities are expected. The density of the ester decreases with increasing length of the acid chain moiety. The aromatic benzoate is an exception; in each series of glycerol or polyglycerol esters the benzoate derivative is the most dense. With esters of a given acid, increase in the size of the polyol results in an increase in density.

The solubility of the esters in water, alcohols and cottonseed oil was also determined. The data (Table II) should give an indication of the hydrophilic (or lipophilic) nature of the esters. All the monoesters except the benzoates were either soluble or readily dispersible in water. The increasing molecular weight of the aliphatic chain tended to lower solubility whereas an increase in molecular weight of the polyol moiety tends to increase solubility in water. The glycerol esters, having fewer free hydroxyl groups, had the least attraction for water. The hydrophilic nature of the polyglycerol esters is further indicated by data in Table III. These values show the per cent water absorbed when water was added to the stirred ester until a persistent haziness formed. The polyglycerol esters showed a greater affinity for water than the glycerol esters. With but one exception, esters in the triglycerol series were less hydrophilic than those of the hexaglycerol series; the decaglycerol esters absorbed the most water. In a given series of polyol esters, an increase in the molecular weight of the aliphatic chain of the component acid resulted in less water-binding capacity of the ester. The caproate and benzoate esters did not absorb as much water as would be expected from their relatively low molecular weights. The amount of water imbibed by the benzoate series of esters was intermediate between the caprate and laurate.

All esters were found to be completely miscible in 95% ethanol but only the homologous series of glycerol and triglycerol esters were completely miscible with isopropanol (Table II). Hexaglycerol esters were soluble at the 1% level but at the 10% level they were only dispersible. Although the caprate and laurate esters were soluble in isopropanol at the 1% level the decaglycerol esters were less easily dispersed than the other esters.

In the final series of solubility tests, refined cottonseed oil was used as the diluent. The results show that the decaglycerol esters were insoluble at even low concentrations whereas only the monoacetate and monobutyrate of hexaglycerol were insoluble. The other hexaglycerol esters, were dispersible at both the 1% and 10% levels. Although the triglycerol monoesters of two, four and six chain acids were soluble, the increasing lipophilic nature of the esters was noted in the esters of 9, 10, and 12 carbon acids. These esters were soluble in the cottonseed at the 1% level and could be readily dispersed at the 10% level. Furthermore, the glycerol esters showed the greatest lipophilic activity.

In general the solubility studies indicated that, as expected, the decaglycerol esters were the most hydrophilic whereas the glycerol monoesters were the least hydrophilic. Within each homologous series, increasing chain length decreased the hydrophilic nature of the monoester. In no case have we found literature values indicating complete solubility of mono-oleates or stearates of hexa- and decaglycerols in oils. In the case of triglycerol esters of the longer chain length acids, there is apparently good solubility at low levels but at levels above 1% or 2% the products are only dispersible (6,7).

Since the longer chain monoesters of several of the polyglycerols have been found to be useful as dispersants or emulsifiers in diverse applications, a simple test for emulsifying action was devised. Ten per cent monoester was dispersed in 65% water, mixed with 25% oil, and twice run through a hand homogenizer. A 4 oz. oil sample bottle was filled and allowed to stand three weeks. At this time the amount of emulsion remaining was observed and scored. If no emulsion remained it was given a zero score, whereas those that showed no separation were given a score of four. Intermediate values were assigned to the partially separated suspensions.

Stable emulsions were not formed with the polyglycerol or glycerol monoesters of acetic, butyric, or caproic acids under the conditions of the test (Table IV). In fact, there was nearly complete separation into oil and water layers in less than a day. The caprylate esters were only slightly more effective but again, no stable suspensions were found. The most stable emulsions were those containing glycerol monolaurate, triglycerol monopelargonate, or triglycerol monolaurate followed by the decablyderol esters of the same acids.

The ability to have polyglycerol esters of varying chain length and varying polymer length strongly indicates the broad scale range of hydrophilic to lipophilic products which should have potential utilization in the clinical and dietary applications.

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