

POLYGLYCEROLS AND POLYGLYCEROL ESTERS AS POTENTIAL WATER ACTIVITY REDUCING AGENTS. CHEMISTRY AND SENSORY ANALYSIS

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1. INTRODUCTION

The development of commercially acceptable intermediate moisture foods for human consumption depends on the use of efficient, safe, and palatable water vapor pressure reducing compounds. Many of these humectant substances act through different mechanisms of "binding" water, thus and restricting the availability of water for microbial growth. In general, the materials used today belong in the categories of salts, sugars, and polyols, with the latter offering particular promise (12, 26). In practice, considerable use has been made of glycerol and propylene glycol, which in general, have a deleterious effect on taste characteristics (burning sensation, etc.) of the food product. Other compounds, such as sucrose, corn syrup, sorbitol and dextrose, are restricted to formulations where sweetness is desirable.

An examination of the published literature (7, 17) reveals both a continuing interest in intermediate moisture foods and a persisting problem due to the lack of suitable substances to reduce water activity. A successful water vapor pressure reducing agent should meet the following criteria :

1. safety (approval by the appropriate national health agency) ;
2. efficiency in lowering water activity without any adverse effects on the host product ;
3. quantitative prediction of water activity lowering effect ;
4. low chemical reactivity ;
5. ease of incorporation ;

6. low cost.

As is the case with other research centers, especially in industry, our laboratories have maintained a long, though fluctuating, interest in intermediate moisture foods, both through in-house and contract work (11).

During the last two years our attention has focused on certain groups of non-ionic surface active agents, known as polyglycerols and polyglycerol esters, as possible water activity reducing substances. The polyglycerols are formed by intermolecular dehydration of glycerol heated in the presence of either alkaline or acidic catalysts (22). Most often alkaline catalysts such as sodium hydroxide or sodium acetate, at 250-275°C are used in an inert atmosphere of nitrogen or carbon dioxide. Esterification with fatty acids is often accomplished at 190-220°C resulting in a mixture of linear and cyclic esters. In commercial preparation, the complexity of the mixture of the esters is due to the composition of the starting fatty acids, the position and extent of esterification, and the number of ether linkages present. By changing the degree of polymerisation of the glycerol and the extent of esterification the hydrophylic-lipophylic balance (HLB) can vary from about 4 to about 13 (3, 21), and therefore the physical properties and functionality of these compounds in foods.

Table I shows some of the main functional properties and examples of foods in which the polyglycerol ester compounds are used. In earlier years the usefulness of these agents in foods was severely limited due to the presence of undesirable colors and flavors. Subsequent improvements to the manufacturing process resulted in a better control of composition and in refinements which reduced the presence of objectionable impurities. An extensive patent and other literature exist on the synthesis, chemistry, and physical properties and uses of these compounds (2, 8, 10, 14, 19, 24, 25, 27, 28).

Garti and Aserin (18), using HPLC, showed that any theoretical calculation of the product composition of polyglycerol esters could not be correct since the fatty acid radicals are not distributed at random among all available hydroxyl groups, the internal positions (secondary hydroxyls) of the glycerol polymer being esterified with greater difficulty than the primary hydroxyl groups.

Neissner (23) reported that two-dimensional TLC on boric acid-impregnated silica gel 60 precoated plates was a simple, useful method for separating fatty acid polyglycerol esters into a larger number of compounds, providing an insight into their complex character and allowing identification of the individual compounds. Babayan and McIntyre (3) reported on the physical and chemical properties of mono- and diesters of short and medium chain acids of polyglycerols. Polyglycerol esters become more hydrophilic as the molecular weight of the polyol increases ; they become less hydrophilic as the length

Table I. Uses of polyglycerol esters in foods.

<u>Role related to functionality</u>	<u>Foods where used</u>
Emulsifiers	Margarines, shortenings, confectionary products
Stabilizers	Sweetened citrus oil beverages
Antispattering agents	Frying fats
Aerating agents	Lipid-based confections
Anti-bloom agents	Chocolate formulations
Crystallization inhibitors.	Salad and cooking oils
Dough improvers	Bread and bakery products
Whiteners	Coffee
Flow property modifiers	Chocolate

of the aliphatic chain of the fatty acid used in esterification increases. Short and medium chain fatty acid polyglycerol esters are promising in applications where surface activity, emulsification and solubilization of oil and water systems are desired.

The literature on the physicochemical foundations of water binding by polyglycerol esters in food emulsions is relatively sparse (8, 16). Hemker (20) reported on the liquid crystalline types and the crystalline gel state of tri- and octaglycerol esters. Triglycerol monoesters showed hexagonal liquid crystalline activity as well as limited regions of stable α crystalline gels. Octaglycerol monoesters exhibited primarily hexagonal liquid behavior which (below their Kraft point) formed stable α -gels. In general, water as well as other polar liquids function as crystalline modifying solvents that effectively alter simple liquid-to-solid phase transformations of amphiphilic molecules upon cooling to include the many mesomorphic structures. The functional properties of polyglycerol esters are largely predicted from their crystalline associative properties at the emulsion interface.

The functionality (emulsification properties) of the polyglycerol esters is often discussed in terms of their hydrophilic-lipophilic balance (HLB)

$$HLB = 20 (1 - S/A)$$

where S = saponification value of the ester and A = acid value of the fatty acid used in the ester preparation. The higher the HLB value, the greater its hydrophilic property, the HLB ranging from 0 to 20. However, no direct, straightline relationship exists between HLB and functional properties (20).

Figure 1, reported by McIntyre (21), shows the range of HLB values

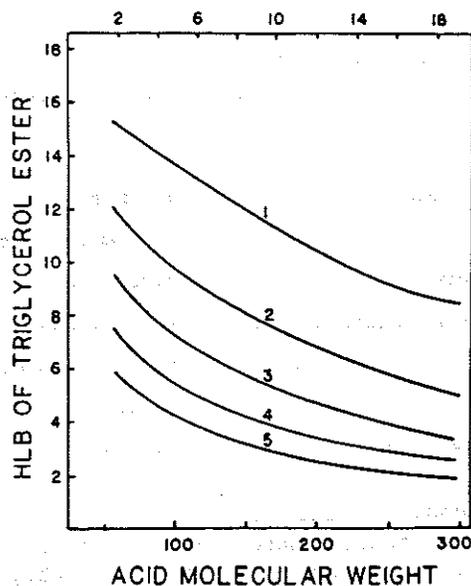


Figure 1. Effect of fatty acid chain and degree of esterification on the HLB of triglycerol esters (21).

of compounds theoretically possible to obtain by esterifying triglycerol with organic acids. The number over the horizontal line shows the degree of esterification, i.e., the number of molecules of the straight chain organic acid combined with one molecule of triglycerol. A decrease in the molecular weight of the fatty acid results in an increase of the hydrophilic nature of the ester, whereas an increase in the number of fatty acid moieties will result in a more lipophilic product. For example, the HLB values range from 1.9 for the penta-stearate to 8.8 for the monostearate; the corresponding palmitate esters range from 2.1 to 9.3.

2. NUTRITIONAL ASPECTS AND SAFETY

The literature on the metabolism of polyglycerols and their fatty acid esters is limited. In the first metabolic study reported in the English literature, Bodansky et al. (9), using albino rats fed a basic diet supplemented either with lard (5 or 10 %) or polyglycerol ester of stearic and oleic acids (5 or 10 %), reported that the rate of growth of both the lard and polyglycerol ester fed animals was normal or better than the basic diet fed animals. Histological examination of tissues disclosed no abnormalities in either of the experimental groups. In other experiments using polyglycerol esters of commercial oleic acid and linseed oil, the growth was normal or better than normal in all groups. Examination of fecal lipids showed

complete utilization of the polyglycerol esters of oleic and linoleic acids, as well as of the linseed oil and other fats used. The composition of the depot fat was only slightly influenced by the kind of fat incorporated into the diet. Babayan (1) used polyglycerol esters of fatty acids derived from cottonseed and peanut oils in feeding experiments with rats. He studied the gain in weight, intestinal absorption, and epididymal fat composition, together with post-mortem histological examination of tissues. No adverse effects of the polyglycerol diets were found. The polyglycerol and lard fed rats (both at 8 % of the diet) were heavier than those fed the basic diet. The fecal lipids of the test groups resembled those of the control groups. The glycerine content of the lipids extracted from depot fat suggested that only triglycerides were present or that at least no appreciable polyglycerol amounts were deposited. Autopsies at the end of the experiment and histological examination of the liver, kidney, and ileum showed no abnormality.

Polyglycerol esters of fatty acids up to and including decaglycerol esters, may be used in foods under the U.S. Federal Food, Drug, and Cosmetic Act, provided they meet some special requirements of the type of oils and fatty acids used in their preparation, and they are used in amounts not greater than that required to produce the desirable effect (13, 15).

3. EXPERIMENTAL WORK

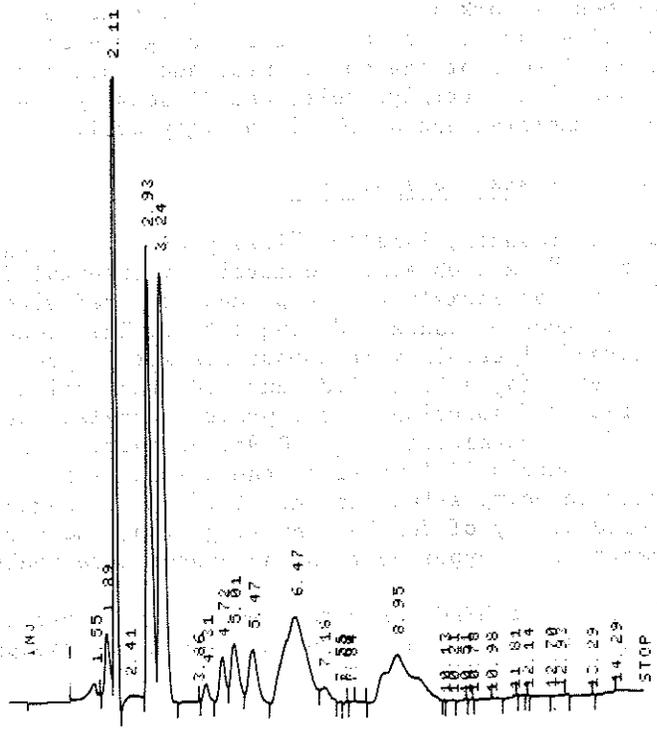
The experimental work performed in our laboratories encompassed : 1) the chemical separation of commercial polyglycerol products, identification of some of the components, and synthesis of linear diglycerols and linear triglycerols, and 2) sensory evaluation of solutions of commercial and synthetic polyglycerol.

3.1. Chemical analysis and synthesis

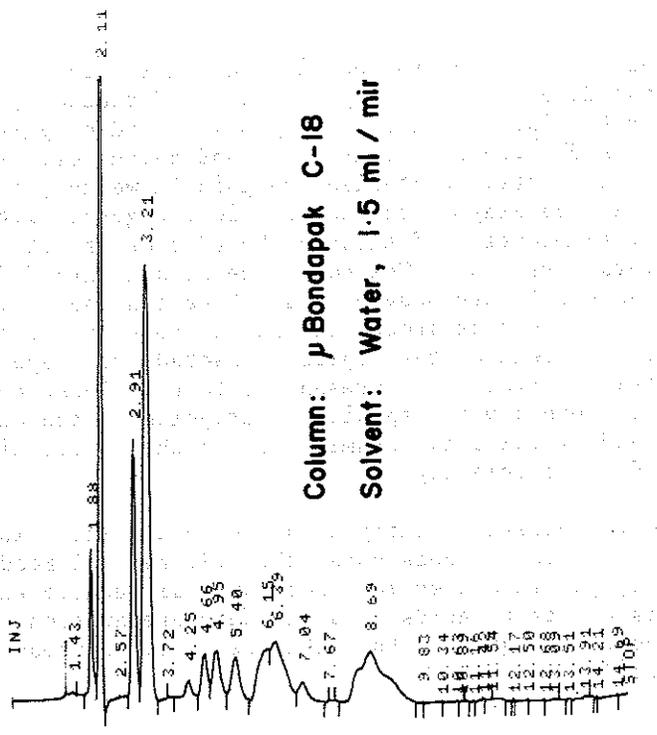
Polyglycerol products, labelled "Triglycerol", "Hexaglycerol", and "Decaglycerol" were obtained commercially (Capital City Products Company, Division of Stokely Van Camp) and compared with glycerol as to their water vapor pressure reducing effect. The products labeled "tri" and "hexa-" glycerols were comparable with glycerol in reducing the water activity ($a_w = 0.84, 0.81$ and 0.81 respectively for 50 % solutions). The 50 % solution of the product labeled "deca-glycerol" exhibited on first examination $a_w = 0.96$. However, this product was found later to contain 30 % water ; otherwise it was similar in its water activity reducing effect to the "tri" and "hexaglycerol". The products seemed worthy of further investigation, and high performance liquid chromatography appeared to be an appropriate analytical method.

Figure 2 shows the HPLC chromatograms of the commercial "triglycerol" and "hexaglycerol", each separated on a reverse phase column

" TRIGLYCEROL "



" HEXAGLYCEROL "



Column: μ Bondapak C-18
Solvent: Water, 1.5 ml / min

Figure 2. HPLC chromatograms of commercial "triglycerol" and "hexaglycerol".

with water as eluent. Experimental conditions are stated on the Figure. More details will be published in a separate paper (4).

The striking characteristics of the chromatograms are their complexity and similarities. Each product is a mixture of polyglycerol compounds; one can distinguish at least 15 peaks. The first major peak (at 2.11 min) is glycerol (ca 20 %). The third major peak at 3.24 min. corresponds to linear diglycerols (25-30 % of the mixture), as verified by the synthesis results described later. The peaks eluting between 8 and 10 min. (10-12 % of the mixture) correspond to linear triglycerols. Similar results, not shown here, were obtained by the separation of the commercial "Decaglycerol" where the diglycerols were still the major components (ca 18 %).

Figure 3 shows the three isomers of diglycerol, neglecting cyclic isomers formed by elimination of two molecules of water. The linear isomer is most likely to be the major product in a non-specific condensation. It should be emphasized that each of these are not simple compounds, due to the existence of optimal isomers. Optical isomerism is unlikely to affect the water activity depression, but it may make a difference in taste.

Figure 4 shows the isomers of triglycerol, disregarding cyclic forms and chirality. The linear triglycerol at the top left is that most likely to be the major product in a non-specific condensation due to the higher reactivity of the primary hydroxyl groups. The three chiral centers give rise to four isomers (two meso forms and a pair of DL-isomers).

In view of the complexities of the commercial products, it was considered desirable to obtain homogeneous samples of linear diglycerol and linear triglycerol in order to compare their water activity reducing effect against glycerol. Figure 5 shows the synthesis of linear diglycerol.

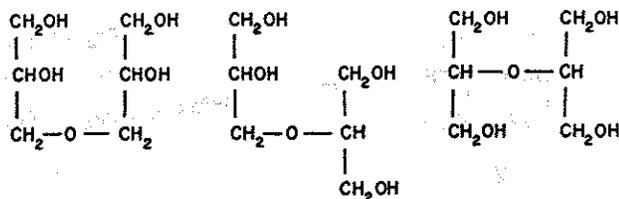


Figure 3. Isomers of di-glycerol.

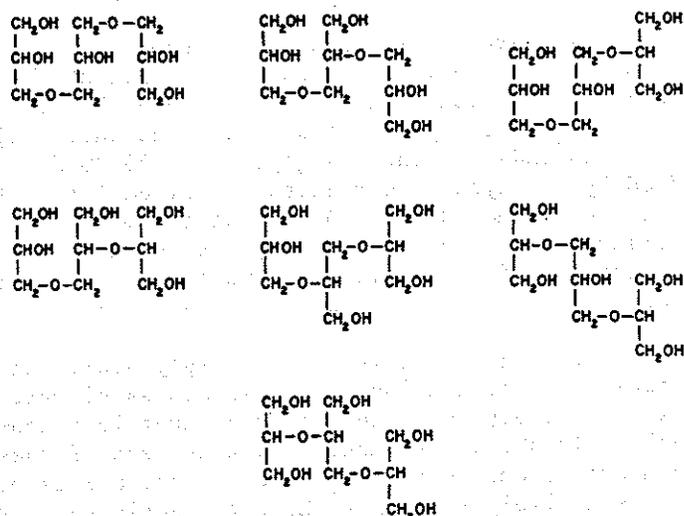


Figure 4. Isomers of tri-glycerol.

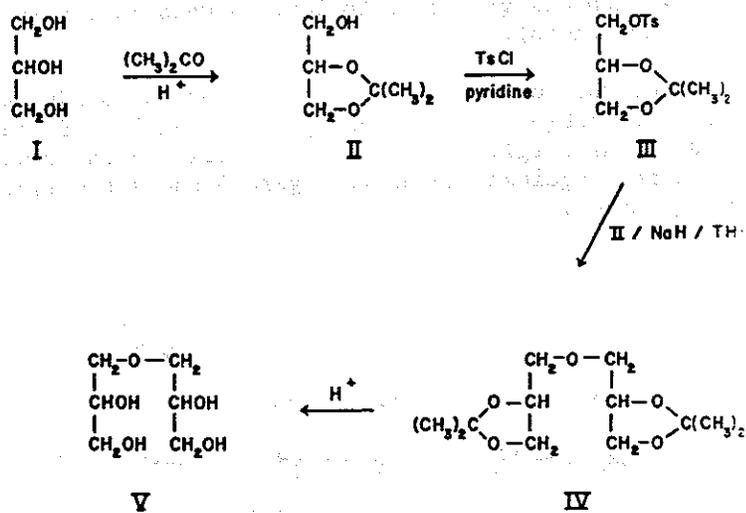


Figure 5. Synthesis of linear triglycerol.

In this procedure, glycerol was treated with acetone and an acidic catalyst to give isopropylidene glycerol, compound II. Treatment of II with tosyl chloride in pyridine, gave the tosylate of isopropylidene-

dene glycerol, compound III. Compounds II and III were condensed under basic conditions to form di-isopropylidene-diglycerol, compound IV. The isopropylidone groups of IV were cleaved by dilute acid to give the linear diglycerol, compound V.

A similar route has been followed to synthesize the linear triglycerol. Figure 6 shows the HPCL fractionation of linear triglycerol, using the recycle mode of the liquid chromatograph.

On the ninth cycle the larger peak was resolved into three component peaks, which are in the expected ratio. One of the meso isomers, corresponding to the slowest moving peak, was obtained crystalline.

3.2. Sensory analysis

3.2.1. Method

a. Subjects. Twenty employees of the U.S. Army Natick Research and Development Laboratories volunteered as subjects. Age of subjects ranged from 19 to 43 years. None were smokers. All had previously participated in taste and acceptance studies and were familiar with the psychophysical methods employed.

b. Samples. Test samples consisted of five concentrations (20.0, 10.0, 5.0, 2.5, and 1.25 % w/w) of sucrose (reagent grade), glycerol (certified ACS), the commercial triglycerol (Capitol City Products Co., Columbus, OH), the synthetic linear diglycerol, and the synthetic linear triglycerol. In addition to these 25 test samples, distilled water was included as a control sample. All test compounds were mixed with distilled water the day before the test and stored overnight. On the morning of the test, all samples were removed from storage and allowed to equilibrate to room temperature (23°C).

Column: μ Bondapak C-18

60cm x 7.8mm

Solvent: Water / CH₃CN (99:1)

3 ml / min

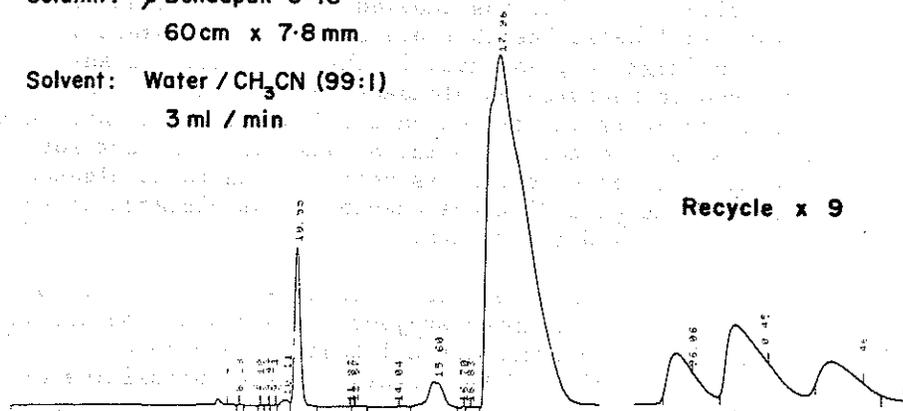


Figure 6. HPLC fractionation of linear triglycerol.

c. Procedure. Subjects were asked to judge the odor intensity, odor pleasantness (or unpleasantness), taste intensity and taste pleasantness (or unpleasantness) of each sample. Judgments of odor intensity and pleasantness/unpleasantness were made by placing the sample cup to the tip of the nostrils and inhaling once. Judgments of taste intensity and pleasantness/unpleasantness were made by having the subject pinch his/her nostrils closed. The subject then sipped the entire contents (5 ml) of the test cup, held it in his/her mouth for three seconds, and expectorated. Immediately after expectorating, subjects made their judgments of taste intensity, followed immediately by their judgment of pleasantness and/or unpleasantness. Subjects then rinsed with distilled water and awaited the next trial. Samples were presented randomly, a 60 second inter-stimulus interval separated all trials, and a distilled water pre-rinse was used.

Judgments of odor and taste intensity were made using the method of modulus-free magnitude estimation. Subjects judged the magnitude of the first sample by assigning an arbitrary number to it. Subsequent judgments were made relative to the first, so that if the second stimulus appeared to be one-third as intense as the first, it was assigned a number one-third as large; if it appeared twice as intense as the first, it was assigned a number twice as large, etc. Each stimulus was also profiled for taste quality, by having the subject divide his estimate of overall intensity among the four basic taste qualities (salty, sour, sweet, bitter).

Judgments of odor and taste pleasantness/unpleasantness were made using a 20-cm line scale. The left end-point was labeled "extremely unpleasant", the right end-point was labeled "extremely pleasant", and the mid-point was labeled "neither pleasant nor unpleasant". Subjects made ratio judgments, so that, if the odor/taste of any sample was perceived to be twice as pleasant (or unpleasant) as the first stimulus, a hash-mark was placed on the line at a distance that was twice the distance from the mid-point as was the hash-mark for the first stimulus. Samples perceived as being one-third as pleasant (unpleasant) were placed at a distance one-third the distance of the first hash-mark from the mid-point, etc.

3.2.2. Results. All judgments were first "equalized" to account for differences in internal moduli among subjects. Medians of the equalized magnitude estimates of overall taste intensity were then calculated. Figure 7 is a plot of the relative taste intensities of the five test compounds. The data are plotted relative to sucrose, which has a value of 1.0. Except for the linear triglycerol at the lowest three concentrations, 0.1, 0.4, and 0.7 log percent concentrations (1.25, 2.5, and 5.0 % w/w), all of the test compounds were perceived to be of equal or lesser taste intensity than sucrose. Overall, the commercial triglycerol was perceived to be the least intense.

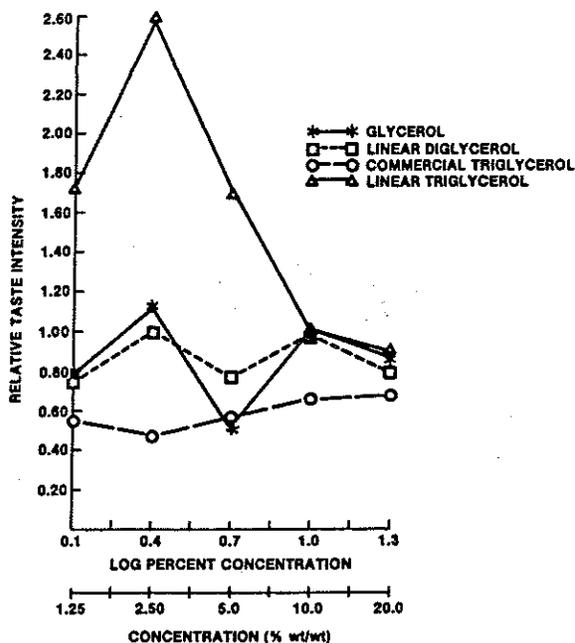


Figure 7. Plot of the relative taste intensities of the test compounds as a function of concentration. The data are indexed relative to sucrose, which has a value of 1.0 at all concentrations.

Friedman ANOVA's conducted on the taste intensity data at each concentration showed significant differences across compounds ($p < .01$) at all concentrations except at 10 % w/w, as reflected in the data of Figure 7. (Note that the difference between the commercial triglycerol and each of the other compounds at 10 % w/w was not sufficient to produce an overall significant effect of compound). Post hoc comparisons of the mean values confirmed that the linear triglycerol was perceived to be significantly more intense than sucrose (and all other compounds) at the lowest three concentrations, while the commercial triglycerol was perceived to be significantly less intense than sucrose at these same concentrations. The only other significant differences were between sucrose and glycerol at 2.5 % and 5.0 % w/w.

The data in Figure 7 reflect judgments of overall taste intensity, independent of taste quality. In order to assess differences in taste quality among the compounds, the magnitude estimation data were analyzed by taste quality. The median magnitude estimate assigned to each taste quality in the profiling procedure was calculated. Analysis of these data revealed that both sucrose and glycerol were predominantly sweet at all concentrations, although glycerol possessed some bitterness, particularly at the lower concentrations. Although

the commercial triglycerol had moderate sweetness at the highest concentrations, it also had a significant bitter component at all concentrations. (Note, however, that some of the bitterness at the two lowest concentrations may be to the commonly observed "water taste" phenomenon (5, 6), since this bitterness occurred at the lowest concentrations of all compounds and was also elicited by the distilled water control samples.)

Unlike glycerol and the commercial triglycerol, the profiles for the two linear polyglycerols possessed significant sour components. In the case of the linear diglycerol, the sourness was present together with bitterness and sweetness. In the case of the linear triglycerol, sourness and bitterness were the only salient qualities of the solutions.

Figure 8 is a plot of the median judgments of taste pleasantness/unpleasantness as a function of concentration for each of the test compounds. The curves drawn through the data summarize the trends.

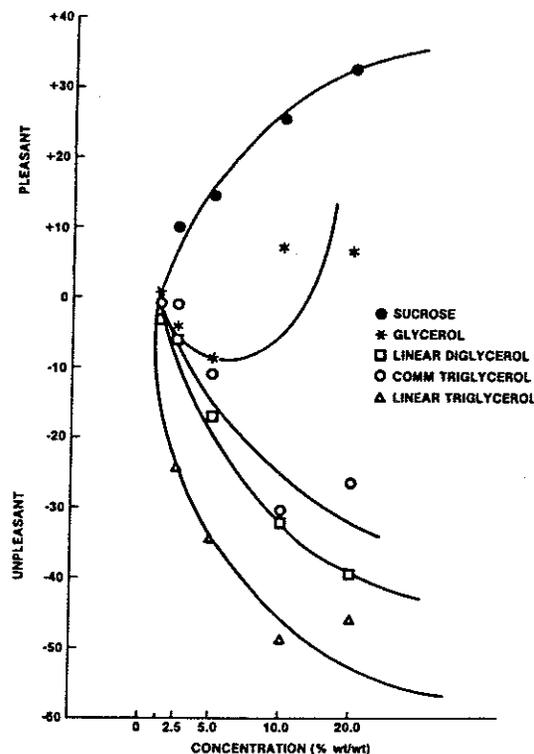


Figure 8. Plot of the median pleasantness/unpleasantness ratings of each compound as a function of concentration. Zero (0.0) on the ordinate reflects a judgment of "neither pleasant nor unpleasant". Pleasantness ratings are indicated by positive values and unpleasantness is indicated by negative values.

For all compounds, the pleasantness/unpleasantness of the lowest concentration is near zero (0.0), indicating "neither pleasant nor unpleasant". As concentration increases, the pleasantness/unpleasantness of all of the polyglycerols undergoes a negative deceleration, with solutions becoming more unpleasant with increases in concentration. Sucrose, on the other hand, exhibits a negatively accelerating function, with solutions becoming more pleasant with increases in concentration. Glycerol exhibits a non-monotonic function, with pleasantness decreasing and then increasing as a function of concentration. Only the sucrose and glycerol solutions were described as pleasant at any concentration.

Friedman ANOVA's conducted on the judgments of taste pleasantness/unpleasantness at each concentration revealed a significant effect of compound at all but the lowest concentration. Post-hoc analyses showed sucrose to be significantly more pleasant than all of the other compounds at each concentration except 2.5 % wt/wt, where sucrose was not significantly different from glycerol. The linear triglycerol was significantly less pleasant than all of the other compounds at 10 % wt/wt and was significantly less pleasant than all but the linear diglycerol at 5.0 and 2.5 % wt/wt. The other significant differences were between glycerol and the linear diglycerol at the two highest concentrations, and between glycerol and the commercial triglycerol at 5.0 % wt/wt.

Although all of the test compounds had salient taste characteristics, only the linear polyglycerols had salient odor characteristics. Friedman ANOVA's and post-hoc contrast tests conducted on the odor intensity data revealed that the two linear polyglycerols were not significantly different at any concentration, but both had significantly higher odor intensity than all of the other test compounds at each concentration. Similar results were found for the odor pleasantness/unpleasantness judgments. Concerning the quality of the odors of the polyglycerols, subjects described them as being "acidic" or of "burnt caramel" character. In all cases they were described as unpleasant.

3.3.3. Discussion of sensory analysis. The data in Figure 7 allow direct comparisons of the taste intensity of the five compounds as a function of concentration. Compared to sucrose, the linear diglycerol exhibits a very high relative taste intensity. Glycerol and the linear diglycerol exhibit relative taste intensities that are equivalent to or less than sucrose. Only the commercial triglycerol exhibits a lower relative taste intensity than sucrose at all concentrations.

Since a low relative taste intensity is a desirable characteristic for any compound that is to be used as a humectant, the commercial triglycerol seems to have the most potential for use, since its

relative taste intensity was approximately 60 % of that for sucrose throughout the concentration range. Unfortunately, the data in Figure 8 show that all of the polyglycerols, including the commercial triglycerol, have a strong negative hedonic quality. This fact makes all of the polyglycerols unlikely candidates for use as humectants. The source of the negative hedonic taste characteristic of the polyglycerols appears to be the bitterness associated with each, as well as the sourness associated with the linear diglycerol and linear triglycerol.

It is also clear from the sensory data that the linear polyglycerols have a significant odor component that is not present in the sucrose or glycerol solutions, nor in the commercial triglycerol that was tested, except at the highest concentration. Moreover, the odor component of these compounds has an unpleasant quality that is commonly described as burnt caramel or acrid. The chemical origin of this odor quality may be due to the formation of small amounts of volatile unsaturated compounds during the synthetic procedures. Since the products were not obtained in crystalline form, complete removal of these contaminants was not achieved.

Of particular importance and interest to understanding the relationship between the chemistry of the polyglycerols and their perceived taste is the difference observed between the commercial triglycerol and the linear triglycerol. The former had a significantly lower taste intensity (Fig. 7), much greater sweetness, negligible sourness, higher taste pleasantness/unpleasantness (Fig. 8) and negligible odor, as contrasted with the linear triglycerol. However, these differences can be explained through examination of the HPLC analysis of the commercial triglycerol, which showed it to be a mixture of twenty compounds, of which over 17 % was glycerol. Since the pure glycerol in this study had comparable taste intensity to the commercial triglycerol (Fig. 7), was predominantly sweet, lacking any sour quality, had high taste pleasantness/unpleasantness (Fig. 8), and had no odor, it is reasonable to conclude that the taste and odor characteristics of the commercial triglycerol were greatly determined by the glycerol component of the mixture. The synthetic tri-glycerol, having no other chemical components, reflects the true taste and odor characteristic of triglycerol.

Of some future interest is the fact that linear di- and tri-glycerols have very low vapor pressures and, if pure, are unlikely to have detectable odors. The present data clearly demonstrate that the pure commercial polyglycerol has low utility, due to its odor and taste characteristics. Whether the purified forms of the synthetic materials will have greater utility depends entirely on empirical results of psychophysical tests. Three of the four possible isomers of linear triglycerol have now been obtained in crystalline form (and therefore in a more highly purified state). If these can be prepared economically in amounts sufficient for psychophysical tes-

ting, it would be instructive to determine a) if they have more acceptable odor and taste characteristics, and b) how stereochemical changes affect their sensory qualities.

4. FUTURE WORK

We hope that our brief review of the subject and the experimental work presented here will activate interest and catalyze further research on polyglycerols and their esters in foods. A great deal more needs to be done on the separation, identification, and synthesis of the individual compounds constituting the commercial mixtures. Although the water activity reducing effects of the isolated compounds would probably be similar, at least among the linear forms (considering the abundance of hydroxyl groups exposed for binding), this needs to be tested experimentally. Basic work on the structuring of water molecules and modes of binding could be useful in predicting the water activity reducing effect. The determination of the moisture sorption isotherms of the great number of individual compounds would be a logical step next to their isolation, together with the application or development of equations to predict the water activity of solutions of different solute concentrations. Finally, and probably the most important, the safety and sensory characteristics of the isolated compounds need to be examined.

REFERENCES

1. Babayan V.K. (1964). *J. Am. Oil Chem. Soc.* 41, 434
2. Babayan V.K. (1968). *Food Product Development* April-May.
3. Babayan V.K. and McIntyre R.T. (1971). *J. Am. Oil Chem. Soc.* 48, 307
4. Ball D.H. and Alabran D.M. (In preparation) *Analytical and Synthetic studies of polyglycerols.*
5. Bartoshuk L.M. (1968). *Percept. and Psychophys.* 3, 69
6. Bartoshuk L.M., McBurney D.H. and Pfaffmann C. (1964). *Sci.* 143, 967
7. Beary E.G. (1967). U.S. Army Natick Laboratories Bibliographic Series 67-1. Defense Technical Information Center, AD656927, Cameron Station, Alexandria, VA 22314.
8. Benson F.R. (1967). In "Nonionic Surfactants" (M.J. Schick, ed.) pp 247-299, Marcel Dekker, New York.
9. Bodansky M., Hermann C. and Cambell K. (1938). *Biochem. J.* 32.
10. Brankamp G.W. (1970). U.S. Patent # 3489573.
11. Brockman M.C. (1970). *Food Technol.* 24, 60
12. Chirife J. and Fontan C.F. (1980). *J. Food Sci.* 45, 1717
13. Code of Federal Regulations (CFC) (1982). CFC 21, 8 172.854, April.
14. Dai Nippon Sugar Manufacturing Co. Ltd. (1970). Japanese Patent 29 411/70, 29 412/70.
15. Federal Register (1970) Food additives. Polyglycerol esters of fatty acids. 35 (225, Nov. 19) 17781.
16. Friberg S. (1976). *Food Emulsions.* Marcel Dekker, New York.
17. Garber E.B. and Kapsalis J.G. Water Activity and Moisture Relationship in Foods : A Bibliography with Summaries. (in press)
18. Garti N. and Aserin A. (1982). *J. Am. Oil Chem. Soc.* 59, 7, 317.
19. Garti N., Aserin A. and Lindner C. (1981). *Bakers Digest* 55, 4, 19, 24.
20. Hemker W. (1981). *A.O.C.S.* 58, 114
21. McIntyre R.T. (1979). *J. Am. Oil Chem. Soc.* 56, 835a.
22. Miner C.S. and N.N. Dalton (1953). In "Glycerol" p 366, Reinhold, New York.
23. Neissner R. (1980). Polyglycerols and Partial Fatty Esters of Polyglycerols (Preparation, Chemical Constants, TLC Separation). Polyglycerine und fettsaeure-polyglycerinpartialester (Herstellung, Kennzahlen, DC-Trennung).
24. Noznick P.P. and Tatter C.W. (1970). U.S. Patent # 3 514 298.
25. Rossen J.L. (1970). U.S. Patent # 3 528 823.
26. Sloan A.E. and Labuza T.P. (1975). *Food Product Dev.* 9, 7.
27. Stenzel W.R. and Franzke C. (1977). *Lebensmittelindustrie* 24, 11, 503.
28. Stewart M.F. and Hughes E.J. (1972). *Process Biochem.* 7, 12, 27.