Methyl Glucoside Fatty Acid Diesters

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Since free hydroxyl groups in many of the nonionic-type of surface-active agents contribute to the hydrophilic properties of these products, the polyhydric alcohols are valuable raw materials for the manufacture of such surfactants. A major consideration in the selection of a polyhydric alcohol for this purpose is its hydroxyl content and molecular structure. In order to investigate the effect of the methyl glucoside configuration on the surface-active properties of its esters, a study was undertaken to develop suitable techniques for the preparation of diesters of this cyclic polyhydric alcohol by direct esterification.

Synthesis of various fatty acid esters of methyl glucoside, a cyclic polyhydric alcohol containing four reactive hydroxyl groups (Figure 1), has been reported by a number of workers. From the transesterification of olive oil with methyl glucoside, Irvine and Gilchrist (1) isolated an ester, which they claimed was a methyl glucoside mono-oleate. Also, by a similar procedure, Wolff and Hill (2) reported the preparation of mono-, di-, and trioleate esters of this polyol, using methyl oleate instead of the triglyceride. By direct esterification with linseed fatty acids Gibbons and Janke (3) prepared drying oil type of tetraesters of methyl glucoside.

To the best of our knowledge there has been no detailed information published in any technical journal on the direct esterification of methyl glucoside with fatty acids to produce diesters or on the evaluation of the surface-active properties of any of the methyl glucoside partial esters heretofore reported. Hence this paper will describe procedures found useful for the direct esterification of methyl glucoside with fatty acids to yield diesters. In addition, the effect of these diesters on surface tension of aqueous systems will be given.

Experimental and Results

Esterification Procedures. The diesterifications of methyl glucoside with various fatty acids have been carried out in the laboratory both by the solvent and by the fusion-reaction techniques described below.

Solvent Method. To a closed reaction vessel, equipped with a mechanical stirrer, thermometer, gas inlet tube, and a water trap (Dean-Stark tube) fitted with a water-jacketed reflux condenser, were charged the methyl glucoside, fatty acids, catalyst, and enough xylene to give a good reflux at 180°C. While being stirred under a blanket of carbon dioxide, the contents were heated rapidly to 180°C. At this temperature the xylene began to reflux vigorously and formed an azeotrope with the water of esterification, removing it from the reaction zone, thus speeding up the rate of esterification. Xylene also helped to maintain constant temperature, which was gradually raised during the course of the reaction by removal of some xylene through the water trap. After the theoretical amount of water of reaction was obtained (as measured by that collected in the trap), the xylene was distilled off. The last traces of xylene were removed from the reaction product by increasing the rate of carbon dioxide sparge. The product was then treated with activated carbon or aqueous hydrogen peroxide, as described below, to improve color.

Fusion Method. To a closed reaction vessel, fitted with a mechanical stirrer, thermometer, gas inlet tube, and a vapor outlet were charged the methyl glucoside, fatty acid, and catalyst. With good agitation and a carbon dioxide sparge, at the rate of approximately 0.02 to 0.04 cu. ft./min./gal., the contents were heated to the desired reaction temperature (180° to 190°C.). The carbon dioxide sparge facilitated removal of the water of reaction, thus speeding up the rate of esterification. When the reaction was completed (as determined by acid number), the ester was decolorized as described below. The products ob-

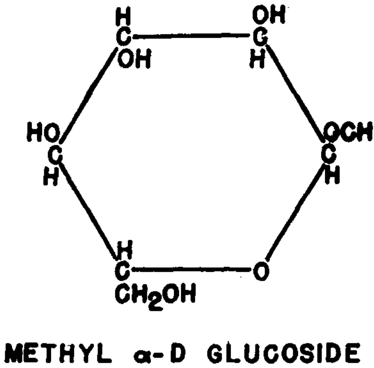

Fig. 1. Methyl α-D glucoside.

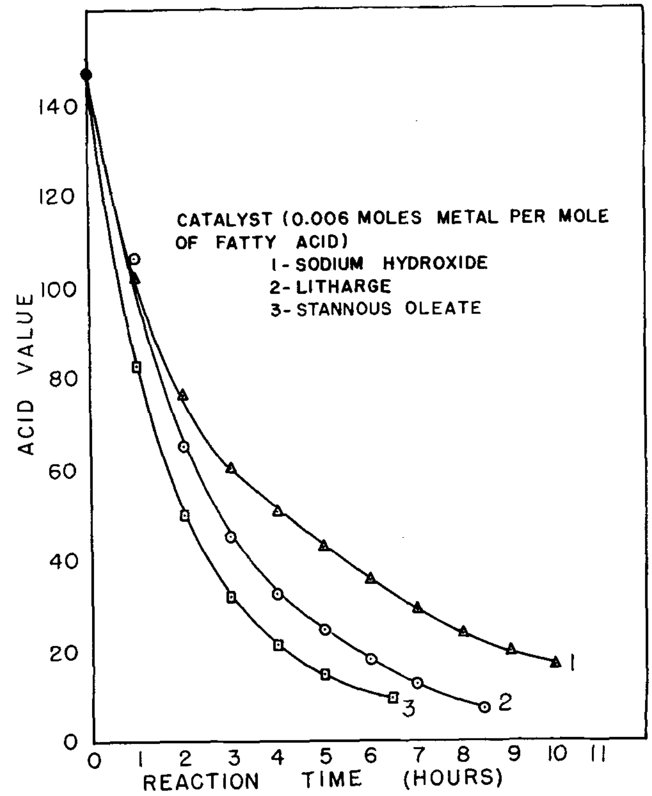

Fig. 2. Esterification of 2 moles of oleic acid with 1 mole of methyl α-D glucoside at 180°C.

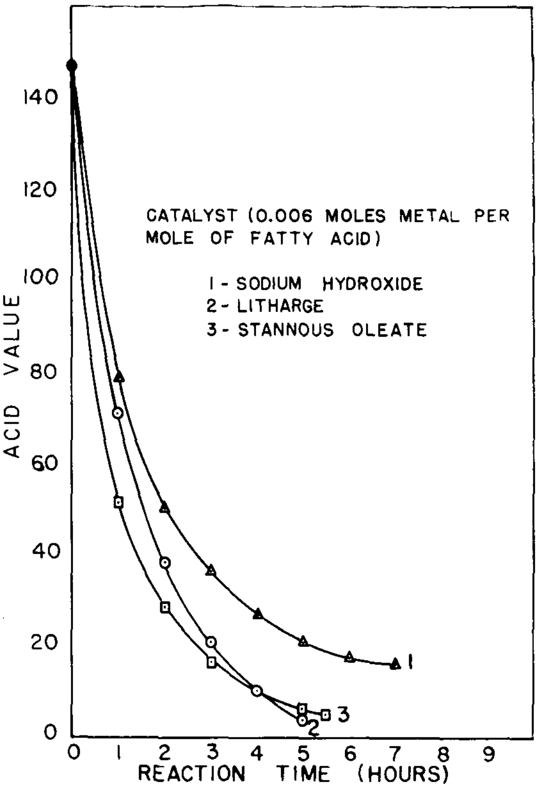

FIG. 3. Esterification of 2 moles of oleic acid with 1 mole of methyl α-D glucoside at 195°C.

tained by this method were comparable in properties to those made by the solvent technique. The fusion method has been found more useful for larger-scale preparations in stainless steel equipment.

Esterification Catalysts. In Figures 2 and 3 are shown the rates of esterification of two moles of oleic acid with one mole of methyl glucoside at 180° and 195°C. with various catalysts. These reactions were all run by the fusion technique described above, using litharge, sodium hydroxide, or stannous oleate (Metal and Thermit Corporation or Nuodex Products Company) as catalysts. As would be expected, at 195°C. the rate of esterification with each catalyst was more rapid than with the same catalyst at 180°C. However the 180°C. reactions gave somewhat lighter-colored products.

For diesterification, litharge has been found to give the best results from the standpoint of the time required to achieve the desired acid value (below 10), color of the final products, and catalyst cost. On completion of the esterification, the lead can be removed from the ester product by addition of adipic acid on the cooling cycle at 150°C. The adipic acid (0.7 parts per part of litharge used) forms insoluble lead adipate, which can then be removed by filtration either before or after bleaching.

In preparing the methyl glucoside diesters listed in Table I, the solvent method was used by employing reaction temperature ranges of 180° to 200°C. Since litharge gave good results in the rate studies, this compound was employed as the catalyst.

With equal molar quantities of fatty acids and methyl glucoside, esterifications in the presence of either litharge or sodium hydroxide catalysts at 170° to 190°C. yield products which contain diester with approximately half the methyl glucoside remaining unreacted. The methyl glucoside and diesters were separated by diluting the reaction mixture with five times its volume of benzene and allowing it to stand at room temperature for 48 hrs. Approximately half the methyl glucoside originally charged precipitated. This was separated by filtration, recrystallized from methanol, and identified by melting point and optical rotation. The filtrate, on removal of benzene, contained a diester which was characterized by acid number, saponification value, and hydroxyl content. The esters obtained were similar to the products prepared by the reaction of two moles of the same fatty acid with one mole of methyl glucoside in the presence of either of the above catalysts.

Stannous soaps are extremely interesting catalysts for the preparation of methyl glucoside esters. When equal molar quantities of fatty acid and methyl glucoside are esterified in the presence of stannous catalysts, preferably at 170° to 180° C., products are obtained which contain 10% or less of unreacted methyl glucoside. Determination of the unreacted methyl glucoside was done by the solvent-precipitation scheme described above in conjunction with chromatographic analysis of the filtrate residue for free methyl glucoside. Acid value, saponification number and hydroxyl-content analysis of the ester portion indicated better than 50% of monoester content. Studies on these stannous soap-catalyzed esterifications are still in progress and will be the subject of another publication on methyl glucoside monoesters.

Decolorization of Esters. When lighter-colored ester products were desired, either the activated carbon treatment or the aqueous hydrogen peroxide bleach method, described below, gave satisfactory results.

With Activated Carbon. After the esterification was completed, about 2 to 4% by weight of activated carbon (Nuchar CN) was added to the reaction mixture. While being stirred under carbon dioxide, the

TABLE I
Preparation and Properties of Methyl Glucoside Diesters
(Esterification by Solvent Method)

Ester No.	Type	Charge[a] fatty acids (g.)	Cooking schedule		Color[b]	Viscosity[c]	Acid No.	Saponification No.	Hydroxyl content (%)	Surface tension[d]		
										Dynes/cm. at 25°C. % conc. in water		
			°C.	Hrs.						1.0	0.1	0.01
1	Dioleate	560	182–195	7.00	8	V	1.6	151	4.5	28	31	35
2	Dilaurate	412	180–193	5.80	7+	V	4.4	186	6.7	26	28	29
3	Dicaprate	356	180–200	7.33	14	W	13.4	208	6.3	28	32	45
4	Distearate	556	180–200	6.33	Tan	....[e]	1.7	154	4.9	Non-dispersible		
5	Dimyristate	464	180–195	4.75	Tan	....[f]	8.2	176	5.1	Non-dispersible		
6	Dipalmitate	516	180–198	7.00	Tan	....[g]	4.3	163	5.5	Non-dispersible		

[a] Litharge catalyst (0.5% on fatty acids), 194 g. of methyl glucoside (Corn Products Company, Argo Brand Methyl Glucoside J361). [b] Gardner-Holdt (1933) Color. [c] Treated with Nuchar CN at end of reaction. [d] Aqueous surface-tension of water at 25°C. = 72 dynes/cm. [e] Solid m.p. 52–54°C. [f] Solid m.p. 35–37°C. [g] Solid m.p. 38–39°C.

mixture was held at 180°C. for 1 hr. then allowed to cool to 120° to 130°C., and filtered through a diatomaceous earth bed to remove carbon. This method of decolorization is not as suitable for larger-scale preparation as the hydrogen peroxide method outlined below. The quantity of carbon required tends to clog the filters, slowing down the filtration rate.

With Aqueous Hydrogen Peroxide. After the desired degree of esterification was achieved, the reaction mixture was cooled to 80°C. whereupon 3% of aqueous (50%) hydrogen peroxide on the weight of the ester was added slowly with stirring. The mixture was held about an hour to bleach, then the water, added with the peroxide, was removed *in vacuo.* In the litharge-catalyzed reactions bleaching with hydrogen peroxide was done as described above after the addition of adipic acid on the cooling cycle at 150°C. The insoluble lead adipate did not interfere with the bleaching operation and was subsequently removed by filtration.

Characterization of Diesters. Summarized in Table I are the experimental conditions used in the preparation of the various methyl glucoside diesters, together with some of the properties of these products. Surface-tension measurements were made by the Du Noüy aqueous surface-tension procedure at concentrations of 1.0, 0.1, and 0.01% of ester in water. The results of these measurements show that the surface tension of water was appreciably reduced by the addition of as little as 0.01% of the methyl glucoside diesters (Esters 1, 2, and 3). The diesters of the higher saturated fatty acids (Esters 4, 5, and 6) were not dispersible in water, hence no significant surface-tension data could be obtained.

Summary and Conclusion

Procedures are described for the preparation of methyl glucoside diesters by direct esterification, using a ratio of one mole of methyl glucoside with two moles of fatty acids. Rate studies indicated that lead or stannous soaps are more effective catalysts than the sodium soaps for speeding up this esterification. With equal molar quantities of methyl glucoside and fatty acid, the lead and the sodium soap catalysts give products containing predominantly diester and half the methyl glucoside remaining unreacted. Under the same conditions stannous soap catalysis gives high yields of monoesters containing only very small percentages of unreacted methyl glucoside. From the standpoint of speed of reaction, color of the final products, ease of removal of catalyst from the ester products, and catalyst cost, litharge is the preferred catalyst for the preparation of methyl glucoside diesters.

Properties of various methyl glucoside fatty acid diesters, prepared on a laboratory scale, are given. Du Noüy surface-tension measurements indicate that small quantities of the methyl glucoside dilaurate, dicaprate, or dioleate are quite effective in lowering the surface tension of water.

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ABSTRACTS . . . . R. A. REINERS, Editor

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• Fats and Oils

The Autoxidation of Unsaturated Compounds. X. Isolation of Methyl Linoleate Hydroperoxides and Polymeric Autoxidation Products of Methyl Linoleate. W. Kern and H. W. Schnecko (Organic Chemistry Institute of the Univ. Mainz). *Die Makromolekulare Chemie* 32, 184–190 (1959). It is possible to isolate pure methyl linoleate hydroperoxide from autoxidized methyl linoleate by countercurrent distribution. Application of the method to highly autoxidized oils (up to 200 mol % oxygen) yields secondary products; the content of hydroperoxide decreases rapidly. The autocatalytic character of the autoxidation can be observed up to a conversion of 100 mol %.

XI. The Catalysis of the Autoxidation of Methyl Linoleate with Methyl Linoleate Hydroperoxide. W. Kern, L. Dulog, and G. Selz. *Ibid.,* 191–196 (1959). Methyl linoleate hydroperoxide was isolated from autoxidized methyl linoleate by countercurrent distribution and was added to pure methyl linoleate as a catalyst for its autoxidation. The identical effect of added methyl linoleate hydroperoxide with the autocatalyst of the autoxidation reaction is demonstrated by the results of a kinetic experiment.

The Cultivation of Perilla Ocimoides and Perilla Nankinensis and Studies of Their Oils. P. Mazhdrakov and As. Popov. *Compt. rend acad. bulgare sci.* 11, 197–200 (1958) (in German). Of the two plants, *Perilla nankinensis* is the better suited for growing in Bulgaria because of the shorter growing season, but hardier strains should be sought. The oil of *Perilla nankinensis* has a lower iodine number (173 *versus* 178–81) but shows superior drying properties. It contains 42.6% linoleic acid and 22.4% linolenic acid. Other usual characteristics are reported. (*C. A.* 53, 15593)

The Color of Milk Fat. L. Radema. *Offic. Orgaan. Koninkl. Ned. Zuivelbond* 50, 216–17 (1958); *Dairy Sci. Abstr.* 20, Abstr. No. 1448. The color of milk fat was determined spectrophotometrically over a one-year period in the mixed milk received at the experimental dairy of the Netherlands Institute for Dairy Research. Converted to carotene, the lowest and highest butterfat values recorded were 2.4 in early April and 7.8 mg./kg. at the end of May. (*C. A.* 53, 15400)

Fatty Acid Composition of Food Fats and Oils. L. R. Dugan, Jr. *Am. Meat Inst. Foundation, Circ.* No. 36, 15 pp. (1957); *Dairy Sci. Abstr.* 20, Abstr. No. 433 (1958). The fatty acid composition of various fats and oils was investigated. Butter contained 57% saturated fatty acids, of which 40% were short-chain acids of less than 16 carbons. The effects of hydrogenation are also given. (*C. A.* 53, 15410)

The Effect of Wrapping Paper on Fat Stability. Z. Kwapniewski, A. Rutkowski, and B. Kubik. *Przemysł Spożywczy* 12, 412–15 (1958). Acid parchment, parchment, half-parchment, and white and gray cardboard accelerated the autoöxidation of fat. Porosity of the paper and its content of iron and copper had the greatest effect on deterioration of fat. Impregnation of the paper with 0.01% octyl gallate increased considerably the stability of the fat. (*C. A.* 53, 15410)