Fatty Acid Esters of Methylglucoside Prepared by the Alcoholysis Reaction

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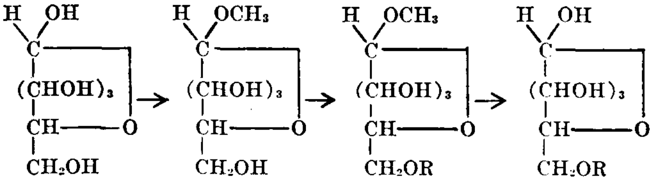
THE preparation of fatty acid esters of sugars has been attempted repeatedly, but either the yields of sugar esters were unsatisfactory or the methods used were too cumbersome to be of practical value. Berthelot (1) attempted to prepare glucose and sucrose esters from the sugars and fatty acids without catalysts. The use of acid catalysts for the preparation of sugar esters has been reported (2), and the preparation of sugar esters from the sugar and acid anhydrides or halides (3) has been described. The aldehyde group of glucose is quite labile to alkali; thus basic catalysts appear unsuitable for the preparation of glucose esters.

In the search for an economical method of preparing glucose esters it appeared that by protecting the aldehyde group of the glucose, the alkali catalyzed alcoholysis reaction could be applied, and the glucose derivative obtained on removal of the protective group as indicated by the following formulas:

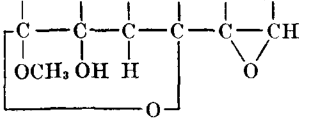


R = fatty acid radical

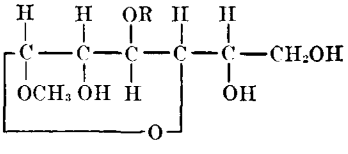
α-Methylglucoside was chosen as the glucose derivative because it is readily available, alkali stable, and smoothly hydrolyzed to glucose on warming with dilute acid. It was found, however, that the acetal linkage of the fatty acid ester of methylglucoside could not be so easily broken; in fact, the ester linkage was hydrolyzed as readily as the acetal on refluxing in 0.1 N acid. That this was not due to the water insolubility of the glucoside ester was shown by refluxing the compound in an acid solution of water and alcohol in which it was soluble at the boiling temperature.

The preparation of glucoside esters, however, revealed several new and interesting features which will be reported in this paper.

Methylglucoside palmitates and stearates have been prepared by the reaction of the acid chlorides and α-methylglucosides in the presence of quinoline (4). The preparation of α-methylglucoside mono-oleate has been reported by Irvine and Gilchrist (5). On heating olive oil and α-methylglucoside to 225°C. in the presence of sodium methoxide catalyst these authors obtained a reaction product to which they ascribed formula I.



I



II

R = oleoyl radical

This compound was assumed to result from dehydration of the glucoside mono-oleate II, originally formed but not isolated.

On repeating Irvine's work little evidence for dehydration was found. The amount of water collected in a dry ice trap was insufficient to account for complete dehydration. The reaction product was then purified as described (5) and found to contain from 13 to 15% of free fatty acid (calc'd as oleic). The amount of methylglucoside recovered from the reaction mixture indicates that the reaction could not have gone to completion. It is therefore apparent that a mixture of glucoside ester (or anhydro-glucoside ester), free fatty acid, and olive oil represents the final reaction product.

The alcoholysis of soybean oil by α-methylglucoside under various conditions was then investigated. It was found that the fatty acid content of the reaction product could be considerably decreased by reducing the amount of sodium methoxide or hydroxide catalyst. The conversion yield, representing the amount of the reaction product (glucoside ester), was determined from the quantity of glucoside that entered the reaction. This yield passes through a maximum in the neighborhood of 0.3% of catalyst, calculated as sodium based on the amount of glyceride used (Table I). The conversion yield is lower than the total amount of isolated product because of unchanged soybean oil which cannot be readily separated from the glucoside ester.

TABLE I

% Catalyst	% FFA	% Conversion	% Isolated Product	Sap. Equiv.
2.0	18.6	60	81	413
1.0	11.4	66	84	431
0.5	4.3	65	85	412
0.3	4.1	80	91	448
0.2	2.7	70	86	416

In all these cases a 5% excess of glucoside was used. The glucoside excess can be removed quantitatively from the reaction product by repeated washing with hot water. Under otherwise equal conditions an excess of 3% over the calculated amount of glucoside gives a 60% conversion yield; a 6% excess, 62% conversion; and a 10% excess, 70% conversion. Even with considerable higher excess of glucoside, the conversion yield could not be materially improved.

These reactions were carried out at a pressure of 2 to 3 mm. Hg in order to eliminate by distillation the glycerol formed during the reaction. This procedure was chosen in order to shift the reaction equilibrium toward the desired glucoside ester formation.

Irvine's finding that only a mono-substituted glucoside ester can be obtained from the reaction of triglycerides and glucosides was confirmed. It was also found, however, that no pure compound could be isolated from this reaction.

The preparation of pure glucoside esters by alcoholysis was believed more likely to succeed if both starting materials, the alcohol and the ester, could be removed from the reaction mixture. The triglyceride was therefore replaced by the methyl esters of fatty acids since the latter can be separated from the glucoside ester by distillation.

Alcoholysis of methyloleate by α-methylglucoside in equimolar ratios, catalyzed by sodium methoxide, was therefore carried out. The reaction product was thoroughly washed with acidulated water in order to remove unchanged glucoside. The mixture was then subjected to a vacuum distillation at 0.02 mm. Hg pressure at 200°C. until no more material distilled. This treatment removed methyloleate and oleic acid formed during the reaction. Analytical data of the reaction product (Table II) are in close agreement with the data required for α-methylglucoside mono-oleate.

Although the reaction of triglycerides and methylglucoside gives only monosubstitution of the glucoside, it was found that higher substitution of the glucoside can be obtained when the triglyceride is replaced by monohydric esters of fatty acids. Thus, by permitting two mols of methyloleate and one mol of glucoside to react, a product could be isolated which gave analytical data in close agreement for a di-oleoylglucoside. A ratio of three to one yields a product which is apparently a mixture of di- and tri-oleoyl-methylglucoside, whereas a ratio of four or more methyloleate to one glucoside yields tri-oleoylmethylglucoside (Table II). Although methylglucoside contains four hydroxyl groups, a maximum of only three hydroxyl groups could be esterified by the alcoholysis reaction. The analytical data of the three oleoylglucosides show that the compounds were fairly pure considering the fact that the compounds are oily products which cannot be distilled in a conventional still. Distillation in a molecular still is presently under investigation and will be reported at a later date.

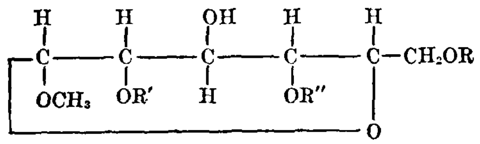
TABLE II

Analytical Data	Methyl-glucoside Mono-oleate	Methyl-glucoside dioleate	Methyl-glucoside trioleate
Sap. equiv.			
Calc'd	458	361	329
Found	435	353	328
% C, H			
Calc'd	$C_{25}H_{46}O_7$ 65.5; 10.01	$C_{43}H_{78}O_8$ 71.5; 10.8	$C_{61}H_{110}O_9$ 74.0; 11.1
Found	66.3; 9.9	71.2; 10.7	73.0; 11.2
% Methoxyl			
Calc'd	6.7	4.3	3.1
Found	6.2	4.2	3.9
Refractive index at 25°C	1.4788	1.4757	1.4747
Iodine value			
Calc'd	55.5	70.2	77.1
Found	59.1	69.1	76.0
Acetyl value*			
Calc'd	288	139	
Found	252	139	
Hydroxyl value**			
Calc'd		155	
Found		151	

* A.O.C.S. method.

** Helrich, V., and Rieman, W., *Ind. Eng. Chem. (Anal. Ed.)* *19*, 691 (1947).

The structure proposed for the mono-oleoyl-methylglucoside is given in formula III.



III: R = *oleoyl radical*
R′ = R″ = H

IV: R = R′ = R″ = oleoyl radical

Methylglucoside contains only one primary hydroxyl group which is the most likely one to be substituted by the reaction of triglycerides and glucoside. The primary hydroxyl groups (α groups) in glycerol react in preference to the secondary group (β group) when triglycerides and glycerol are heated in the presence of alkaline catalysts (6).

In the absence of evidence for dehydration and in view of the fact that tri-substituted glycoside esters could be obtained, thus excluding intermolecular dehydration, structure III represents the most likely formula of the main product obtained on alcoholysis of olive oil by α-methylglucoside. The same structure is assigned to the monosubstituted glucoside obtained from methyloleate and α-methylglucoside.

The di-substituted α-methylglucoside would have a fatty ester group on carbon 2 or 4 in addition to the one on carbon 6.

For the tri-oleoyl-methylglucoside formula IV is proposed since it is most likely on account of steric reasons that the two non-neighboring hydroxyl groups would be substituted.

Experimental

Alcoholysis of Soybean Oil by α-Methylglucoside: A mixture of 75 g. of refined soybean oil, 52.5 g. of α-methylglucoside (m.p. 166-8°) and 0.47 g. of finely powdered sodium hydroxide was heated with vigorous stirring in a 300-cc. distillation flask equipped with a vacuum stirrer. When the temperature reached 200°C. at a receiver pressure of 2-3 mm. Hg, glycerol started to distill. After maintaining the temperature at 225° for 40 minutes the mixture was allowed to cool to 80-90°C. and then poured, with stirring, into a beaker containing 450 ml. of boiling water and 2 ml. of glacial acetic acid. On cooling, the reaction mixture settled at the bottom of the beaker. The water was decanted and washing of the product with boiling water was repeated. The wet product was then dissolved in alcohol and decolorized with carbon. After filtration and evaporation of the alcohol, 101 g. of product was obtained, representing an isolation yield of 82% of theory. The methylglucoside recovered from the water layer weighed 18.8 g., indicating a conversion yield of 68%. The product was a yellow, viscous oil with a free fatty acid content of 3% and a sap. equiv. of 416.

α-Methylglucoside Mono-oleate: A mixture of 38.8 g. (0.2 mol) of α-methylglucoside, 29.6 g. (0.1 mol) of methyloleate, and 0.15 g. of 95% sodium methoxide was heated with stirring at atmospheric pressure to 230° for one-half an hour. The reaction product after cooling to 80°C. was poured into 400 ml. of boiling water containing 0.2 ml. of glacial acetic acid. The ester was then extracted with ether in a continuous extractor. After drying the ether solution over anhyd. sodium sulfate, the ether was evaporated, leaving 38.8 g. of an oily product. This material was heated to 200°C. at 0.02 mm. of Hg until no more distillation occurred. The distillate weighed 5.3 g., containing 5.5% of oleic acid. The residue was then taken up in benzene and decolorized with carbon, leaving 33 g. of methylglucoside mono-oleate. Yield, 72% of theory (based on methyloleate). Analytical data are reported in Table II.

α-Methylglucoside Dioleate: The mixture of 25.3 g. (0.13 mol) of methylglucoside, 77.4 g. (0.26 mol) of methyloleate and 0.4 g. of sodium methoxide was treated as outlined for the mono-oleate. There was obtained 90 g. of material which on vacuum distillation gave 18.4 g. of distillate (8.7% oleic acid) and 70 g. of residue, which analyzed for di-oleoylglucoside (yield 74% of theory) (Table II).

α-Methylglucoside Trioleate: A mixture of 59.2 (0.2 mol) of methyloleate, 9.7 g. (0.05 mol) of methylglucoside and 0.3 g. of sodium methoxide was treated as outlined above. The ester was obtained in a yield of 65% of theory. A ratio of six mols of methyloleate to one of glucoside gave the same product.

Attempted Hydrolysis of the Glucoside Oleates:

A) In aqueous hydrochloric acid.

A solution of α-methylglucoside (giving no Fehling test) was compared with a sample of di-oleoyl methyl glucoside at reflux in 0.1 N hydrochloric acid. After 30 minutes the methylglucoside solution gave a strong Fehling test. The ester was heated for an additional two hours, after which the aqueous layer gave a faint Fehling test. The water insoluble material was extracted with benzene and after evaporation of the benzene the residue was analyzed for dextrose equivalent (d.e.) and free fatty acids (f.a.). The d.e. was found to be 0.4%, thus showing a small amount of acetal hydrolysis; this value is equivalent to 1.4% of glucose di-oleate. The f.a. content was found to be 6% or more than four times the f.a. content of the starting material.

B) In alcoholic hydrogen chloride.

To a boiling solution of 10 g. of α-methylglucoside mono-oleate in 175 ml. of 0.1 N alcoholic hydrogen chloride, water was added dropwise until cloudiness occurred. A total of 33 ml. of water was added. On addition of a few drops of alcohol the cloudiness disappeared. After two hours reflux about 400 ml. of water was added and the material extracted with benzene in a continuous extractor. On evaporation of the benzene, 8.2 g. of residue was obtained which contained 8.5% of fatty acid (compared to 0.3% of the starting material) and gave no Fehling test.

Summary

1. Alcoholysis of triglycerides by methylglucoside gave an impure reaction mixture containing from 60-70% of glucoside-monoesters.

2. The mono-, di-, and trioleoyl methylglucosides were prepared by alcoholysis of methyloleate with α-methylglucoside.

3. Hydrolysis of the glucoside esters of fatty acids to dextrose esters could not be achieved. The ester linkage hydrolyzed in preference to the acetal linkage.

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☆ ☆ ☆ ABSTRACTS ☆ ☆ ☆

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