Methyl Alpha-D-Glucoside Drying Oils

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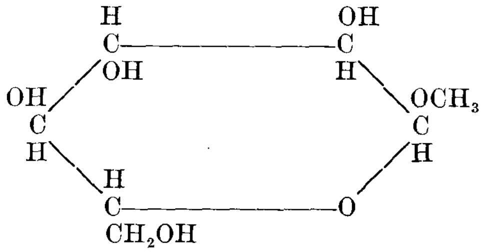
DRYING oils prepared by the direct esterification of linseed fatty acids with polyhydroxy compounds such as pentaerythritol, polypentaerythritol, sorbitol, and inositol have been described in the literature (1, 2, 3, 4). These synthetic oils are reported to have improved drying properties over the natural product, linseed oil.

Dextrose, a relatively inexpensive compound, might be expected to give synthetic oils of similar nature except for the fact that, at the temperatures required for direct esterification with fatty acids, this sugar is readily decomposed. However methyl alpha-D-glucoside, a derivative of dextrose having the following stereochemical configuration, has been found sufficiently heat-stable to withstand direct esterification with fatty acids without apparent decomposition.



To the best of our knowledge there are no earlier reports of successful direct esterification of methyl alpha-D-glucoside with fatty acids. In this paper therefore we wish to describe our investigation of the direct esterification of this polyol with linseed fatty acids and to set forth the evaluation of the resulting esters as drying oils in 25-gallon oil length varnishes.

Experimental and Results

Preparation of Oils. In this work a high purity, commercial grade of methyl alpha-D-glucoside was used (Corn Products Refining Co.'s methyl alpha-D-glucoside—R3). It is a white, crystalline, nonhygroscopic solid melting at 165-166°C. The linseed fatty acids were a distilled grade (Archer-Daniels-Midland Co. water-white distilled grade).

The esterifications were carried out in a 3-liter flask equipped with a mechanical stirrer, thermometer, gas inlet tube, and a Dean-Stark water removal trap fitted with a condenser. Heat was effected by means of a hemispherical electric mantle controlled by a variable transformer.

The reactants were charged to the flask at room temperature and carbon dioxide sparging begun at the rate of approximately 200 ml. per minute. While stirring, the contents were heated to the desired temperature and then enough xylene was added through the condenser to maintain a steady reflux.

In preparing methyl alpha-D-glucoside esters, it was observed that products of lighter color could be obtained if the reaction temperature was held between 190° and 200°C. (374° and 392°F.) until approximately 50% of the esterification was completed (as measured by water recovered in trap) instead of heating directly at 230°C. (446°F.).

Table I summarizes several esterifications made with methyl alpha-D-glucoside, glycerol, and pentaerythritol. In the methyl alpha-D-glucoside and glycerol reactions the following heating cycle was employed: 190° to 200°C. (374° to 392°F.) for 2 hours, then 210° to 220°C. (410° to 428°F.) for 2 hours, and finally 230° to 235°C. (446° to 455°F.) until the water recovery essentially ceased. With the pentaerythritol esters the temperature was taken directly to 225° to 230°C. (428° to 446°F.) and held until no further water of esterification was obtained.

To provide sufficient polyol, 5 to 10% excess hydroxyl is often employed in industrial practice to obtain low acid numbers in a reasonable length of time. It can be observed from Table I (preparations 4, 5, 6, 8, and 10) that an excess of hydroxyls appreciably affects the reaction by giving esters with relatively lower acid numbers compared to those made using a ratio of 4 mols of fatty acid to 1 mol of methyl alpha-D-glucoside.

Methyl alpha-D-glucoside has four hydroxyls available for esterification—one primary and three secondary. The rate of reaction however indicates that two of the four hydroxyls have approximately equal reactivity and are esterified more rapidly than the other two. Experimental evidence of this behavior is the fact that the reaction of 1 mol of fatty acids with 1 mol of methyl alpha-D-glucoside yielded a product containing mostly diester, with practically half of the methyl alpha-D-glucoside unreacted.

TABLE I

Esterification of Polyols with Linseed Fatty Acids

Prepn. No.	Polyol	Mol Ratio Linseed Fatty Acids to Polyol	Catalyst % Based on Fatty Acids	Total hrs. for Reaction	Max. Temp.	Properties of Esters			
					(°C.)	Viscosity[c] (poises)	Color[d]	Acid No.	Saponification No.
1	Methyl α-D-glucoside	4: 1.00	None	10.0	233	1.00	15	28.6	178
2	Methyl α-D-glucoside	4: 1.00	CaO-0.13	7.0	235[b]	1.40	13	21.5	176
3	Methyl α-D-glucoside	4: 1.00	PbO-0.5	8.3	235	1.65	13	12.3	172
4	Methyl α-D-glucoside	4: 1.10	None	10.0	235	1.25	16	18.6	171
5	Methyl α-D-glucoside	4: 1.05	CaO-0.13	10.5	237	1.25	15	16.8	171
6	Methyl α-D-glucoside	4: 1.05	PbO-0.5	7.5	235	1.65	13	4.2	176
7	Glycerol	3: 1.00	None	8.0	230	0.40	9	17.0	188
8	Glycerol	3: 1.05	PbO-0.5	4.8	230	0.40	12	3.0	186
9	Pentaerythritol[a]	4: 1.00	None	5.0	230	1.00	9	17.3	186
10	Pentaerythritol	4: 1.05	None	4.5	228	1.00	8+	11.6	184

[a] Pentaerythritol—Pentek (Heyden Chemical Corp.).
[b] Final hour, heated at 260°C.
[c] Gardner bubble viscometer.
[d] Gardner-Hellige color comparator.

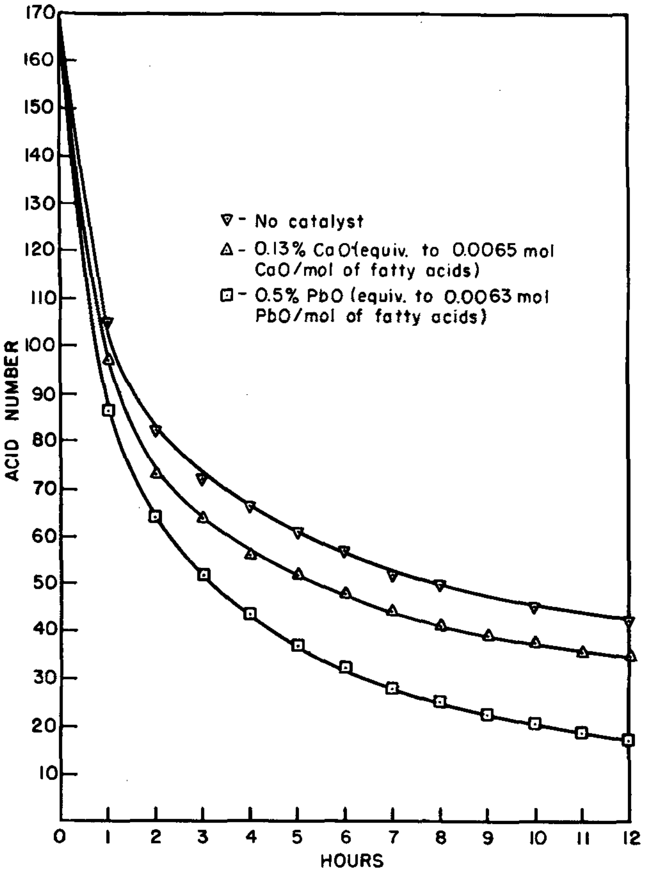


Fig. 1. Esterification of 4 mols of linseed fatty acids with 1 mol of methyl α-D-glucoside at 200°C. (392°F.).

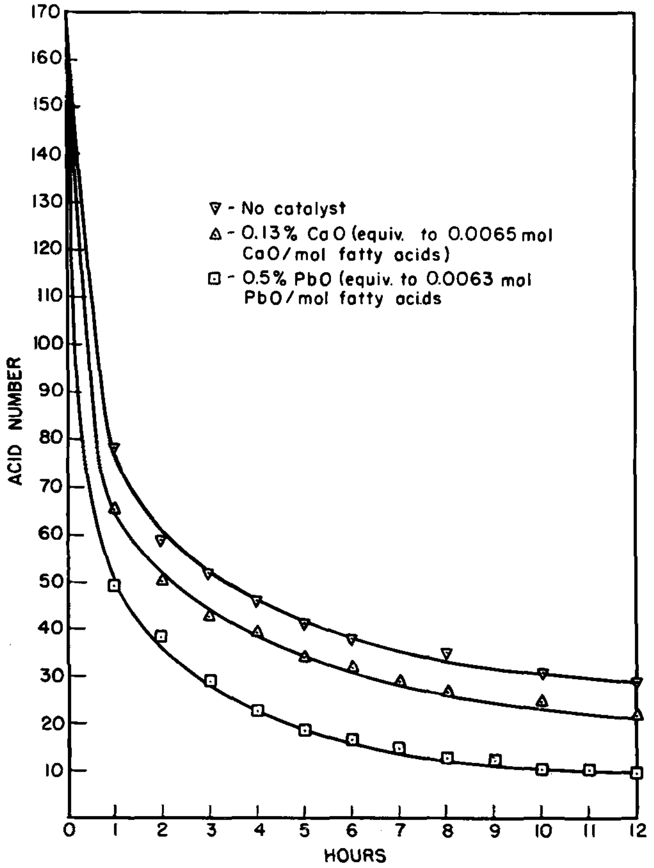


Fig. 2. Esterification of 4 mols of linseed fatty acids with 1 mol of methyl α-D-glucoside at 230°C. (446°F.).

The rate of esterification of 4 mols of linseed fatty acids with 1 mol of methyl alpha-D-glucoside at both 200°C. (392°F.) and 230°C. (446°F.) with and without catalysts is shown in Figure 1 and 2. These experiments were carried out using a ratio of 4 mols of linseed fatty acids to 1 mol of glucoside with a xylene azeotrope in a carbon dioxide atmosphere. Samples were withdrawn periodically and, after removing the solvent *in vacuo,* the acid numbers determined. It can be seen that at both temperatures the catalysts accelerate the rate of reaction, with litharge being more effective than calcium oxide for this purpose.

Bodying of Oils. The bodying characteristics of the methyl alpha-D-glucoside, glycerol, and pentaerythritol linseed fatty acids drying oils presented in Figure 3 were determined at 310°C. (590°F.). The procedure outlined by Von Mikusch (6) was employed. This method embraces heating the oil in an atmosphere of carbon dioxide, periodically withdrawing samples, cooling them quickly to 25°C., and determining the viscosities by the Gardner bubble viscometer. The oil was heated rapidly to the desired temperature and, when samples indicated the viscosity had reached 2.5 poises, timing was begun. The oils used in this study were preparations 1, 3, 7, and 9, Table I.

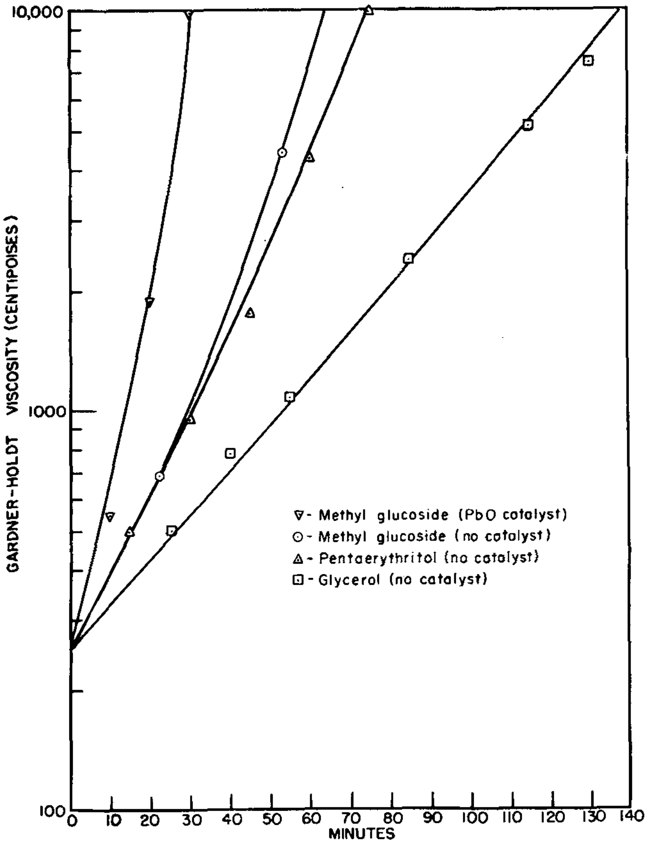


Fig. 3. Bodying of esters of linseed acids and various polyols at 310°C. (590°F.).

The methyl alpha-D-glucoside oils possess more rapid bodying characteristics than either the pentaerythritol or glycerol oils and are somewhat similar to those of inositol (4), which forms a hexaester with linseed fatty acids. The rapid bodying rate of the litharge-catalyzed methyl alpha-D-glucoside oil may be due to the presence of traces of lead not completely

TABLE II

Preparation and Properties of 25-Gallon Oil Length Varnishes

Drying Oils	Table I Prep. No.	Cooking Schedule			Gardner[b] Viscosity 25°C. (77°F.)	Color[c]	Tack-Free Time (hr.)	5%[d] Alkali Resistance (hr.)	Water Resistance 48 hr. (70°F.)	Sward Hardness[e] after			
Linseed Fatty Acid Esters of		Heat-Up[a]		Holding									
		Temp. (°C.)	Time (min.)	Time (min.)						24 hr	48 hr	72 hr	96 hr
Methyl α-D-glucoside No Cat.	4	300	23	35	G	16	2.25	26	o.k.	20	34	34	34
Methyl α-D-glucoside PbO Cat.	6	300	22	25	D	14	3.25	41	o.k.	24	34	34	34
Glycerol PbO Cat.	8	300	25	80	G	12	3.75	12	o.k.	8	18	18	18
Pentaerythritol No Cat.	10	300	25	60	F	9	3.50	41	o.k.	14	22	22	22

[a] Time required to reach temperature.
[b] Gardner bubble viscometer.
[c] Gardner-Hellige comparator.
[d] Hours to failure.
[e] Rocker standardized at 100 on glass.

removed by filtration of the oil before the bodying studies were run.

Cooking and Comparison of Varnishes. The methyl alpha-D-glucoside, pentaerythritol, and glycerol oils listed in Table I, preparations 4, 6, 8, and 10, were cooked into 25-gallon oil length varnishes, using a p-phenyl-phenol oil-soluble resin (Bakelite BR-254). The litharge-catalyzed methyl alpha-D-glucoside and glycerol oils were heated at 90°C. (194°F.) for 1 hour with 0.5% phthalic anhydride, according to the procedure of Jordan and Wittcoff (5), to form insoluble lead phthalate, which was then removed by filtration. Cooking was carried out in a 1-liter flask equipped with a stirrer, inlet tube for carbon dioxide sparging, and a hemispherical electric mantle for heating. After the varnish had been cooked to a satisfactory "string" it was allowed to cool, then diluted to 60% solids with a solvent mixture comprising 20% xylene and 80% VM&P naphtha (by volume). A naphthenate drier consisting of 0.5% lead, 0.05% cobalt, and 0.025% manganese on the basis of drying oil was added 24 hours prior to testing.

Films were cast on 3 x 5 glass plates at 0.003 inch thickness with a Bird applicator, and drying times and Sward hardness tests were then determined at 70°F. and 50% relative humidity. The drying time was found by pressing down on the film with a finger, then lifting away. The time at which the finger came free without raising the plate from the table has been recorded as the tack-free time. Films for alkali and water resistance were prepared by dipping 1 x 8 inch test tubes in the varnishes and permitting these to dry in an inverted position for 96 hours at 70°F. and 50% relative humidity before testing.

The cooking schedules and the results of the film tests for the different varnishes are given in Table II. It can be seen from these data that methyl alpha-D-glucoside-linseed fatty acids drying oils cook rapidly into varnishes which are fast drying, have good alkali and water resistance, and set up to relatively harder films than similar glycerol or pentaerythritol oil varnishes. In addition, the adhesion of methyl alpha-D-glucoside oil varnishes to glass plates appeared superior to those prepared from the glycerol or pentaerythritol oil varnishes.

Summary

Drying oils have been prepared by the direct esterification of methyl alpha-D-glucoside and linseed fatty acids. Litharge is an effective catalyst for this reaction. These methyl alpha-D-glucoside oils possess more rapid bodying characteristics at 310°C. (590°F.) than similar synthetic glycerol or pentaerythritol oils.

With Bakelite BR-254 resin the methyl alpha-D-glucoside oils cook rapidly into 25-gallon oil length varnishes that dry quickly to hard films with good alkali and water resistance and excellent adhesive properties.

Acknowledgment

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