POLYHYDRIC ALCOHOL ESTERS OF FATTY ACIDS

THEIR PREPARATION, PROPERTIES, AND USES

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Received July 23, 1943

The methods of preparation, the physical and chemical data, and the industrial applications of the higher fatty acid esters of polyhydric alcohols and of polyhydroxy ethers are reviewed. Triglycerides are not included.

In the course of studies concerning the polyhydric alcohol esters of the higher fatty acids, it becomes apparent that there is a need for a complete and systematic survey of all facts recorded in the literature about the preparation, properties, and uses of this group of substances. While much work has been done, much information has been omitted, and there are many contradictory statements. Reviews thus far published have surveyed only part of the subject (124, 223, 382, 400, 452); this literature review is meant to fill the gap.

To clarify the scope of this review, polyhydric alcohol esters of higher fatty acids shall be defined to include the esters of the higher fatty acids (i.e., straight-chain monocarboxylic acids, from C_8 up) with the polyhydric alcohols (i.e., diols, triols, tetrols, pentitols, hexitols), the polyhydroxy ethers (i.e., the polyalkylene glycols, polyglycerols, polymerized pentaerythritol or hexitols, hydroxyalkyl ethers of polyhydric alcohols), and the simpler carbohydrates (mono-, di- and tri-saccharides).

While definitely within this group, synthetic and natural triglycerides had to be excluded as they have been amply covered by the literature on fats and oils.

Polyhydric alcohol esters of higher fatty acids are not a new group of chemicals. The first glycerides were prepared as early as 1853 (38), erythritol, dulcitol, mannitol, and glucose esters in 1855 (40), and the first glycol esters in 1859 (563). Yet the first patent on glyceride manufacture was granted only in 1907 (546), and another fifteen years passed before industry began to take an interest in the polyhydric alcohol esters. Today, however, a considerable patent literature is witness to their growing industrial importance.

Two basic types of polyhydric alcohol esters can be distinguished: (*1*) those in which all alcoholic hydroxyl groups have been esterified; (*2*) those in which only part of them have been esterified. They will be referred to as the completely and the partially esterified polyhydric alcohols.

There are no distinct borderlines between these two groups. Similar methods of preparation, similar properties, and similar uses make it very difficult to consider them separately. However, the partially esterified polyhydric alcohols have received much more attention because of certain surface-modifying properties inherent in them. While both groups have much in common with the glyceride fats, it will be seen that considerable modification of properties is possible when triglycerides are replaced by mono- or di-glycerides, or by esters of other polyhydric alcohols.

It is possible to modify the polyhydric alcohol esters further, chiefly for use as surface-active agents, by the introduction of sulfuric, sulfonic, sulfoacetic, phosphoric, boric acid and other radicals. Such materials, though important, are beyond the scope of this survey.

I. PREPARATION OF THE POLYHYDRIC ALCOHOL ESTERS OF HIGHER FATTY ACIDS

All polyhydric alcohol esters can, in general, be prepared by the same basic methods which were originally worked out for the preparation of the glycerides. These basic methods are: *(1)* direct esterification of hydroxyl groups with fatty acids or anhydrides, with or without a dehydrating agent; *(2)* esterification by means of fatty acid halides with removal of hydrogen halide; *(3)* reësterification; *(4)* reaction of halogen groups with fatty acid salts, with formation of metal halide; *(5)* hydrolysis; *(6)* addition of alkylene oxides to compounds containing hydroxyl or carboxyl groups. Etherification, by dehydration, may accompany esterification or reësterification.

For greater clarity, however, the methods have been arranged according to the starting materials employed:

A. Polyhydric alcohols.
B. Fully esterified polyhydric alcohols.
C. Anhydro derivatives of polyhydric alcohols.
D. Substituted derivatives of polyhydric alcohols.
E. "Protected" derivatives of polyhydric alcohols.
F. Compounds related to polyhydric alcohols.

A. PREPARATION FROM POLYHYDRIC ALCOHOLS

A. Direct esterification

The direct reaction of polyhydric alcohols with fatty acids is the oldest recorded, and probably the simplest, way in which to make polyhydric alcohol esters. Its advantages are simplicity of equipment, operation, and control, and the ready commercial availability of raw materials. However, it has several disadvantages. Even though some esterification occurs at ordinary temperatures, if given enough time (39), its progress is slow at low temperatures and long heating or high temperatures are required to carry the reaction to completion. It cannot be used, therefore, when there is danger of undesirable chemical changes (polymerization, dehydration, resinification, or charring) in a reactant under these conditions. The greatest disadvantage of the method, however, is observed when polyhydric alcohols are to be only partially esterified. In such cases, mixtures of more and less completely esterified polyhydric alcohols form, even if a large excess of the alcohol is used. Most polyhydric alcohols are not, or are only poorly, miscible with the fatty acid, even at elevated temperature, while their ester products are. Thus, the fatty acids react with the ester products rather than with the polyhydric alcohols themselves, yielding more highly esterified products than intended. It may be stated at this point that various improvements in the method have been made which have wholly or partially eliminated its disadvantages. Thus, by the use of catalysts, mutual solvents, carrier solvents and traps, improved agitation, and the passage of currents of inert gas, better and more homogeneous products may now be obtained in shorter time and with greater yield.

Unaided direct esterification of polyhydric alcohols, like other esterifications, is increased in speed when the temperature is raised. The proportion of the reactants, the speed of moisture removal, the size of the batch, and the use and efficiency of agitation also strongly influence its progress. The more complex polyhydric alcohols seem to esterify more slowly than the less complex ones, but the data appearing in the literature allow no reliable conclusions. The esterifications were often not carried to completion, or were stopped at an indefinite point. Thus, reactions carried out in sealed tubes can be expected to have reached an equilibrium point, but not completion. Hence, data on reaction time are approximations at best. These esterifications have usually been carried out at 150° to 250°C., and preferably as high as the boiling or decomposition points of the reactants allowed (tables 1, 2, and 3).

TABLE 1

Esterification of glycols and ether-glycols with fatty acids, without catalyst

GLYCOL	TIME	REACTION TEMPERATURE	REACTION CONDITIONS	REFERENCES
	hours	°C.		
Ethylene glycol		100	Sealed tube	(518)
		150	Special stirring, CO_2	(370)
	4–7	170–210	Open vessel	(101, 158, 473, 474)
			Reflux or partial reflux	(407, 482, 483)
	5–11	200–205	Special stirring, CO_2	(73, 424)
		Above 210		(287, 353)
1,2-Propylene glycol	7–8	157–167	Open vessel	(262)
	6–8	210–230	CO_2	(353)
1,3-Propylene glycol		170–180	Open vessel	(262)
Diethylene glycol	2½	180–210	CO_2	(158)
	6–8	210–230	CO_2	(353)
Triethylene glycol	6	180–210	CO_2	(158)
Polyethylene glycol		130		(275, 302, 488)
		200		(131)

In the case of mono- and di-glycerides, the course of reaction has been more carefully studied: when 1 mole of glycerol and 1 mole of fatty acid (oleic, palmitic, stearic) are reacted at 215–220°C. under a pressure of 30–40 mm. of mercury, the

TABLE 2

Esterification of glycerol with fatty acids, without catalyst

TIME	REACTION TEMPERATURE	REACTION CONDITIONS	REFERENCES
hours	°*C.*		
114	100	Sealed tube	(38, 39)
114	100	Open retort, collecting water of reaction	(97)
5–8	160–180	Sealed tube	(42, 379, 441, 545)
4–45	150–160	Open vessel, CO_2	(259, 370)
6–52	200–220	Sealed tube	(38, 39, 42, 253, 264, 379)
2–50	170–220	Open vessel, inert gas; also in retort, collecting water of reaction	(73, 87, 97, 157, 187, 241, 249, 250, 325a, 335, 370, 537)
4–8	170–200	Vacuum	(28, 187, 352, 441, 546)
	230–250	Autoclave	(189, 481)
½–5	220–260	Open vessel, inert gas	(87, 155, 156, 157, 287, 335, 370, 453)
5–40	200–250	Vacuum	(28, 68, 548)
7–10	250–275	Sealed tube	(39, 364)
		Partial reflux, allowing elimination of water	(407)
3–6	280–290	Vacuum	(189, 390)

TABLE 3

Esterification of higher polyhydric alcohols with fatty acids, without catalyst

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	REACTION CONDITIONS	REFERENCES
	hours	°*C.*		
Polyglycerol		250	Sealed tube	(133, 264)
Glycerol trihydroxyethyl ether	2	175		(274, 288, 308, 487)
	10	205		(274, 288, 308, 487)
Erythritol		200–250	Sealed tube	(40, 44, 375)
		200–205	Open vessel	(477)
Pentaerythritol	6	180, 200, 220, 240		(56)
	6–10	200–220		(53)
		220–235		(87)
Hexitols	15–20	200–260	Sealed tube	(40, 41, 44)
	3–10	200–260	Open vessel or vacuum	(53, 87, 273, 286, 288, 370, 418)
Hexitol hydroxyethyl ethers	3–10	170–210		(274, 288, 487)
Glucose, sucrose	50–60	120	Sealed tube; poor yields	(40, 43)
Trehalose		180	Sealed tube	(43)

bulk of fatty acid disappears in about 2 hr., but an excess of unreacted glycerol remains. Monoesters form initially, but after the first half hour diesters prevail. If the reaction is continued after all fatty acid has reacted, the amount of monoglycerides again increases and the unreacted glycerol is used up (28).

At 160–180°C., 50–70 per cent of the fatty acid is esterified in about 4 hr. Depending upon the ratio of glycerol (1–10 moles) to fatty acid (1 mole), however, only 32–46 per cent of the esters formed are monoglycerides (259).

A mixture of monoglycerides and diglycerides forms when 0.8–1.4 moles of glycerol are reacted with 1 mole of fatty acid. Esterification was found almost complete after 15–20 hr. at 170–180°C., and after 3 hr. at 230–240°C. At lower temperatures, less mono- and di-glycerides were formed than at higher temperatures. If lauric or oleic acid was used, chiefly mono- and di-glycerides were formed, but with stearic acid di- and tri-glycerides prevailed (335).

No detailed study seems to have been made on any of the other polyhydric alcohols, with the possible exception of a study on pentaerythritol (56) and on erythritol esters (477).

Many catalysts speed up the esterification of polyhydric alcohols. Acidic, neutral, and alkaline catalysts have been suggested, but no systematic investigation of the comparative merits of these catalysts has ever been recorded.

Dry hydrogen chloride gas has been suggested for the esterification of glycols (128, 139, 557), polyglycols (199, 339), glycerol and polyglycerols (38, 128, 139, 187), pentaerythritol, hexitols, and sugars (53, 139, 294) at temperatures ranging from 100° to 260°C. However, products containing chlorine may result from its use (38, 39, 53, 187).

The esterification of glycols (94, 199, 339, 432, 439, 557), glycerol andpolyglycerol (39, 131, 147, 432, 439, 457), pentaerythritol, hexitols, and sugars (53, 147, 274, 288, 432, 487), and hydroxyalkyl ethers of glycerol or hexitol (274, 288, 487) may be catalyzed by sulfuric acid. However, sulfuric acid readily affects the color and purity of most chemicals coming in contact with it (39, 53), and cannot be used indiscriminately.

Phosphoric acid has also been used repeatedly (39, 199, 274, 288, 459). Boric acid is suggested for the higher polyhydric alcohols and their hydroxyalkyl ethers (274, 288, 294, 304, 487); anhydrous sulfur dioxide gives good color to reaction products of glycerol, but at the same time it isomerizes oleic acid and probably other unsaturated acids (187).

Acid salts, such as zinc chloride, calcium chloride, or copper sulfate, as well as certain phosphates, have been suggested as catalysts (33, 53, 139, 154, 271, 294, 557). Zinc chloride, particularly, is described as an ingredient of certain solid surface catalysts used at high temperatures, where at least one of the reactants is present in vaporized or finely suspended (mist) form.

A group of catalysts widely used for the esterification of polyhydric alcohols is that of organic sulfonic acids, such as the sulfonic acids of benzene, toluene, naphthalene, or camphor, and the so-called Twitchell reagents (table 4). They possess the effectiveness of sulfuric acid, but do not have its carbonizing action, and may be used in very small quantities. However, while increasing the ester yield, the presence of such sulfonic acids in the preparation of monoglycerides will lower the monoglyceride yield (259). This, of course, may be true for all catalysts.

Acetyl chloride has recently been suggested as a catalyst for the esterification of glycol in the cold (183).

The finely powdered metals, such as zinc, tin, iron, manganese, platinum, antimony, bismuth, lead, and titanium, or combinations of metals such as zinc–copper or zinc–silver are used as catalysts, either in suspension in the reacting medium or precipitated on a porous base. Shortened reaction time and light-colored products are said to be thus obtained in the esterification of glycols (297, 386), glycerol (205, 297, 298, 480), polyglycerol (491, 495), and erythritol (518).

TABLE 4

Esterification of polyhydric alcohols with higher fatty acids, using sulfonic acid catalysts

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	CATALYST (SULFONIC ACID)	REFERENCES
	hours	°*C.*		
Glycol	4–5	Benzene reflux	Aromatic	(103)
	4	120, 140, 180	Camphor	(259)
			Naphthalene	(329)
			Twitchell reagent	(147, 432)
			Alkyl or aryl	(316)
		150	Twitchell reagent	(258, 384)
Glycerol	4, 6	100	Twitchell reagent	(139, 321, 544)
	4–5	Benzene reflux	Aromatic	(57)
	½–4	120–180	Camphor	(89, 259)
	1	140	*p*-Toluene	(54, 57)
			Naphthalene	(329)
	4	160–180	Naphthalene and camphor	(260, 314)
			Twitchell reagent	(147, 432)
			Alkyl or aryl	(316)
	3	Dioxane reflux	Twitchell reagent	(457)
Others			Twitchell reagent	(16, 147)

Amphoteric metallic oxides, such as titanium dioxide (93), bismuth oxide (298), and tin or aluminum oxides (267, 272, 300), have been mentioned as catalysts. However, basic oxides, basic salts, and particularly alcoholates and soaps have found much wider acceptance for this purpose (table 5). There seems to be no evidence as to whether or not this basic group yields more valuable catalysts than the acid group. For many commercial uses a soap content of a polyhydric alcohol ester is not undesirable; thus there is no objection to the use of alkaline catalysts.

In the preparation of partial esters of polyhydric alcohols, a large excess of polyhydric alcohol is normally necessary to produce a preponderance of the desired partial esters, such as monoesters, over the more highly esterified prod-

TABLE 5

Esterification of polyhydric alcohols with higher fatty acids, using basic catalysts

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	CATALYST	REFERENCES
	hours	*°C.*		
Glycol	2	200	Sodium glycerophosphate	(31, 32)
		230	Zinc, tin, magnesium oxides	(300)
	2–3	180–200	Tin oleate	(254, 270, 284, 296, 299)
	½	230	Metallic soap	(271)
Polyglycols	Few minutes	Reflux	Sodium metal	(540)
	2	200	Sodium glycerophosphate	(32)
Glycerol	1–5	200–220	Sodium hydroxide; calcium, sodium, potassium glyceroxides	(100, 203)
		100–200	Sodium glyceroxide (instead of glycerol)	(99)
	3	275	Potassium soap	(303)
	10	180	Potassium soap	(373)
		170–210	Magnesium oxide	(298)
		180–250	Zinc, magnesium oxides	(272, 300)
	4–5	170–250	Tin, zinc, aluminum, and magnesium soaps	(267, 281, 293)
	2–7	180–200	Tin oleate	(254, 270, 284, 296, 299)
	½	230	Metal soaps	(271)
Polyglycerols		250–300	Potassium hydroxide	(461)
	1–1½	220–230	Alkaline catalyst from glycerol polymerization	(160, 161, 228, 236, 238, 240, 241, 250)
	2¼	205		
	16	190–200		
	4–5	260	Sodium acetate	(491, 495)
	16	190–200	Sodium glyceroxide	(228)
			Magnesium oxide, trisodium phosphate	(415)
Pentaerythritol	5	220	Sodium hydroxide	(203)
	1–4	240	Lead, calcium, zinc, sodium oxide	(14, 143)
	3½	190	Lead oxide	(504)
Mannitol	8½	180	Lead oxide	(504)
	5	220	Sodium hydroxide	(203)
Quebrachitol	8	235–245	Magnesium oxide	(315)

ucts; pure materials are not obtained even then, and the purification takes time and is not always successful. The use of mutual solvents, such as the phenols (69, 89, 147, 259, 260, 314, 432) or ethers such as dioxane (457), permits using only a slight excess of polyhydric alcohol, yet gives a higher percentage of partial esters.

To esterify polyhydric alcohols at lower temperatures, carrier solvents may be used. Their function is to remove water by maintaining the reaction mixture at its boiling point. If these solvents are immiscible with water, the azeotropic distillate may be condensed into a Bidwell–Sterling tube, where the water may be separated from it and the carrier may be returned into the reaction vessel, allowing the continuous use of a small amount of solvent. Toluene, xylene, ethylene dichloride, carbon tetrachloride, secondary amyl alcohol, or closely boiling naphthas are such solvents (94, 103, 147, 181, 316, 432). If a water-miscible solvent is used, the removal of the water from the vapors may be accomplished by drying agents, notably calcium carbide (103) or calcium chloride (316, 457).

Most polyhydric alcohol–fatty acid reactions are heterogeneous, at least during the initial stage. Consequently, the speed and course of reaction can be greatly influenced by efficient agitation. In many investigations no such agitation has been used. On the small scale, a rapid current of air, carbon dioxide, or another inert gas has often been considered sufficient agitation. The stirring and water-removing effect of a current of gas may be combined with the mixing action of mechanical stirring by introducing the gas into the center of the stirrer vortex, thus "whizzing" it throughout the reaction mixture. This procedure is stated to shorten the reaction time and to yield purer materials (73, 370).

Such currents of inert gases, e.g., carbon dioxide, nitrogen, or hydrogen, and also a vacuum, have been used to protect reaction mixtures, as well as to help the removal of moisture. Their influence has been studied on the reaction of glycerol with oleic acid (187). In this case, carbon dioxide gave products of good color, while nitrogen and reduced pressure did not. In no case was the rate of reaction influenced by the use of vacuum or inert gas under the conditions studied.

Information on reaction yield is not always given in the literature and is often ambiguous. In the patent literature, "yield" indicates, as a rule, the total of the useful product which need not be further purified and may contain a variety of ingredients. However, in technical papers "yield" refers to the purified products, generally excludes by-products and fractions which are not fully pure, and ignores solvents or auxiliary reagents. Products are often obtained from a reaction which has not been carried to completion. Sometimes the yield is based on one, not all, of the reactants used. It was, therefore, not possible to survey yield to advantage.

It was stated initially that polyhydric alcohol esters can be subdivided into two basic groups: completely esterified and partially esterified compounds. Esters of the former group are accessible by comparatively simple methods. Preparation of members of the latter group has given considerable trouble, because of the tendency to form mixtures. In direct esterification an excess of polyhydric alcohol is used to obtain incompletely esterified materials. A survey of the literature shows excesses of up to 33 moles of glycol for each mole of fatty acid (183, 259, 473, 474), and up to 11.5 moles of glycerol to 1 mole of fatty acid (28, 33, 38, 39, 42, 46, 59, 97, 103, 241, 249, 250, 253, 259, 260, 264, 314, 335, 352, 441, 457, 459, 537, 544, 548). With the higher polyhydric alcohols, such as erythritol, pentaerythritol, or mannitol, a greater excess seems to be of little value in securing a preponderance of lower esters (53, 56, 418, 477, 504, 518).

Continuous esterification at elevated temperatures is described in a series of patents. The polyhydric alcohol and the fatty acid are brought to react in vaporized form or in the form of mists, and are introduced through spray nozzles into a reaction chamber. The ester product collects in condensed form, owing to its higher boiling point (68, 93, 254, 270, 271, 272, 284, 285, 296, 300). This procedure may be carried out in special reactors designed to allow the mixture to pass through at varying speed or temperature (298).

When an excess of polyhydric alcohol is used, it will generally separate at the end of the reaction as an immiscible layer, or it may be washed out with water. In the case of products which are highly dispersible in water, such as polyglycerol esters, this is not possible, but washing may be carried out with certain concentrated salt solutions (185, 358, 359, 362, 363).

Excess fatty acids may be removed from polyhydric alcohol esters by neutralizing them to form soap, and extracting the esters with ether or with chlorinated solvents, such as dichloroethylene (90).

Ether alcohols, obtained by reacting alkylene oxides (or other anhydro derivatives of polyhydric alcohols) with the polyhydric alcohols, may be esterified with fatty acid in the manner described (274, 275, 288, 302, 308, 487, 488).

Partially esterified polyhydric alcohols may be further esterified with fatty acids, just as the polyhydric alcohols from which they are derived. This method does not furnish well-defined esters and offers no particular advantages as a reliable tool. Thus, glycerides were heated with an excess of fatty acid for 3 to 8 hr. at 200–270°C. (38, 39, 42, 253, 264), or with a sulfonic acid catalyst for 5 hr. at 120–130°C. (377). Mannitol diester has been further esterified in 20 to 30 hr. at 220–230°C. (53). Several technical applications are known: for instance, the neutralization of acidic oils (480, 536), the reësterification of certain partial esters of drying oil fatty acids (144), and the production of mixed esters (238, 241, 249, 250).

2. Reaction of polyhydric alcohols with anhydrides of fatty acids

Esterification with acid anhydrides is carried out in solvents at temperatures not exceeding 100°C. Materials such as glycerol, pentaerythritol, sorbitol, sugars, inositol, or quebrachitol may be reacted under the action of ketene gas, in the presence of condensation catalysts (sulfuric, hydrofluoric, perchloric acids; zinc chloride; benzenesulfonic acid) (145). Sucrose, dissolved in ten times its weight of monochloroacetic acid, may be reacted with fatty anhydrides, alone or mixed with acetic anhydride, using catalysts such as sulfuryl chloride or mag-

TABLE 6

Reaction of polyhydric alcohols with fatty acid halides

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	REMARKS	REFERENCES
	hours	*°C.*		
Ethylene glycol	24	In the cold; later 60	Pyridine	(514, 521, 555)
	48–72	In the cold	Quinoline	(564)
		Up to 180	No solvent used	(420)
1,2-Propylene glycol	2–3	95–100	No solvent used	(1)
			Pyridine	(514)
1,3-Propylene glycol			Pyridine	(515)
1,3-Butylene glycol			Pyridine	(514)
1,4-Butylene glycol			Pyridine	(514)
Glycerol	½	125–130	Tertiary amine	(192, 269)
Erythritol			Formation of tri- and tetra-esters	(477)
Pentaerythritol	24	In the cold; later 60	Pyridine (6 moles)	(3)
			Pyridine	(274, 288, 487)
Mannitol	24	In the cold: later 60	Pyridine (10 moles)	(521)
Sorbitol	Several	Room	Pyridine	(274, 288, 487)
Dulcitol			Quinoline	(406)
l-Arabinose		50	Quinoline, chloroform	(406)
Glucose	24	Room; later 60	Pyridine (up to 15 moles	(60, 228, 231, 232, 521)
	8–12	60	Pyridine	(95)
		In the cold	Pyridine	(25, 265, 292, 465, 484)
	12	In the cold	Pyridine	(565)
Glucose (α)	4–6 (total 24)	Cold; −10, later 60	Pyridine (up to 25 moles)	(256, 565)
	72–96	15–18	Pyridine (up to 25 moles)	(256)
Glucose (β)	¼ – ½ (total 24–72)	Cold; 10	Pyridine	(565)

TABLE 6—*Continued*

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	REMARKS	REFERENCES
	hours	°*C.*		
α-Methyl-*d*-glucoside.		50	Quinoline, chloroform	(405a, 406)
Sucrose.	½ - 3 (total 4–48)	Room, 60	Pyridine (38 moles)	(256)
		70–80	Pyridine	(25, 265, 292, 465)
	½	125–130	Tertiary amine	(192, 269)
Raffinose.			Hendeca ester	(256, 406)
α-Monoglyceride.	24	Cold	Pyridine, benzene	(377)

nesium perchlorate (371). Hydrol sugars and fatty anhydrides are reacted for 8 to 12 hr. at 100°C. (95, 120). α-Glucose pentacaproate has been obtained from glucose and caproic anhydride (256), and methylene glycol dimyristate from paraformaldehyde and myristic anhydride, by heating them to 100°C. with zinc chloride (514).

3. *Reaction of polyhydric alcohols with fatty acid halides*

Polyhydric alcohol esters may be obtained by dissolving an anhydrous polyhydric alcohol in a large excess of an anhydrous tertiary amine, such as pyridine, quinoline, or trimethylamine. A fatty acid halide, usually a chloride, is added to the solution, preferably dissolved in a chlorinated solvent such as chloroform. This method allows the use of low temperatures, but anhydrous working conditions are essential and the reagents are comparatively expensive (table 6). The reaction products are purified by pouring them into dilute aqueous mineral acid to remove all the excess amine and its halide salt. The ester product, recovered as a supernatant layer or by extraction, is treated to remove free acidity. This method is most suited to the preparation of the fully esterified product. Where pure partial esters are desired, certain modifications of the method are more suitable. These will be discussed later.

The amines may also be replaced by metallic halides which help to liberate hydrogen halide (192, 269). In another variation the polyhydric alcohol and the fatty halide are mixed directly, eliminating the free hydrogen chloride by means of a current of gas (1, 420). It has also been proposed to react the fatty acid halide with a tertiary amine first, filter off the precipitate of hydrochloride salt, and react the filtrate with a polyhydric alcohol (269, 283).

Evidence exists that a mixture of more and less esterified materials is formed with this method in at least some cases (256, 477, 484). No clearly defined yield data could be assembled.

4. Reësterification of fatty acid esters with polyhydric alcohols

One of the most widely used methods for the preparation of polyhydric alcohol esters is based upon the reësterification of fatty acid esters, and especially of the naturally available triglyceride fats. The reaction can proceed without a catalyst, but may be considerably speeded up if catalysts are used. Reësterification reactions involving polyhydric alcohols have been carried out along two different lines: (*1*) with elimination of the alcohol previously present in the fatty acid ester, usually by distillation (this is practical only if the polyhydric alcohol introduced for reaction has a higher boiling point than the alcohol present in the ester); (*2*) by allowing all ingredients to remain in the reaction product, even if esters of different alcohols are present in the resulting material.

TABLE 7

Reactions of polyhydric alcohols with alkyl esters

Polyhydric alcohol: glycerol

ESTER	TIME	REACTION TEMPERATURE	REMARKS	REFERENCES
	hours	°C.		
Ethyl......	102	100	Incomplete reaction; HCl catalyst	(38, 39)
		270	Incomplete reaction; autoclave, no stirring	(219)
	15	270–280	Open vessel, 94% conversion	(219)
Isoamyl....	15	270	Open flask, 100% conversion	(219)
Methyl.....		100	Incomplete reaction; HCl catalyst	(450)
	5, 48	70	Presence of acetone, HCl catalyst; forms isopropylideneglyceride	(450)
	24	100	Sodium methylate catalyst, in pyridine	(450)
Cetyl.......		200	Contradictory results; catalyst: zinc	(336, 404)
Alkyl.......			Sodium methylate or sulfonic acid catalysts; glycerol may be replaced by erythritol, arabitol, xylitol, mannitol, sorbitol, etc.	(204)

The most thoroughly studied example of the former type (reësterification with elimination of the lower boiling alcohol) is the reaction of alkyl esters with glycerol (219). It has been shown that under suitable conditions this reaction is reversible and is forced to go in the direction of glycerides only when the other alcohol is forced out by heat (table 7).

Only a few attempts have been recorded to replace the glycerol of triglycerides by higher boiling polyhydric alcohols, because of the high temperature required to distill off the glycerol. In the presence of a strong catalyst, sodium methylate, olive oil and tristearin have thus been reësterified with mannitol by raising the temperature to 275°C., while keeping the pressure at 14 mm. of mercury (190, 319, 354). Similarly, olive oil has been reacted with α-methyl-*d*-glucoside, by heating them to 220°C. under a pressure of 10 mm. of mercury (318). Sorbitol or pentaerythritol esters may be prepared similarly, using sodium methylate, but sulfuric or phosphoric acids have also been mentioned as catalysts (14, 143).

The second method, in which both the alcohol originally present and the alcohol added for reaction remain in the reaction product, has found very wide application in industry. Any type of alcohol can be used. Naturally, unless the polyhydric alcohol added is identical with the alkyl radical of the ester—usually glycerol—a mixture of esters will result. For many technical purposes, however, such mixtures have proven extremely useful. Often compounds with properties superior to those of the individual ingredients may be obtained. As in the case of direct esterification, the reaction runs only towards an equilibrium and the product is always a mixture (404, 405).

TABLE 8

Reësterification of triglycerides by polyhydric alcohols, without catalyst

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	REMARKS	REFERENCES
	hours	*°C.*		
Ethylene glycol...	1–2	200	Presence of ethanol, benzene, hydrogen gas under 90 atmospheres pressure has no effect; water slows reaction; autoclave	(338, 404, 405)
	9–13	200	Autoclave	(404)
Glycerol..........	1–9	200	Pyridine speeds reaction; ethanol has no effect	(404)
	2	200	Reflux	(57)
	22	200	Sealed tube	(38, 39)
	3	170–220	Partial reaction	(336)
	1–5	225–250	Partial or poor reaction; addition of monoglyceride speeds it	(336, 428, 429, 430, 435, 436, 470)
	1–5	270–290	Moisture formed in side reactions may be removed by partial reflux	(78, 79, 167, 329, 391, 392, 489, 499, 543, 564)
			No details available	(12, 28, 78, 79, 108, 109, 114, 115, 374, 529, 530)
Quebrachitol.....			No details available	(315)

Reësterification may be carried out without a catalyst but has been found to be speeded up greatly by catalysts, especially basic ones. Investigations on glycerol and pentaerythritol show this particularly well (57, 336). Of the few neutral and acid catalysts mentioned, it is stated that they are weak or ineffective (404). This type of reaction is reviewed in tables 8, 9, and 10.

As can be seen from these tables, the alkalis, alkali carbonates, alkali alcoholates, or generally any alkaline substance capable of forming soaps, as well as the soaps themselves, are the strongest and most frequently used reësterification catalysts.

TABLE 9

Reësterification of triglycerides by polyhydric alcohols, using alkaline catalysts

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	CATALYSTS AND CONDITIONS	REFERENCES
	hours	*°C.*		
Ethylene glycol	1	200	Potassium carbonate	(404)
	2	150	Soap, alcoholate	(153, 427, 434)
Propylene glycol	¼–2	180–200	Potassium soap	(558)
Diethylene glycol		Reflux	Sodium metal	(149)
Glycerol	72	25	Sodium methylate, pyridine; poor reaction	(450)
	1–3	170–205	Potassium carbonate, sodium bicarbonate	(201, 202, 336)
	⅛ to 4	140–205	Sodium (potassium) glyceroxide or alcoholate; soap; alkali; sodium acetate	(54, 81, 82, 83, 84, 85, 149, 150, 151, 152, 153, 235, 239, 425, 426, 427, 434)
			Sodium metal	(426)
	2–5	200–220	Potassium carbonate; borax (poor); sodium hydroxide	(203, 336, 404)
	1½–5	240–290	Sodium (potassium) hydroxide; sodium carbonate; soap; sodium alcoholate	(249, 250, 303, 334, 336, 453, 471, 504, 506, 543)
	¼	290	Trisodium phosphate, sodium carbonate; nitrogen gas	(564)
	1½	Reflux	Sodium hydroxide or glyceroxide; in dioxane	(458)
Polyglycerol	1–3	250–265	Sodium hydroxide; sodium acetate	(160, 161, 168, 236, 238, 240, 241, 250, 451, 491, 492, 495)
Erythritol	5	220	Sodium hydroxide	(203)
Pentaerythritol	2½	205–210	Potassium hydroxide or alcoholate; alkalies	(14, 54, 57)
Sorbitol		240–280	Alkali	(303)
Mannitol	5	220	Sodium hydroxide	(203)

The usefulness of certain basic salts, notably borax and trisodium phosphate, is doubtful. Other metallic oxides also act as catalysts, their effectiveness falling off in proportion to their alkalinity; calcium hydroxide or oxide, litharge, and magnesium oxide are preferred. The presence of water retards reësterification, and should be avoided (150, 151, 391, 392, 404, 499). Metals, particularly when combined with fatty acid, are fairly good catalysts (336).

While most of the reëesterifications are based on the triglycerides, the method has been shown to be capable of generalization, by reacting glycol with glycol dipalmitate in the presence of trisodium phosphate (564).

TABLE 10

Reësterification of triglycerides by polyhydric alcohols, using metal or metallic oxide catalysts

POLYHYDRIC ALCOHOLS	TIME	REACTION TEMPERATURE	CATALYSTS AND CONDITIONS	REFERENCES
	hours	°C.		
Ethylene glycol.....	1–2	170–190	Litharge	(558)
		180–200	Tin	(490, 494)
Glycerol............	$\frac{1}{4}-\frac{1}{2}$	200–280	Litharge	(54, 144, 170)
	1–2	200–280	Zinc oxide	(54, 404, 543)
	1–4	200–275	Calcium oxide, magnesium oxide, calcium glyceroxide	(54, 57, 301, 404, 543)
			Iron oxide, cobalt oxide	(54)
	3–5	170–250	Tin, zinc, aluminum metals, alone or with fatty acid	(224, 336, 480, 490, 494)
	1	230–250	Alumina, clay, infusorial earth; (hydrogen gas)	(10)
Erythritol..........		180–200	Tin	(490, 494)
Polyglycerol........		180–200	Tin	(490, 494)
Pentaerythritol.....	3	220–270	Calcium oxide	(57)
	$\frac{1}{4}$	280	Litharge, calcium oxide: effective. Magnesium oxide: less effective. Zinc, iron, cobalt oxides: ineffective	(54, 144)
Sorbitol, mannitol..			Litharge	(144)
Mannitol, sorbitol..		180–200	Tin	(490, 494)

Reëesterification with alcohols is just one separate case of a more general type of reaction by which radicals in esters can be interchanged with alcohols, acids, or other esters. It may also be carried out simultaneously with esterification (336, 405).

Where the presence of soap in products resulting from reësterification is objectionable, methods have been suggested for its removal. The most usual method is its decomposition with acid (81, 82, 83, 84, 85, 235, 239, 453, 471). To avoid the formation of free fatty acid, the soap removal may be carried out by reaction with certain halogen-containing compounds, such as halohydrins, or with other compounds capable of yielding acid, such as the sulfuric esters of the polyhydric alcohols, thus yielding an ester and an inorganic salt (201, 202). The soap may also simply be removed by extraction of the ester with a suitable solvent (90, 331).

As in esterification, partial esters are formed if an excess of polyhydric alcohol is used, but unless sufficient soap is used or formed, the excess of polyhydric alcohol is not compatible with the resulting ester and must be drained or washed off. Under certain conditions, a very large excess of polyhydric alcohol can be kept homogeneously mixed with the product or reacted with the product (303, 458). Where the ester products are water soluble, unreacted excess of polyhydric alcohol may be removed by washing with certain salt solutions (185, 358, 359, 362, 363).

To produce special "cuts" of polyhydric alcohol esters by reësterification, the following procedure has been suggested: reësterification of triglycerides (with monohydric or polyhydric alcohols); fractionation of the products by liquid–liquid extraction, using mixtures of solvents which will separate into two liquid layers; and, finally reësterification of the fractionated esters (having higher or lower iodine values) with polyhydric alcohols, such as glycols, glycerol, erythritol, arabitol, xylitol, mannitol, or sorbitol. The preferred catalyst suggested is sodium methylate (203).

Reactions between polyhydric alcohols, fatty acids, and polyhydric alcohol esters must be considered reversible. Disproportionation of monoglycerides by heating them *in vacuo* at elevated temperatures is one interesting example. Monoglyceride thus turns into diglyceride and finally into triglyceride, with loss of free glycerol (220, 564).

5. Etherification of polyhydric alcohol by reaction with partially esterified polyhydric alcohols

As previously mentioned, reësterification of oils with polyhydric alcohols may be carried out with a large excess of polyhydric alcohol. This excess is said to react with the esterification product, yielding a homogeneous material (303, 458). Similarly, fatty acids may be reacted with a large excess of polyhydric alcohol, for example, in the presence of a mutual solvent, a water carrier, and a suitable catalyst, notably sulfuric or certain sulfonic acids (147, 432). Apparently the polyhydric alcohol present in excess reacts with the partial esters, forming esters of polyhydroxy ethers. Thus, mono- or di-glycerides either previously prepared, or formed *in situ*, form polyglycerol esters with excess glycerol. Water split out in reactions of this type has been observed to be more than that theoretically expected, a fact which has been explained as being caused by "side reactions" (57, 73, 151, 153, 264, 370). Etherification of glycols during reactions with fatty acids in the presence of dehydrating catalysts has also been mentioned (557).

B. PREPARATION FROM FULLY ESTERIFIED POLYHYDRIC ALCOHOLS

1. Reaction of fully esterified polyhydric alcohols with water

Polyhydric alcohol esters are formed by the reaction of polyhydric alcohols with fatty acids with the elimination of water. Reversing this reaction, it should be possible to obtain the partial esters which are formed during the hydrolysis of polyhydric alcohol esters. However, partial esters are very difficult to catch in this way, because most of them hydrolyze too quickly (378, 542a). A small quantity of mono- and di-glycerides can be isolated from glycerides that have been autoclaved with water for several hours (378). Similarly, losses of glycerol in fat splitting have been explained by the formation of partial glycerides (317). Naturally, this is not a practical method.

2. Reaction of fully esterified polyhydric alcohols with concentrated sulfuric acid

Hydrolysis of glycerides may be carried out with concentrated sulfuric acid in the cold. It was found (214, 218, 537) that if concentrated sulfuric acid was allowed to act on triglycerides at temperatures up to 70°C., 50 to 65 per cent of the material was hydrolyzed to free fatty acid and glycerol, while the remaining glycerides presented a mixture of triglycerides with diglycerides and a small percentage of monoglycerides. This seems to happen during the sulfonation of oils. Sulfonated oils contain considerable amounts of diglycerides in their neutral oil fraction (350).

3. Reaction of fully esterified polyhydric alcohols with alkali

Though in a survey in 1913 (378) it was stated that it had not been possible to find mono- or di-glycerides when interrupting the alkaline hydrolysis of triglycerides at an early stage, it was nevertheless admitted that their existence—at least temporarily—was possible. In later years, a number of patents were taken out along these lines, claiming that a mixture of mono-, di-, and tri-glycerides together with soap is obtained when triglycerides are treated with alkali. One such method involves heating the triglycerides to about 200–220°C., and adding alkali (anhydrous or as a concentrated aqueous solution), heating for 5 to 10 min., and cooling rapidly (249, 234, 235). The products may be plunged into cold water and their alkalinity partly neutralized with acids.

Another method is based upon the treatment of triglycerides with alkali in the cold in the presence of suitable solvents such as glycols or glycol-ethers (127, 330, 331, 505). While not yielding pure products, this method can obviously be used where the presence of soap is not undesirable.

4. Reaction of fully esterified polyhydric alcohols with alcohols

Polyhydric alcohol esters, such as triglycerides, can be reësterified with monohydric alcohols, forming monohydric alcohol esters. Initially, partial polyhydric alcohol esters are still found in the product, but finally polyhydric alcohol (glycerol, in the case of triglycerides) separates and the partial esters disappear. Materials of this type have been prepared and can be easily analyzed, after removal of the free alcohol, by distillation, or merely by determination of the acetyl value (1, 217, 219, 404, 469, 541).

C. PREPARATION FROM ANHYDRO DERIVATIVES OF POLYHYDRIC ALCOHOLS

A different approach to the preparation of polyhydric alcohol esters is by the addition reaction of anhydro derivatives of polyhydric alcohols and fatty acids. Such anhydro derivatives are the alkylene oxides (e.g., ethylene oxide, propylene oxide, glycide) or their halogen derivatives (e.g., epichlorohydrin). Instead of fatty acids, their anhydrides or halides may also be used.

To carry out this reaction, the low-boiling alkylene oxide is introduced into a pressure vessel containing the fatty acid and usually a catalyst. The reaction mixture is heated and stirred under pressure until enough of the alkylene oxide has been absorbed. A reaction of this type will normally yield only partial esters containing free hydroxyl groups (table 11).

Fatty acids may be esterified, and the products etherified by using an excess of the anhydro polyhydric alcohols, forming polyalkylene glycol esters, or polyalkoxy-polyhydric alcohol esters (table 12).

Partial polyhydric alcohol esters, obtained otherwise, may likewise be reacted with anhydro derivatives of polyhydric alcohols. An example is the reaction of a glycerol monoester with two or more parts of ethylene oxide (275, 302, 488).

Products obtained by reaction of anhydro-polyhydric alcohols with carboxylic acids may be purified by liquid–liquid extraction of the crude reaction products (279).

D. PREPARATION FROM SUBSTITUTED DERIVATIVES OF POLYHYDRIC ALCOHOLS

1. Reaction of polyhydric alcohol halides with salts of fatty acids

Reactions of halides of polyhydric alcohols with metallic salts of fatty acids (soaps) also yield polyhydric alcohol esters. Though this method has been used for numerous investigations in the past, its value has been reduced considerably by the discovery that, owing to acyl migration, fatty acid radicals are not necessarily introduced to take exactly the place of the halogen. The products are impure, and their purification is complicated.

The halide is mixed and heated with anhydrous soap for a number of hours, usually with stirring or shaking. The reaction has been carried out either in sealed tubes or under reflux. The polyhydric alcohol ester or esters and the unreacted fatty acid are recovered as an oil or solid, and there is a precipitate of inorganic halide salts. Unreacted organic halide and unreacted soap may also be present. The polyhydric alcohol ester may be purified by dissolving the oil layer in a suitable solvent (which will not dissolve soap and inorganic salts), such as ether, filtering, neutralizing the free fatty acid with alcoholic alkali, evaporating the solvent, and extracting and filtering once more. The extract thus obtained is washed with water, dried, and evaporated to yield the polyhydric alcohol ester. The yield from this type of reaction is stated to be poor.

TABLE 11

Condensation of fatty acids with anhydro derivatives of polyhydric alcohols

ANHYDRO POLYHYDRIC ALCOHOLS	TIME	REACTION TEMPERATURE	CATALYSTS, REMARKS	REFERENCES
	hours	°C.		
Ethylene oxide...	Several		Sodium hydroxide, autoclave	(496, 524)
	6	160	Zinc chloride, boric acid	(282)
		Elevated	Titanium dioxide, aluminum oxide, sodium chloride	(268)
Alkylene oxide....		Elevated	Mineral acid, acid salts, basic salts	(266, 366, 367, 368)
		Elevated	Fatty acid anhydride used	(516)
Glycidol..........	5	100	Secondary reaction, when iodohydrin is heated with silver soap; slow and incomplete	(221)
			Alkalies, alkaline salts, organic acids, or acid-reacting salts	(412a)

TABLE 12

Condensation of fatty acids with an excess of anhydro derivatives of polyhydric alcohols

ANHYDRO POLYHYDRIC ALCOHOLS	REACTION TEMPERATURE	CATALYSTS, REMARKS	REFERENCES
	°C.		
Alkylene oxide (ethylene, propylene)...........	130–140	2 moles or more of oxide for 1 mole of fatty acid	(278)
Ethylene oxide..........	160	4 moles or more of oxide for 1 mole of fatty acid; sodium hydroxide, sodium alcoholate	(312)
Alkylene oxide..........	80–250	6 to 50 moles of oxide for 1 mole of fatty acid; acids, alkalies, active carbon or clay	(275, 302, 488)
Glycidol................	150	Sodium hydroxide: 2 moles or more for 1 mole of fatty acid	(276)
Epichlorohydrin........	50–100	Aluminum chloride, iron chloride, boron trifluoride, sodium aluminum chloride; chlorine atom may be reacted further	(291, 517)
Glycidol and other alkylene oxides............		Alkalies, alkaline salts, organic acids, acidic salts	(412b)

TABLE 13

Reaction of polyhydric alcohol halides with fatty acid salts (soaps)

HALOHYDRIN	TIME	REACTION TEMPERATURE	METAL SALT USED; REMARKS	REFERENCES
	hours	*°C.*		
1-Chloroethanol	18–20	105–115	Ag	(474)
1,2-Bromoethane	Several	Reflux	Ag	(420, 563)
	10	180	Ag; sealed tube	(421a)
	3	130–140	K; open flask, nitrogen gas	(532)
		150	K; sealed tube	(532)
	48	140	Na	(88)
1,2-Chloroethane	10–15	180	K; excess halide yields chloroethyl esters	(351)
		200	Li	(518)
	1	150	Na; started as aqueous gel, dehydrated during reaction	(21, 22)
		160–180	K, Na, Li, Ca; in ethanol under pressure	(460)
1-Monoiodohydrin	2	100	K; forms diglycerol ester as by-product	(221)
		100	Ag; forms AgI, free acid, glycidol, impure esters	(221)
	4–10	110	Na; flask, reflux, or sealed tube	(13, 225, 252, 537)
		80–170	Na	(548)
	6	150–160	Na; reflux or sealed tube, CO_2	(441)
	4–6	140–150	Na (in dibutyl ether); sealed tube	(11, 344)
	12	160	K; hydrogen gas	(322)
	6	180	K; sealed tube, CO_2	(351)
	⅙	112	Pb; CO_2	(75)
1-Monochlorohydrin	10	180	Ag	(379)
2-Monochlorohydrin			K; halide used not pure	(171)
1,3-Dichlorohydrin	4	110	Na	(13)
	6–8	140–150	Na; sealed tube, CO_2	(225)
	8–9	140–150	Na	(172, 252, 537)
	10	170	Na; stoppered flask	(353)
	6–8	180	Na	(441)
			Na	(354, 459)
		120–140	K; CO_2	(216)
	9–10	140–150	K	(207, 208, 213)
	2½–9	160–170	K	(64, 213)
	12	160	K; hydrogen gas	(322)
	3½	160–170	K; in xylene	(539)
			K	(218)
	⅙	112	Pb; CO_2	(75)
	6	140–150	Pb	(537)

TABLE 13—(*Continued*)

HALOHYDRIN	TIME	REACTION TEMPERATURE	METAL SALT USED; REMARKS	REFERENCES
	hours	°C.		
1,2-Dibromohydrin	6–8	140–150	Na; sealed tube	(225, 449)
	72	120–135	Na; sealed tube	(449)
	6	175–180	Na; sealed tube	(441)
	12	180–200	Na; sealed tube	(449)
	6–8	150	K	(211)
	3¼	160–170	K	(539)
	4	122	Pb; under pressure	(449)
1,2-Dichlorohydrin	10	112	Pb; CO_2	(75)
1,4-Dichloro-2,3-butanediol			Na; impure erythritol derivatives	(477)
2,3-Dichloro-1,4-dioxane	25	152–156	Free acid used, freeing HCl; in xylene	(510)
	14	161–190	Free acid used, freeing HCl; in xylene	(510)
Halohydrin			Any soap	(128, 488)

The preferred metallic salts for this reaction are sodium or potassium soaps, but lead and silver soaps have also been used. In the case of silver the reaction does not proceed satisfactorily. While silver chloride is formed at once, glycidol and free fatty acid form instead of the expected glycerol ester. On further heating, these materials yield a mixture of esters (221) (table 13).

This method has also been tried for further reaction of esters of polyhydric alcohol halohydrins, such as 1-lauro-3-chlorohydrin, with soaps of fatty acids (209).

2. *Reaction of sulfuric acid esters of polyhydric alcohols with fatty acids*

Sulfuric acid esters are formed in the reaction of polyhydric alcohols with cold concentrated sulfuric acid. With glycerol, diesters of sulfuric acid are formed, probably accompanied by small amounts of other esters. These sulfuric acid esters react with free fatty acids dissolved in concentrated sulfuric acid. At low temperatures, such as from 40° to 75°C., a homogeneous solution results, and after several hours fairly large quantities of polyhydric alcohol esters of fatty acid have formed. The original method of purifying these esters (by extracting the strongly cooled mixture with ice-cold ether and diluting this with ice-cold water) gives poor yields, because of hydrolysis and side reactions (such as the formation of ethyl esters of fatty acids). This is avoided by pouring the reaction mixture into ammonium sulfate solution, followed by washing and then extracting with ether (59, 60). High-molecular-weight fatty acids (e.g., stearic) give better ester yields with this method than do fatty acids of lower molecular weight (e.g., lauric).

A considerable amount of unreacted fatty acid is recovered in the crude ether extract. This must be neutralized into soap and removed as such. (See table 14.)

TABLE 14

Reaction of sulfuric acid esters of polyhydric alcohols with fatty acids

POLYHYDRIC ALCOHOL	TIME	REACTION TEMPERATURE	REMARKS	REFERENCES
	hours	°C.		
Glycerol	3	70	Glycerol:H_2SO_4, 1:4 by weight; fatty acid: H_2SO_4, 2:3 by weight; yield varies from 34 to 80% according to method of purification	(206, 207, 537, 548)
	4	50–60	Glycerol:H_2SO_4, 1:4.35 by weight; yield varies	(213, 215, 538)
Mannitol	3	65–75	1 g. mannitol to 7.5–10 cc. of H_2SO_4; yields mannide, mannitan esters; yield, 50%	(58, 59)
		38–40	Mannitol:H_2SO_4, 1:20 by weight; yield varies from 45 to 85% according to method of purification; mannitan, isomannide ester	(59, 60, 323)

3. *Interchange of polyhydric alcohol esters of volatile acids with fatty acid esters of volatile alcohols*

Another method of making polyhydric alcohol esters is by the reaction of short-chain fatty acid esters of polyhydric alcohols, such as glycol diacetate, with short-chain monohydric alcohol esters of long-chain fatty acids, such as methyl stearate. The two volatile radicals combine to form a volatile ester, methyl acetate, leaving the polyhydric alcohol ester behind. This reaction may be carried out at relatively low temperature (414).

E. PREPARATION FROM "PROTECTED" DERIVATIVES OF POLYHYDRIC ALCOHOLS

1. *Reaction of polyhydric alcohol halohydrins with fatty acid halides*

The first step of this reaction consists in treating a polyhydric alcohol halohydrin (e.g., monochloroethanol, 1-monoiodopropanediol, 1,3-dichloropropanol) with a fatty acid halide at room temperature or at a slightly elevated temperature. The hydrogen halide liberated may be driven off by a current of air (210), or may be neutralized by a tertiary amine such as quinoline (8, 20, 177). An attempt to use this for a reaction with erythritol 1,4-dichlorohydrin has also been recorded (477).

The halogen-containing ester is now treated at 120–130°C. with an equal weight of silver nitrite to remove the halogen groups (171, 172, 208, 209, 210, 212, 218, 322, 459, 539). This procedure requires 5–14 hr. and is usually carried out in an atmosphere of hydrogen. Silver oxide has also been used (420). A much better yield may be obtained if the reaction is carried out in a solvent, such as 90 per cent ethyl alcohol. Seventy-five per cent of the expected yield has been obtained thus after only half an hour (8, 20, 177).

As a result of acyl migration, however, the partial esters produced do not necessarily contain the acyl group where the hydroxyl group had been in the halohydrin; hence this method has little value as a reliable tool. 2-Acylglycerides prepared by it were found to be merely 1-acylglycerides, which may readily be obtained otherwise (171, 172).

Esters obtained by this method are purified by ether extraction (in the presence of a little hydrochloric acid to remove all excess silver salt), neutralization, and filtration.

2. Reaction of isopropylidene derivatives of polyhydric alcohols with fatty acid halides, and tertiary amines

The first successful method to direct the fatty acid radical into a well-defined position in the glycerol molecule was found in the acylation of isopropylidene derivatives of glycerol. In reacting glycerol with acetone by the action of dry hydrogen chloride gas, 1,2-isopropylideneglycerol is always formed. After reacting this with the fatty acid halide, usually in the presence of pyridine or quinoline, the isopropylidene group is removed by short contact in the cold with concentrated hydrochloric acid, dilution with cold water, and purification of the water-insoluble ester.

While thus far recorded only in connection with glycerol esters, this method is likely to be of general value, as the formation of isopropylidene derivatives of other polyhydric alcohols, such as mannitol, has been shown to be possible, and it is likely that they will lend themselves to the same reaction.

With glycerol, this method is the most reliable known to obtain 1(or alpha)-monoesters. It has been used to prove that all older methods yield primarily 1-acyl or 1,3-acyl esters with glycerol. The method usually gives good yields.

The isopropylidene group is introduced by allowing anhydrous, freshly distilled glycerol to stand with acetone saturated with dry hydrogen chloride over fused anhydrous sodium sulfate. The hydrogen chloride in excess is then removed, the acetone distilled off, and the isopropylidene glycerol itself is rectified by distillation.

The isopropylidene product is reacted with a fatty acid halide (chloride) and a tertiary amine in the usual manner, usually at room temperature or below. Purification of the isopropylideneglycerol ester consists in removal of the pyridine or quinoline by pouring it into *N*/2 sulfuric acid in the presence of ether, washing, and recovery of the ester. A variation of the method, much simplified, has also been proposed (376): isopropylideneglycerol is reacted with the fatty acid itself by passing in dry hydrogen chloride gas for 15 min., and the product is poured into water.

The isopropylidene group is then removed from the ester by the action of concentrated hydrochloric acid, at room temperature, for about 30 min. (8, 8a, 20, 23, 52, 64a, 65, 66, 171, 176, 376, 450, 533, 548). This may be carried out in the presence of a solvent, such as ether. For esters of the lower members of the fatty acid series, such as lauric acid, the hydrolysis must be carried out at −15°C. to 0°C. and must not last more than 5 to 10 min. (171, 176, 450, 459, 564). Another method of hydrolysis consists in treatment with *N*/4 sulfuric acid at 45°C., followed by neutralization with barium hydroxide (20).

When glycerol and the methyl ester of a fatty acid are refluxed in acetone in the presence of hydrogen chloride gas, a large quantity of isopropylidene monoglyceride forms, from which monoglyceride can be recovered (450).

3. Reaction of benzylidene derivatives of polyhydric alcohols with fatty acid halides and tertiary amines

A second method developed to yield well-defined glycerol derivatives is based upon the reaction of benzaldehyde with glycerol, which yields 1,3-benzylideneglycerol. The purified benzylideneglycerol is treated at room temperature for 18–24 hr. with fatty acid chloride in the presence of a tertiary amine, such as pyridine, and is purified as described previously for this type of reaction.

The purified 2-acylbenzylideneglycerol is suspended in absolute alcohol, and hydrogenated in the presence of a palladium black catalyst for 1½ to 2 hr. at room temperature. A 2(or beta)-monoglyceride can be obtained by crystallization from the resulting solution (36, 121a, 522).

This method was the first one which yielded true 2-monoglycerides, and may yet find more general application; benzylidene derivatives of higher polyhydric alcohols, such as mannitol or sorbitol, have already been prepared.

4. Reaction of carbobenzyloxy derivatives of polyhydric alcohols with fatty acid halides and tertiary amines

A recent method for the formation of 1,2-acylated glycerol (122) is the following: 3-monosodium glyceroxide is prepared and reacted with benzylchloroformate ($C_6H_5CH_2OCOCl$) in dry benzene, yielding 3-carbobenzyloxyglycerol. This glycerol compound is reacted with a fatty acid chloride in the presence of quinoline, yielding a 1,2-diacylated material. The resulting 3-carbobenzyloxy-1,2-diglyceride is purified, suspended in absolute alcohol, and treated with hydrogen in the presence of palladium black. The 1,2-diglyceride can be recovered from the solution.

5. Reaction of trityl ethers of polyhydric alcohols with fatty acid halides and tertiary amines

Glycerol forms well-defined 1-mono- and 1,3-ditrityl (or triphenylmethyl) ethers. These may be used for the preparation of 2-monoglycerides and 1,2-diglycerides. Initially, the removal of the trityl group with hydrogen bromide or hydrogen chloride gas, yielding triphenylmethyl halide, was attempted (324, 549, 550, 551), but was found to cause acyl migration. By carrying out the removal of the trityl group by hydrogenation in the presence of palladium-charcoal or platinum dioxide catalyst, triphenylmethane and 2-monoglyceride or 1,2-diglyceride form without acyl migration (123, 552, 554).

This method may well lend itself to the preparation of other polyhydric alcohol esters (553). For instance, 1,6-ditrityl mannitol has already been prepared.

6. Reaction of the benzyl ethers of polyhydric alcohols with fatty acid halides and tertiary amines

Another method for the preparation of 1,2-diglycerides (179, 512) consists in introducing a benzyl ether group into isopropylideneglycerol, removing the isopropylidene group by refluxing with dilute sulfuric acid, and reacting the resulting 1-benzyl ether of glycerol with fatty acid chloride in the presence of a tertiary amine in the known manner. The 1,2-diglyceride is then obtained by catalytic hydrogenation of the purified product. The use of acetic acid as a solvent for the hydrogenation may well have caused the discrepancy in melting points of the products obtained by this method and by the trityl method.

7. Reaction of sulfuric acid esters of halohydrins of polyhydric alcohols with fatty acids

A variation of a method previously reported consists in preparing sulfuric acid esters from halohydrins such as glycerol monochlorohydrin or dichlorohydrin by the action of concentrated sulfuric acid (208, 214) or of chlorosulfonic acid (537) in the cold, and by reacting the product with fatty acid. In the former method, the fatty acid is introduced dissolved in two times its weight of concentrated sulfuric acid. Reaction is carried out for from 1 to 3 hr. at 45–70°C., and the ester product is purified by diluting with ether, washing, neutralizing the usually large excess of unreacted fatty acid, and extracting (sometimes distilling). The halogen is removed by heating with silver nitrite at 110–120°C. This requires at least equal weights of silver nitrite, gives a poor yield, and causes acyl migration, thus offering no advantages over other methods.

F. PREPARATION FROM RELATED COMPOUNDS BY SPECIAL METHODS

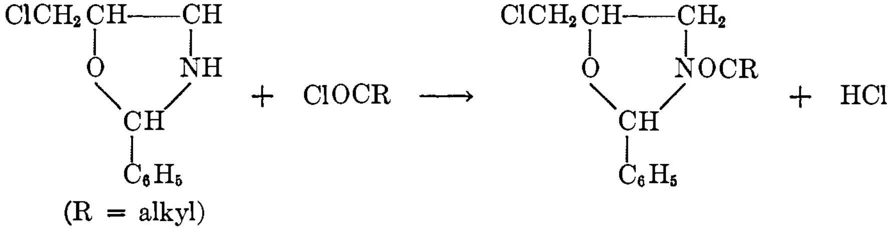
Special methods which have been tried for the preparation of certain polyhydric alcohol esters are briefly reviewed here because they may offer more general application in the future.

The oxidation of allyl esters of fatty acids with potassium permanganate in acetone leads to 1-monoglycerides, but in very poor yields (30 per cent maximum) (450).

The catalytic reduction of diacyldihydroxyacetone yields mixtures of 1,2- and 1,3-diglycerides. No details of this method were found (222).

The addition of hypoiodous acid to an allyl ester of fatty acid leads to 1-acyl-2-iodohydrin; this, on reaction with an alkali soap, is said to form a 1,2-diglyceride, but most likely the product is a 1,3-diglyceride, owing to acyl migration (191).

1-Monoglycerides have been prepared as follows (35): Phenylchloromethyloxazolidine is reacted with a fatty acid chloride and pyridine, yielding 2-phenyl-3-acyl-5-chloromethyloxazolidine:



This is split by fuming hydrochloric acid, removing benzaldehyde. The product, $ClCH_2CHOHCH_2NHOCR$ (3-chloro-2-hydroxy-1-acylaminopropane), can be caused to rearrange to the hydrochloride of 3-acylated-2,3-dihydroxypropylamine by boiling it with water. The product, $RCOOCH_2CHOHCH_2NH_2 \cdot HCl$, will form 1-monoglyceride on diazotization with nitrous acid.

Glycol diesters have been prepared by reaction of the cyclic glycol-ether dioxane by reaction with fatty acid halides, thus opening the ether linkages (547).

II. PROPERTIES OF POLYHYDRIC ALCOHOL ESTERS

Considerable experimental data have been assembled regarding the physical and chemical properties of the polyhydric alcohol esters. Yet only certain esters have been investigated thoroughly and much of the data are not reliable because the esters were made by faulty methods. A good deal is known about the properties of the fatty acid esters of ethylene glycol, propylene glycol, glycerol, mannitol, and glucose, but very little or nothing at all was found about the others, notwithstanding the fact that many of these other compounds are frequently mentioned in the patent literature.

Most of the common data have been compiled in tables 16 to 23. Chiefly, these include the melting points, density, refractive index, solubilities, boiling ranges, optical rotation, and some chemical data such as saponification, iodine, and acetyl values. Certain other, less usual facts are available which do not stand out in the tables. They are briefly discussed here.

A. TRENDS

Certain regularities and trends are revealed by a study of the physical and chemical properties of the polyhydric alcohol esters. Unfortunately, the available information is too incomplete to enable one to arrive at more definite conclusions with authority.

It is well known, of course, that the melting points and boiling points of the polyhydric alcohol esters increase in proportion to the increase of the chain length of their acid radicals, while, in general, their solubility decreases. It is also known that lower melting and more soluble esters are formed from the unsaturated carboxylic acids than from the corresponding saturated acids.

Among the esters of the glycols, the diesters appear to be distinctly higher melting than the monoesters (262, 263). On the other hand, the monoesters of glycerol are higher melting than the corresponding diesters (259). The melting points of the esters of erythritol, mannitan, and glucose, too, seem to increase in proportion to an increasing number of unesterified alcoholic hydroxyl groups. The 2- and the 1,2-glycerides are distinctly lower melting than the 1- and 1,3-glycerides.

The esters of polyhydroxy ethers, such as diethylene glycol, triethylene glycol, polyglycols, polyglycerols, and hydroxyalkyl ethers of polyhydric alcohols, appear, from the meager data available, to be soluble in a wider range of solvents and to have lower melting points than the esters of the corresponding polyhydric alcohols. Among the derivatives of mannitol (and probably of the other hexitols), the melting point of certain partly acylated materials (e.g., diesters) drops, while the solubility rises, as hydroxyl groups are eliminated with the formation of inner ethers, such as mannitan or mannide.

TABLE 15

Melting points of palmitates in °C.

	MONO	DI	TRI	TETRA	PENTA	HEXA	OCTA	HENDECA
Methylene glycol		49.5						
Ethylene glycol	52.5	72						
1,2-Propylene glycol	55–56	69.5–70						
1,3-Propylene glycol	42–43.5	56.5						
1,3-Butylene glycol		39–40						
1,4-Butylene glycol		63						
Glycerol: 1-; 1,3-	77	72.5	65					
Glycerol: 2-; 1,2-	69	64						
Erythritol		99.5–101	81–8					
l-Arabinose				69.5				
α-Methyl-*d*-glucoside			77	69				
α-Glucose					72–75			
β-Glucose					68–72			
Mannitol						64.5		
Dulcitol						74		
Sucrose							54–55	
Raffinose								52–3

To indicate roughly the melting-point relations of the various polyhydric alcohol esters, the palmitates (which are the most thoroughly documented) may be chosen for comparison (table 15).

B. MELTING POINTS

The melting points given in the literature show large discrepancies (20, 450). In many cases it is necessary to blame this on lack of purity of the material investigated, such as may be caused by impure raw materials or by untrustworthy methods of preparation. However, it has been shown reliably that certain polyhydric alcohol esters, notably the glycerides, exist in several poly-

TABLE 16

*Physical and chemical properties of glycol esters**

ESTER	MELTING POINT	SOLUBILITY	OTHER DATA	REFERENCES
	°C.			
Methylene glycol dimyristate	49.5	Acetone: moderately soluble, crystallizes on cooling Benzene, carbon tetrachloride: soluble		(514)
Ethylene glycol				
Monolaurate	27.5	Ether: very soluble hot, cold		(259)
Dilaurate	49; 52; 54	Acetone: moderately soluble, crystallizes on cooling Ether: soluble hot, crystallizes on cooling Benzene, carbon tetrachloride: easily soluble	Boils at 188°C. (0 mm. Hg)	(45, 259, 351, 398a, 514, 515)
Dimyristate	63; 64	Acetone: moderately soluble, crystallizes on cooling Ether, benzene, carbon tetrachloride: soluble	Boils at 208°C. (0 mm. Hg)	(351, 514, 515)
Monopalmitate	47.5; 48; 49; 51–52.5; 51.5	Ethanol (absolute), in grams per 100 g.: 1.62 (0°C.); 5.76 (7.4°C.); 10.67 (16°C.); 24.08 (25°C.) Acetone, ether: soluble, crystallizes on cooling Chloroform: crystallizes on cooling	Density (at melting point), 0.8786 Refractive index, 1.4411 Molecular weight: 297 (in camphor), 270 (in retene); calculated, 300	(183, 249, 408, 473, 474, 564)

Dipalmitate..........	65; 68.7–68.9; 69; 70; 70.5; 72	Ethanol (absolute), in grams per 100 g.: 0.018 (0°C.); 0.087 (25°C.); 0.109 (28°C.); 0.31 (38°C.) Acetone: moderately soluble Ethyl acetate: soluble Ether: crystallizes on cooling Benzene, chloroform, carbon tetrachloride: easily soluble	Boils at 226°C. (0 mm. Hg) Density (at melting point), 0.8594 Refractive index, 1.4378 Crystals: birefringent radial-symmetrical masses	(2, 45, 259, 351, 398a, 408, 421a, 473, 474, 514, 515, 521, 555, 564)
Monomargarate (heptadecoate)......	50.2; 53.2	Ethanol (absolute), in grams per 100 g.: 1.72 (0°C.) Ethanol (hydrous): very soluble, crystallizes on cooling	Refractive index, 1.4440	(473, 474)
Dimargarate (heptadecoate)......	65.5; 70.4	Ethanol (absolute), in grams per 100 g.: 0.024 (0°C.); 0.101 (25°C.) Ethanol (hydrous): poorly soluble, crystallizes on cooling	Density (at melting point), 0.8605 Refractive index, 1.4392	(473, 474)
Monostearate.........	56; 58.5	Ethanol (absolute), in grams per 100 g.: 0.67 (0°C.); 4.17 (25°C.); 10.61 (29°C.) Ethanol (hydrous): soluble Ether: very soluble cold	Density (at melting point), 0.8780 Refractive index, 1.4310	(259, 473, 474)
Distearate...........	73; 75–76.5; 75.8; 76; 77; 79	Ethanol (absolute), in grams per 100 g.: 0.01 (0°C.); 0.028 (25°C.); 0.037 (28°C.); 0.112 (40°C.) Ether: soluble hot, crystallizes on cooling	Boils at 241°C. (0 mm. Hg) Density (at melting point), 0.8581 Refractive index, 1.4385	(45, 103, 103a, 259, 351, 398a, 420, 421a, 473, 474, 555, 563)

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* Certain data have already been given in the text, but all references to cover them are entered here, because many original papers were not accessible to the author for detailed information.

TABLE 16—*Continued*

ESTER	MELTING POINT	SOLUBILITY	OTHER DATA	REFERENCES
	°*C*.			
Ethylene glycol—*Cont.* Distearate—*Cont.*		Benzene, nitromethane: soluble	Molecular weight: 497, 524, 530, 532 (in benzene); 489, 496, 575, 580 (in nitromethane); calculated, 594.6 Crystals: birefringent radial-symmetrical masses Saponification value: 187.5, 189.4; calculated, 188.7	
Monoöleate	1		Boils at 190–200°C. (0.05 mm. Hg); 200–220°C. (7.3 mm. Hg) Refractive index, 1.4600 (27°C.) Saponification value, 165.9; calculated, 170 Acetyl value, 153.5	(88, 259, 404)
Dioleate		Ether: soluble	Boils at 183–185°C. (3 mm. Hg) Density, 0.906 (25°C.) Refractive index, 1.4492 (70°C.) Specific refraction, 0.3038; calculated, 0.305	14, 421a, 424, 518, 532)

			Saponification value: 190.5, 192; calculated, 190 Iodine value: 84.5, 79.8–81	
Dilinoleate			Density, 0.916 (25°C.) Specific refraction, 0.30648; calculated, 0.302 Saponification value, 189.5; calculated, 191 Iodine value, 169.6	(414, 424)
Dieleostearate			Density, 0.921 (35°C.) Molecular weight, 556 (in stearic acid); calculated, 586 Crystallizes on standing (forms oxidation products) Saponification value, 211.5; calculated, 191 Maleic anhydride addition value, 79.8	(386, 414)
Monoester of coconut oil fatty acid	28–30; 42	Ethanol, acetone: soluble Isopropanol, glycol, glycerol, toluene, naphtha, linseed oil, mineral oil: soluble		(158, 200)

TABLE 16—*Continued*

ESTER	MELTING POINT	SOLUBILITY	OTHER DATA	REFERENCES
	°C.			
Ethylene glycol—*Cont.*				
Monoester of commercial stearic acid	59–61	Ethanol, acetone: soluble hot, crystallizes on cooling Toluene: soluble hot, cold Naphtha, mineral oil: soluble hot		(200)
Monoester of commercial oleic acid		Ethanol, acetone, toluene, naphtha, mineral oil: soluble	Crystallizes on standing	(200)
Monoester of rapeseed oil fatty acid			Saponification value, 167 Viscosity, 6.74° Engler (20°C.); 10.74° Engler (10°C.)	(258, 566)
Monoester of linseed oil fatty acid			Density, 0.9214 (30°C.) Refractive index, 1.4748 (20°C.) Saponification value, 171; calculated, 174 Acetyl value, 168	(73)
Diester of linseed oil fatty acid			Boils at 212°C. (2.5 mm. Hg); 250°C. (30 mm. Hg)	(139, 370)

			Refractive index, 1.4856, 1.4779 Molecular weight, 603; calculated, 602 Saponification value: 203.7, 294.2; calculated, 187 Iodine value: 160.2, 125.7	
Monoester of tung oil fatty acid...........			Density, 0.9495 (30°C.) Refractive index, 1.4956 (20°C.) Saponification value, 175; calculated, 176 Acetyl value, 130	(73)
Monoester of castor oil fatty acid........		Ethanol, acetone: soluble Toluene, naphtha: poorly soluble Mineral oil: insoluble		(200)
1,2-Propylene glycol				
Dilaurate.............	35	Acetone: crystallizes on cooling Benzene, carbon tetrachloride: easily soluble		(514, 515)
Dimyristate...........	41.5	Acetone: crystallizes on cooling Benzene, carbon tetrachloride: easily soluble		(514, 515)
Monopalmitate........	54.3; 55–56	Ethanol, in grams per 100 g.: 0.0193 (0°C.); 0.0907 (15°C.)	Refractive index, 1.4405	(261, 262)

TABLE 16—*Continued*

ESTER	MELTING POINT	SOLUBILITY	OTHER DATA	REFERENCES
	°C.			
1, 2-Propylene glycol—*Cont.*				
Dipalmitate	52.5–54.5; 68.8; 69.5–70	Ethanol, in grams per 100 g.: 0.00516 (0°C.); 0.0115 (15°C.) Acetone: moderately soluble, crystallizes on cooling Benzene, carbon tetrachloride: easily soluble	Refractive index, 1.4364	(262, 408, 514, 515)
Monostearate	59.5	Ethanol, in grams per 100 g.: 0.0211 (0°C.); 0.034 (15°C.)	Refractive index, 1.4424	(262)
Distearate	40; 72.3	Ethanol, in grams per 100 g.: 0.0012 (0°C.); 0.0063 (15°C.) Ether: soluble	Refractive index, 1.4366 Saponification value, 190.8; calculated, 184.7	(1, 262)
Dioleate			Saponification value, 191.5; calculated, 186	(1)
Monoester of coconut oil fatty acid		Ethanol, acetone, toluene, naphtha, mineral oil: soluble		(200)
Ester of commercial stearic acid	33–35; 37; 37–39	Ethanol: soluble hot Acetone: soluble hot, cold Toluene, naphtha, mineral oil: soluble hot		(49, 50, 200)
Monoester of commercial oleic acid		Ethanol, acetone, toluene, naphtha, mineral oil: soluble		(200)

Ester of linseed oil fatty acid			Boils at 218–220°C. (5 mm. Hg) Refractive index, 1.4812 Saponification value, 204.58; calculated, 182 Iodine value, 131.1 Molecular weight, 403; calculated, 616	(139)
Monoester of castor oil fatty acid		Ethanol, acetone, toluene, naphtha: soluble Mineral oil: poorly soluble, soluble hot		(200)
1,3-Propylene glycol				
Dilaurate	38–39	Acetone: crystallizes on cooling		(515)
Dimyristate	49–49.5	Acetone: crystallizes on cooling		(515)
Monopalmitate	42–43.5			(409)
Dipalmitate	54.2–55.5; 55.5; 56.2; 56.5	Ethanol, in grams per 100 g.: 0.0244 (0°C.); 0.0517 (15°C.) Acetone: crystallizes on cooling	Refractive index, 1.4374	(262, 408, 409, 515)
Monostearate	60.5	Ethanol, in grams per 100 g.: 0.01431 (0°C.); 0.0305 (15°C.)	Refractive index, 1.4437	(262)
Distearate	64.7	Ethanol, in grams per 100 g.: 0.00126 (0°C.); 0.00381 (15°C.)	Refractive index, 1.4397	(262)

TABLE 16—*Concluded*

ESTER	MELTING POINT	SOLUBILITY	OTHER DATA	REFERENCES
	°C.			
1,3-Butylene glycol				
Dilaurate	16.5	Acetone–petroleum ether: soluble, crystallizes on cooling Benzene, carbon tetrachloride: soluble		(514, 515)
Dimyristate	29.5–31	Acetone: soluble Benzene, carbon tetrachloride: soluble Acetone–petroleum ether: crystallizes on cooling		(514, 515)
Dipalmitate	39–40	Acetone: soluble Benzene, carbon tetrachloride: soluble Acetone–petroleum ether: crystallizes on cooling		(514, 515)
1,4-Butylene glycol				
Dilaurate	45.5	Acetone: poorly soluble Benzene, carbon tetrachloride: soluble		(514)
Dimyristate	55	Acetone: poorly soluble Benzene, carbon tetrachloride: soluble		(514)
Dipalmitate	63	Acetone: poorly soluble Benzene, carbon tetrachloride: soluble		(514)

morphous forms, and thus have more than one melting point (376, 377, 450). The glycerides occur in an unstable (alpha), a stable (beta), and some also in a metastable (beta′) form. The conversion from the unstable to the stable form at the melting temperature of the lower melting form is almost instantaneous for monolaurin, but requires more than 45 min. for monostearin (376, 377, 450). The stable (beta) form is the one usually obtained by crystallization from solvents; the unstable (alpha) form, which is lower melting, usually forms first when a fused glyceride is cooled. Melting points of glycerides may change on storage (207, 210), and sometimes differ with the methods and solvents used for crystallization (221).

A study of the cooling curves of glycerides reveals further conversion points ("breaks"). Other properties, such as the dielectric constant and the x-ray pattern, also change at these points.

C. DIELECTRIC CONSTANT

The dielectric constants of 1-monostearin and monomyristin have been determined at frequencies of 1000 and 4400 kilocycles per second (47, 48). Sharp changes of the dielectric constant take place at conversion points of the various forms into one another. These forms, their dielectric constants, and their conversion points are given below:

ESTER	DIELECTRIC CONSTANT	CONVERSION (MELTING) POINT
		°C.
1-Monostearin:		
Unstable form	4.96 (at 40°C.)	74
Metastable form		79
Stable form	2.40 (at 40°C)	81.5
1-Monomyristin:		
Unstable form	8.58 (at 38.2°C)	56
Metastable form	2.86 (at 40°C.)	67.5
Stable form	2.41 (at 40°C.)	70.5

These determinations were carried out at 1000 kilocycles per second.

D. CONVERSION OF 2(OR β)- TO 1(OR α)-GLYCERIDES

After satisfactory methods for the preparation of 2-monoglycerides and 1,2-diglycerides had at last been developed, work was done to determine their stability. They were found to be readily converted by acids and alkalies, which cause acyl migration, explaining the large amount of wasted effort to obtain these glycerides. It has now been shown that hydrochloric acid as dilute as 0.0067 *N* caused marked conversion to the alpha ester within 24 hr., although 0.005 *N* hydrochloric acid did not. A 0.0125 *N* ammonium hydroxide solution caused conversion, but a 0.01 *N* solution did not (121a, 122).

TABLE 17

*Physical and chemical properties of ether-glycol esters**

ESTER	MELTING POINT °C.	SOLUBILITY	OTHER DATA	REFERENCES
Diethylene glycol				
Dilaurate	31	Glycol, glycerol, butyl acetate, linseed oil: soluble	Boils at 200°C. (11 mm. Hg) Density, 0.929(24°C.) Molecular weight, 522; calculated, 470.5	(94, 158)
Monoester of coconut oil fatty acid	17–18	Ethanol, acetone: soluble Toluene, naphtha, mineral oil: moderately soluble		(200)
Diester of coconut oil fatty acid		Ethanol, isopropanol: soluble Toluene, naphtha: soluble		(94, 158)
Monoester of commercial myristic acid	35	Ethanol: soluble hot Acetone: soluble hot, cold Toluene, naphtha, mineral oil: moderately soluble		(200)
Monoester of commercial stearic acid	42–43; 55; 58	Ethanol, acetone, toluene, naphtha, mineral oil: soluble hot, crystallizes on cooling		(29, 200, 257, 567)
Monoester of commercial oleic acid		Ethanol, acetone, esters, toluene, naphtha, mineral oil: soluble		(29, 200, 567)
Diester of linseed oil fatty acid			Refractive index, 1.4777	(370)

Monoester of castor oil fatty acid.....		Ethanol, acetone, toluene, naphtha: soluble Mineral oil: poorly soluble		(200)
Triethylene glycol				
Ester of cocoanut oil fatty acid.........		Ethanol, glycol, naphtha, linseed oil: soluble		(158)
Diester of commercial stearic acid		Toluene, benzene, turpentine: soluble		(32)
Tetraethylene glycol				
Monoester of commercial stearic acid..	29–30	Ethanol, acetone, toluene, naphtha, mineral oil: soluble hot	Disperses in hot water	(200)
Diester of commercial stearic acid.....	32–33	Ethanol: soluble hot Acetone: poorly soluble Toluene: soluble hot, cold Naphtha: poorly soluble Mineral oil: soluble	Disperses in hot water	(200)
Hexaethylene glycol				
Monoester of commercial oleic acid....		Ethanol, acetone, toluene: soluble Naphtha, mineral oil: moderately soluble	Disperses in water	(200)
Nonaethylene glycol				
Monoester of coconut oil fatty acid ...		Ethanol, acetone, toluene: soluble Naphtha: moderately soluble Mineral oil: insoluble or poorly soluble	Dissolves colloidally in water	(200)
Diester of coconut oil fatty acid......		Ethanol, acetone, toluene, naphtha: soluble Mineral oil: soluble hot	Disperses in water	(200)

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* Certain data have already been given in the text, but all references to cover them are entered here, because many original papers were not accessible to the author for detailed information.

TABLE 17—*Continued*

ESTER	MELTING POINT °C.	SOLUBILITY	OTHER DATA	REFERENCES
Nonaethylene glycol—*Cont.*				
Monoester of commercial stearic acid..	27–29	Ethanol, acetone, toluene: soluble Naphtha, mineral oil: soluble hot or poorly soluble	Disperses or dissolves colloidally in water	(200)
Diester of commercial stearic acid.....	29–31	Ethanol, acetone, toluene: soluble Naphtha, mineral oil: soluble hot	Disperses in hot water	(200)
Monoester of commercial oleic acid ...		Ethanol, acetone, toluene: soluble Naphtha: moderately soluble Mineral oil: insoluble or poorly soluble	Disperses or dissolves colloidally in water	(200)
Diester of commercial oleic acid.......		Ethanol, acetone, toluene, naphtha, mineral oil: soluble	Disperses in water	(200)
Monoester of castor oil fatty acid.....		Ethanol, acetone, toluene: soluble Naphtha, mineral oil: insoluble	Disperses in water	(200)
Diester of castor oil fatty acid........		Ethanol, acetone, toluene: soluble Naphtha, mineral oil: insoluble	Disperses in water	(200)
Dodecaethylene glycol				
Monoester of coconut oil fatty acid ...	30–39	Ethanol, acetone, toluene: soluble Naphtha, mineral oil: insoluble	Dissolves colloidally in water	(200)
Diester of coconut oil fatty acid.......	30–39	Ethanol, acetone, toluene: soluble Naphtha, mineral oil: poorly soluble	Disperses in water	(200)
Monoester of commercial stearic acid..	36–37	Ethanol, acetone, toluene, naphtha: soluble Mineral oil: poorly soluble hot	Dissolves colloidally in hot water	(200)

Diester of commercial stearic acid	29–30	Ethanol, acetone, toluene, naphtha, mineral oil: soluble hot	Disperses in hot water	(200)
Monoester of commercial oleic acid	30–35	Ethanol, acetone, toluene: soluble Naphtha, mineral oil: insoluble	Dissolves colloidally or disperses in water	(200)
Diester of commercial oleic acid	25–35	Ethanol, acetone, toluene: soluble Naphtha: moderately soluble Mineral oil: poorly soluble	Disperses in water	(200)
Monoester of castor oil fatty acid	25–35	Ethanol, acetone, toluene: soluble Naphtha, mineral oil: insoluble	Dissolves colloidally in water	(200)
Diester of castor oil fatty acid	25–35	Ethanol, acetone, toluene: soluble Naphtha, mineral oil: insoluble	Disperses in water	(200)
Polyethylene glycol				
Diester of coconut oil fatty acid	53–54	Ethanol, toluene: soluble hot Acetone: moderately soluble hot Naphtha, mineral oil: insoluble	Soluble in water	(200)
Diester of commercial stearic acid	52–54	Ethanol, acetone, toluene: soluble hot Naphtha, mineral oil: insoluble	Soluble in water	(200)
(Di)ester of commercial oleic acid	50	Ethanol, acetone, toluene: soluble hot Naphtha, mineral oil: insoluble	Soluble in water	(200, 275, 488)
Diester of castor oil fatty acid	50	Ethanol, acetone, toluene: soluble hot Naphtha, mineral oil: insoluble	Soluble in water	(200)
Dioxanediol (2,3)				
Distearate	84			(510, 511)
Dioleate			Density, 0.904 (20°C.)	(510, 511)

TABLE 18

Glycerol esters: physical and chemical data

ESTER	MELTING POINT* °C.	SOLUBILITY	OTHER INFORMATION	REFERENCES
1-Monocaproate			Boiling point, 162°C. (4 mm. Hg)	(459)
1-Monocaprylate	40		Boiling point, 178–181°C. (5–6 mm. Hg) Refractive index, 1.4309 (85.7°C.) Density, 0.9646 (97.3°C.)	(450, 459)
1-Monocaprate	54; 53; 51.4; 51.2		Refractive index, 1.4331 (85.7°C.) Density, 0.9399 (97.3°C.) Conversion points of unstable forms: 49°; 27°; 8°C.	(20, 376, 450, 459)
2-Monocaprate	40.4		Refractive index, 1.44045 (70°C.)	(522)
1,3-Dicaprate	44.5	Ethanol: crystallizes in cold Light petroleum: gels	Conversion points of unstable forms: 42°; 37°C.	(377)
1-Monoundecoate	56.5		Conversion points of unstable forms: 52°; 36.5°; 3°C.	(376)
1,3-Diundecoate	49		Conversion points of unstable forms: 47°; 43.5°C.	(377)
1-Monolaurate	63.2; 63; 62–3; 62.5; 62; 61.5–62; 61; 60.5–61;	Ethanol (95%): soluble hot, crystallizes on cooling Ethanol (60%): soluble hot	Boiling point, 142°C. (green cathode light vacuum) Refractive index, 1.4350 (85.7°C.)	(20, 23, 35, 64a, 69, 171, 172, 176, 178, 179, 209,

	optically active, 53–4	Ether: (easily) soluble hot; soluble cold, crystallizes on cooling Benzene: poorly soluble Ligroin: crystallizes on cooling, poorly soluble cold Carbon tetrachloride, chloroform: soluble Acetone: easily soluble Carbon disulfide: crystallizes on cooling Ether–ligroin: crystallizes	Density, 0.9248 (97.3°C.) $[\alpha]_D$ of optically active *l*-form: −3.76° (in pyridine) Saponification value: 272.6, 204.2, 200.8, 207.0, 204.6, 204.5 Conversion points of unstable forms: 59.5°; 44(45)°; 15°C.	210, 259, 351, 376, 450, 459, 537, 550, 564)
2-Monolaurate..................	51.1		Refractive index, 1.4424 (70°C.)	(522)
1,3-Dilaurate...................	57; 56.6; 56.5; 56.3; 56; 55; 53	Ethanol (95%): soluble hot, crystallizes on cooling Ethanol (60%): insoluble hot, cold Ether: very soluble Petroleum naphthas: moderately soluble, crystallizes on cooling from ligroin, hexane	Saponification value: 236.4; 243.7; 243.2; 254.8; 250.5; 248.3; 259.8; 244.1 Molecular weight: 511.3, (233.8; 225.9), 517.4 Conversion points of unstable forms: 54°; 49.5°C.	(20, 172, 207, 208, 213, 377, 537, 538, 564)
1,3-Lauromyristate..............	34–5; 40–42			(209)
1,3-Laurostearate...............	45; 52–3			(209)
1-Monotridecoate...............	65		Conversion points of unstable forms: 61°; 50°; 9°C.	(376)
1,3-Ditridecoate................	59.5	Ethanol: crystallizes on cooling Petroleum (light): crystallizes on cooling	Conversion points of unstable forms: 57°; 54.5°C.	(377)

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* Some of the very low, obviously untrustworthy melting points have been omitted, but references for them are entered.

TABLE 18—*Continued*

ESTER	MELTING POINT* °C.	SOLUBILITY	OTHER INFORMATION	REFERENCES
1-Monomyristate	70.5; 70; 69; 68; 67.9, 67.5	Ethanol: poorly soluble cold Ether: easily soluble, crystallizes on cooling Petroleum ether: crystallizes on cooling, poorly soluble Ligroin: poorly soluble Benzene: easily soluble Carbon disulfide: poorly soluble, crystallizes on cooling	Boiling point, 162°C. (green cathode light) Refractive index, 1.4366 (85.7°C.) Density, 0.9121 (97.3°C.) Saponification value: 187.8, 187.7 Conversion points of unstable forms: 67.5°; 56°(57°); 39.5°; 24°(27°)C.	(5, 20, 47, 48, 64a, 104, 172, 212, 323, 351, 364, 376, 450, 459, 564)
2-Monomyristate	61		Refractive index, 1.4420 (70°C.)	(522)
1,3-Dimyristate	68; 65.5; 64.5; 64.4; 63.8; 63.5; 63; 62; 61; 60.5	Ethanol: soluble hot, crystallizes, poorly soluble cold Amyl alcohol: crystallizes on cooling Ether: easily soluble, crystallizes on cooling Benzene: easily soluble Hexane, ligroin: poorly soluble, crystallizes on cooling Chloroform: easily soluble, crystallizes on cooling Carbon disulfide: poorly soluble	Saponification value: 219.7; 218.6 Conversion points of unstable forms: 63°; 60°C.	(20, 172, 207, 208, 212, 252, 323, 364, 377, 564)
1,2-Dimyristate	59			(122)

1,3-Myristostearate	58; 52–3	Ethanol: poorly soluble Ether, chloroform: soluble Carbon disulfide, ligroin: poorly soluble Benzene: soluble		(212)
1,3-Myristolinoleate	38; 15	Ethanol, methanol, ligroin, carbon disulfide: poorly soluble Benzene, ether, chloroform: (easily) soluble		(322)
1,3-Myristoricinoleate	33; 15			(322)
1-Monopentadecoate	72		Conversion points of unstable forms: 69°; 62°; 17°C.	(376)
1,3-Dipentadecoate	68.5	Hexane: crystallizes Hexane–benzene: crystallizes	Conversion points of unstable forms: 66.5°; 63.5°C.	(377)
1-Monopalmitate	78–9; 77.6; 77; 76; 75–75.5; 74–5; 71; optically active, 71–2	Ethanol, in grams per 100 g.: 4.1351 (21°C.); 5.3060 (22°C.); 4.09 g. per 100 cc. (25°C.); crystallizes; poorly soluble cold Methanol, isobutanol: crystallizes Acetone: crystallizes Ether: 2.75 g. per 100 cc. (25°C.); crystallizes Light petroleum: poorly soluble Benzene: crystallizes Pentane, chloroform: soluble	Boiling point, 190°C. (0.1 mm. Hg) Molecular weight, 325–6 Refractive index, 1.4484 (85.7°C.) Density: 0.9014 (97.3°C.); 1.04 g. per cubic centimeter Saponification value: 171, 186, 170, 172, 167.7 Optical rotation of *l*-form: $[\alpha]_D = -4.37°$ (in pyridine) Conversion points of unstable forms: 74°; 65°(66°); 34°C.	(5, 7, 8, 8a, 20, 23, 28, 38, 39, 44, 66, 75, 89, 97, 104, 121a, 122, 171, 176, 178, 179, 210, 225, 259, 351, 376, 383, 447, 450, 459, 561, 564)

TABLE 18—*Continued*

ESTER	MELTING POINT*	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°*C.*			
2-Monopalmitate................	69.5; 69; 68.5; 68	Ethanol: 4.61 g. per 100 cc. (25°C.); moderately soluble, crystallizes Methanol: moderately soluble Ether: easily soluble hot, crystallizes on cooling; 11.15 g. per 100 cc. (25°C.) Ligroin: soluble hot Petroleum ether: poorly soluble hot Benzene: easily soluble hot, crystallizes Chloroform: easily soluble Acetone: moderately soluble Ethyl acetate: easily soluble hot	Refractive index, 1.44605 (70°C.) Molecular weight, 323	(36, 104, 121a, 122, 123, 522)
1,3-Dipalmitate.................	73; 72.5; 72; 70; 69.5; 69; 68.5	Ethanol, in grams per 100 g.: 0.2097 (20°C.); 0.5040 (27°C.); soluble hot, crystallizes on cooling Ether: easily soluble Ether, hexane, ligroin, petroleum ether: crystallizes Chloroform: soluble, crystallizes	Saponification value: 199, 198, 193.3, 194.3, 195.4, 197.6, 196.6 Acetyl saponification value, 239.9 Conversion points of unstable forms: 68°C.	(7, 8, 20, 37, 38, 39, 44, 75, 97, 172, 191, 206, 214, 225, 252, 377, 378, 383, 520, 564)

1,2-Dipalmitate	64; optically active, 67–67.5		Optically active (*d*) form: $[\alpha]_D = -2.3°$ (in $CHCl_3$)	(122, 512)
1,3-Palmitostearate	73.4; 71–71.3	Ether: crystallizes on cooling		(191, 550)
2,3-Palmitostearate	68.5–69.5			(554)
1,2-Palmitostearate	60.5–61			(554)
1-Monomargarate (heptadecoate)	77; 76.4; 75.7	Ethanol, in grams per 100 g.: 0.3015 (0°C.), 0.1015 (0°C.), 1.0545 (15°C.); 0.2650 (15°C.) Butanol: easily soluble Ethyl acetate, acetone: soluble Ether, in grams per 100 g.: 0.1945; 0.0725 (0°C.); 0.7810; 0.2499 (15°C.); poorly soluble cold Benzene: easily soluble Petroleum ether: easily soluble Chloroform, carbon tetrachloride: soluble	Refractive index: 1.4412, 1.4413 (80°C.) Saponification value: 161.1, 164.6 Conversion points of unstable forms: 74.5°; 70°; 28°C.	(378, 539)
1,3-Dimargarate (heptadecoate)	74.5; 71.8; 70.1	Ethanol, in grams per 100 g.: 0.0010; 0.0075 (0°C.); 0.0210; 0.0445 (15°C.) Ethyl acetate, acetone: easily soluble hot Ether, in grams per 100 g.: 0.0565; 0.0745 (0°C.); 0.5150; 0.7435 (15°C.) Petroleum ether, carbon tetrachloride, chloroform: easily soluble	Refractive index: 1.4407, 1.4404 (75°C.) Saponification value: 188.2, 186.0 Conversion points of unstable forms: 71.5°C.	(377, 539)

TABLE 18—*Continued*

ESTER	MELTING POINT*	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
1-Monostearate	83.5; 82; 81.5; 81–81.5; 81–2; 80; 80.9; 79.5–80; optically active, 76–7	Ethanol: moderately soluble hot, crystallizes Methanol, isobutanol: crystallizes Ether: easily soluble hot, poorly soluble cold, crystallizes on cooling Benzene: crystallizes on cooling Petroleum ether: very poorly soluble cold, crystallizes	Boiling point, 260°C. (12 mm. Hg), decomposes; volatile *in vacuo* Refractive index, 1.4400 (85.7°C.) Density, 0.8959 (97.3°C.) Saponification value: 156, 173.2, 155, 149.2, 156.5, 158; (74, 79.88, 75% stearic acid) Molecular weight: 358, 353–4 *l*-Form: optical rotation, $[\alpha]_D = -3.58°$ (in pyridine) Conversion points of unstable forms: 79°; 74°; 47.5°; 42°C.	(8, 20, 23, 28, 35, 38, 39, 44, 48, 89, 176, 178, 179, 208, 217, 219, 221, 225, 252, 253, 259, 260, 264, 314, 351, 370, 376, 450, 550, 564)
2-Monostearate	74.4		Refractive index, 1.44770 (70°C.)	(522)
1,3-Distearate	79.5–80; 79.5; 79.1; 78.5–79.1; 78.5; 77.5–78.2; 78; 77.5; 76.5; 76	Ethanol: poorly soluble hot (1:150); crystallizes Ether: soluble hot, poorly soluble cold Benzene, petroleum ether (ligroin), chloroform, hexane: crystallizes	Molecular weight, 625 Saponification value: 180, 181, 180.6; 186.5; 179.7; 187.2; 179.8; 181.8; 183, 181, 179.3; 180.2; (90.9; 91% stearic acid) Acetyl saponification value, 224 Hehner value, 92.3% Conversion points of unstable forms: 74°C.	(8, 20, 38, 39, 44, 64, 172, 177, 206, 207, 208, 211, 214, 217, 218, 219, 225, 252, 264, 352, 353, 370, 377, 378, 420, 449, 459, 549, 564)
1,2-Distearate	68.5–69; optically active, 74.5–75		*d*-Form: optical rotation, $[\alpha]_D = -2.7°$ (in $CHCl_3$, C., 6.18)	(512, 554)

1-Monoarach(id)ate (eicosanate).		Ether: very poorly soluble cold		(42)
1,3-Diarach(id)ate (eicosanate) ..	75	Ether: very poorly soluble cold, poorly soluble hot Chloroform: easily soluble Carbon disulfide: soluble	Saponification value, 166.34	(42, 206)
1-Monocerotate.................	78.8	Ethanol: soluble hot Benzene: crystallizes		(379)
1,3-Dicerotate..................	79.5	Ethanol: very poorly soluble Ether: poorly soluble Benzene: easily soluble hot		(379)
1-Monomelissate................	91.5–92	Ethanol: soluble hot		(379)
1,3-Dimelissate.................	93	Benzene: soluble hot		(379)
1-Monoöleate...................	Freezes, 0, −6 Melts, 10 Crystallizes on standing. 35–40; 35; 26–27; 23.8–26; 23; 22	Ethanol (90%): soluble 100% Ethanol (80%): soluble 98.2% Ethanol (50%): soluble 97.6% Ethanol (80%): crystallizes Ethyl acetate: soluble 45.4% Acetone: soluble 49.2% Acetone (80%): soluble 100% Acetone (50%): soluble 88.3% Ether: soluble 92.6% Benzene: soluble 98.8% Petroleum ether: soluble 100%, crystallizes on cooling Chloroform: soluble 100% Carbon disulfide: soluble 89.2%	Boiling point: 300°C., decomposes (15 mm.); 238–240°C. (3–4 mm. Hg) Refractive index, 1.4605 Density, 0.947 (21°C.) Saponification value: 157.1, 181.8, 176.7, 159, 157 Molecular weight, 353.5–354 Iodine value: 70.1, 69.4, 70.6, 73.4, 67.22, 68.5	(8, 8a, 11, 13, 28, 38, 39, 44, 89, 155, 156, 225, 259, 260, 314, 325a, 335, 351, 370, 464, 533)

TABLE 18—*Continued*

ESTER	MELTING POINT*	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
1,3-Dioleate	14–16; crystallizes on storage at 15 or less	Ethanol (100%): soluble 90% Ethanol (80%): soluble 87.5% Ethanol (50%): soluble 74.2% Ether: soluble 100% Benzene, petroleum ether, chloroform, carbon disulfide, ethyl acetate: soluble 100% Acetone (anhydrous): soluble 100% Acetone (80%): soluble 75.4% Acetone (50%): soluble 74.2%	Refractive index, 1.4661 Density, 0.921 (21°C.) Saponification value: 182, 183 Iodine value: 80.4; 80.5 Molecular weight, 621	(13, 38, 39, 44, 225, 335, 370)
1-Mono-10,11-isoöleate	49			(65)
Monoelaidate	44.8	Ethanol: crystallizes Ether: very soluble Petroleum ether, chloroform, acetone: very soluble		(66)
1-Monobehenolate	50.5	Ethanol: crystallizes	Saponification value, 139 Iodine value, 61.6	(441)
1,3-Dibehenolate	42.5; 43	Ethanol: crystallizes Ligroin: crystallizes	Saponification value, 156.1 Iodine value, 68.9	(441)
1-Monostearolate	40.5; 40	Ethanol: poorly soluble cold, crystallizes Benzene, ligroin, chloroform: easily soluble	Saponification value, 160 Iodine value, 71.49	(441)

1,3-Distearolate	40; 38.5; 38	Ethanol: poorly soluble cold Ether, benzene, ligroin, petroleum ether, chloroform: easily soluble	Saponification value, 181.6 Iodine value, 82.31	(441)
Dierucate	47	Ethanol: poorly soluble cold, poorly soluble hot Ether, ligroin: easily soluble		(448, 523)
Dibrassidate	65; 67	Ether: poorly soluble		(448, 523)
1-Monolinoleate	14–15; crystallizes only at very low temperatures (−10, −26)	Ethanol, methanol: poorly soluble Ligroin, carbon disulfide: poorly soluble Ether, benzene, chloroform: easily soluble Ether, petroleum ether: crystallizes	Refractive index, 1.4758 Saponification value, 158.5 Iodine value, 142.1	(52, 322)
1,3-Dilinoleate		Ethanol, methanol, ligroin, carbon disulfide: poorly soluble Ether, benzene, chloroform: easily soluble	Saponification value, 180.3 Iodine value, 157.1	(216, 322)
1,3-Linoleoricinoleate				(322)
1-Monoricinoleate	Viscous at −15	Ethanol, methanol, ether, benzene, chloroform: easily soluble Ligroin, carbon disulfide: soluble		(322)
1,3-Diricinoleate		Ethanol, methanol, ether, benzene, chloroform: easily soluble Ligroin, carbon disulfide: soluble		(322)

TABLE 18—*Continued*

ESTER	MELTING POINT*	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
Monoester coconut fatty acid....	40.8; 37.2		Saponification value: 186.5, 227.9, 220.5, 197 Hydroxyl value: 190.5, 244.4	(153, 336, 425, 427, 434)
"Monostearate," commercial.....	61.6; 59		Saponification value: 157, 170.4 Acetyl value, 159.6	(156, 200, 336)
"Distearate," commercial.......	54.5			(157)
Monoester olive oil fatty acid....	Crystallizes on storage		Saponification value, 181.8	(404)
Monoester cottonseed fatty acid..			Saponification value, 152 Acetyl value, 145	(152, 425, 471)
Diester cottonseed oil fatty acid..			Acetyl value, 263.5	(10)
Diester sesame oil fatty acid.....			Oleic acid, 86.41%	(10)
Monoester linseed fatty acid.....			Refractive index: 1.4788; 1.4785 (20°C.) Density: 0.988 (15.5°C.); 0.9818 (30°/15.5°C.) Saponification value: 168, 156.7, 184.9, 162.4, 166 Acetyl value: 156.2, 174.6, 157, 288 Acetyl saponification value: 300.3, 311 Molecular weight: 344.7, 354	(57, 73, 370, 391, 499)

Diester linseed fatty acid			Refractive index: 1.4811; 1.4777 (20°C.) Density, 0.9314 (30°/15.5°C.) Saponification value: 183.3; 184 Molecular weight, 617 Hydroxyl value: 75; 81.2	(46, 73, 370)
Monoester dehydrated castor oil fatty acid			Saponification value, 176.4 Molecular weight, 318.8 Acetyl saponification value, 310.7	(391, 499)
Monoester tung oil fatty acid			Refractive index, 1.4996 (20°C.) Density, 0.9934 (27°/15.5°C.) Saponification value, 161 Acetyl value, 308	(73)
Diester tung oil fatty acid			Refractive index, 1.5000 (20°C.) Density, 0.9718 (27°/15.5°C.) Saponification value, 182 Acetyl value, 83.3	(73)
Monoester teaseed fatty acid			Saponification value: 183.9; 149.5 Acetyl value: 91; 191.2	(336)

TABLE 19

Esters of polyglycerol and glycerol ethers: physical and chemical data

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
Glycerol trihydroxyethyl ether				
Monolaurate.........		Water: soluble		(295)
Monoöleate..........		Water: colloidally soluble		(275, 488)
Diglycerol				
Monostearate........	About 30	Water: disperses Ethanol: soluble hot, crystallizes on cooling Ether: easily soluble	Saponification value (% stearic acid): 65.96 65.88	(264)
Distearate...........	70.5–71.3	Ether: very soluble Petroleum ether–ether: crystallizes on cooling		(221)
Polyglycerol				
Monoester of commercial stearic acid		Water: disperses	Saponification value, 152 Hydroxyl value, 284	(147, 432)
Monoester of lard fatty acid...........			Saponification value, 143 Iodine value, 31.6	(62)
Monoester of commercial oleic acid..			Saponification value, 151 Iodine value, 69.4	(62)
Monoester of linseed oil fatty acid......			Saponification value, 137.2 Iodine value, 116.7	(62)

E. SPECIFIC HEAT AND HEAT OF COMBUSTION

The heat of combustion for 1-monopalmitin was found to be 2778.78 ±0.36 kcal. per mole, and 2788.30 ±0.67 kcal. per mole for 2-monopalmitin. This indicates that conversion from the 2- to the 1-monoglyceride liberates 9.52 kcal. per mole. The heat of combustion calculated for 1-monomyristin is 2464 ±0.59 kcal. per mole (104).

TABLE 20

Erythritol and pentaerythritol esters: physical and chemical data

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
Erythritol				
Dipalmitate	99.5–101		Consists of 85% dipalmitate and 15% monopalmitate	(477)
Tripalmitate	81–83		Consists of 72% tripalmitate and 28% tetrapalmitate	(477)
Mixed tri-tetrapalmitate	80–83		Consists of 57% tripalmitate and 43% tetrapalmitate	(477)
Mixed di-tristearate	62–64.5		Consists of 36% distearate and 64% tristearate	(40, 477)
Tetraoleate			Iodine value, 85.6 Refractive index, 1.4540 (70°C.)	(518)
Pentaerythritol				
Tetrapalmitate	70–70.5	Ethanol: soluble hot, crystallizes on cooling Benzene–ethanol: crystallizes	Stearic acid: 94.15; 94.18	(3)
Oleate			Saponification value: 197.9, 204.1 Iodine value, 73.8 Molecular weight, 1102; calculated, 1184	(53)
Erucate			Saponification value, 209.9 Iodine value, 96.1 Molecular weight, 1609; calculated, 1416	(53)
Ester of linseed fatty acid			Saponification value: 257.1, 212.3 Iodine value: 101.2, 122.1 Refractive index, 1.4900 Molecular weight, 320	(14, 139, 143)

TABLE 21

Pentose and methyl glucoside esters: physical and chemical data

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
l-Arabinose				
Tetrapalmitate.......	69.5	Ethanol: poorly soluble Ether, acetone: moderately soluble Ethyl acetate: poorly soluble Chloroform, benzene: easily soluble	$[\alpha]_D^{19} = +4.24°$	(406)
α-Methyl-*d*-glucoside				
Tripalmitate.........	77	Ethanol: moderately soluble hot Ether, acetone: soluble in boiling solvent Ethyl acetate: moderately soluble Chloroform, benzene: very soluble		(405a)
Tetrapalmitate.......	69	Ethanol: poorly soluble Ether, acetone: moderately soluble hot Chloroform, benzene: easily soluble Carbon disulfide, ligroin: poorly soluble	$[\alpha]_D^{15} = +38.22°$ $[\alpha]_D^{18} = +46.9°$	(406)
Tristearate..........	82	Ethanol, methanol: poorly soluble Acetone: moderately soluble hot Ether, ethyl acetate; moderately soluble Chloroform, benzene: very soluble		(405a)
Tetrastearate.........	68	Ethanol, methanol: poorly soluble Acetone: moderately soluble hot Ether, ethyl acetate: moderately soluble Chloroform, benzene: very soluble		(405a)
Monoester of olive oil fatty acid.........			1-Methoxy-5,6-anhydroglucose-3-oleate	(318)

The molecular heat of combustion with constant pressure is 6979.5 kcal. for glycerol dierucate, and 6953.7 kcal. for glycerol dibrassidate; with constant volume, the values are 6968.2 kcal. and 6942.4 kcal., respectively (523).

The specific heats for the 1- and 2-monopalmitins at 25°C. are 0.436 ±0.001 and 0.439 ±0.001 cal. gram^{-1} degree^{-1}, respectively (104).

F. OPTICAL ROTATION

Many sugar and sugar alcohol esters are optically active (58, 59, 60, 61, 256, 406, 565). All other asymmetric polyhydric alcohol esters are theoretically capable of optical rotation. However, sufficiently well defined pure optical isomerides of the glycerides were obtained only recently. Thus levorotatory 1-monoglycerides (23, 178, 179) and dextrorotatory 1,2-glycerides (512) have been prepared.

G. FLU ORESCENCE

Many polyhydric alcohol esters of fatty acids are strongly fluorescent. Certain commercial esters of glycol, diethylene glycol, polyglycol, glycerol, mannitol, and sorbitol, under radiation of 3650 Å., showed fluorescence varying from blue to green, and from yellow to brown (128a).

H. SURFACE TENSION

The surface tensions (in dynes per centimeter at 97.3°C.) of the 1-monoglycerides have been determined (450) by Sugden's maximum bubble pressure method:

ESTER	SURFACE TENSION	ESTER	SURFACE TENSION
Monocaprylin	26.69	Monomyristin	24.88
Monocaprin	25.43	Monopalmitin	25.54
Monolaurin	25.28	Monostearin	25.07

The surface tension of monolaurin is considerably lower than that of dilaurin and of trilaurin; the interfacial tensions of dilaurin and of trilaurin against alkaline solutions are much lower than against neutral or acid solutions (542a).

Surface action on paraffin and contact angles of glycol diesters have been measured (398a).

I. PARACHOR

The parachor was calculated for the 1-monoglycerides from their surface tension and density, and is given here together with the corresponding theoretical values (450):

ESTERS	PARACHOR		ESTERS	PARACHOR	
	Found	Calculated		Found	Calculated
Monocaprylin	514	529	Monomyristin	740	763
Monocaprin	588	607	Monopalmitin	823	841
Monolaurin	664	685	Monostearin	894	919

TABLE 22

Hexitol, hexitan, and hexide esters: physical and chemical data

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
Mannitan dilaurate.....	122	Water: insoluble Ethanol, methanol: poorly soluble cold Ether: easily soluble cold, soluble hot Benzene: soluble hot, poorly soluble cold Chloroform: poorly soluble Acetone: poorly soluble	$[\alpha]_D = +8.5°$ ($CHCl_3$) Lauric acid: 75.68, 75.79% Density, above 1	(61, 323)
Isomannide dilaurate...	37.5	Ethanol: very soluble cold Ether: very soluble Benzene: soluble cold Chloroform: soluble	Volatilizes slowly *in vacuo* with decomposition Optical rotation, strongly dextrorotatory Refractive index: 1.4570 (40°C.); 1.4500 (60°C.)	(61)
Mannitan dimyristate...		Water: insoluble Ethanol, methanol: poorly soluble cold Ether, benzene, chloroform: soluble Acetone: poorly soluble cold		(323)
Mannitan dipalmitate..		Water: insoluble Ethanol, methanol: poorly soluble cold Ether, benzene, chloroform: soluble Acetone: poorly soluble	Volatilizes *in vacuo*	(42, 323)
Mannitol hexapalmitate.	64.5	Ethanol: poorly soluble hot, cold Ether: easily soluble Petroleum ether, chloroform: easily soluble Ethyl acetate: easily soluble, crystallizes	Palmitic acid: 95.06%	(521)

Mannitan distearate....	116.5; 124; 67–72	Water: insoluble Ethanol: soluble hot, poorly soluble cold (crystallizes) Ether: soluble hot, very poorly soluble cold Benzene: soluble hot, very poorly soluble cold Naphtha: soluble hot Chloroform: 5% soluble, very poorly soluble cold Acetone: poorly soluble (crystallizes) Ethyl acetate: soluble hot	Volatile *in vacuo* Stearic acid: 81.64, 81.45, 80.91, 82.44% $[\alpha]_D^{50} = +8.0°$ ($CHCl_3$) Molecular weight, 704–706.6	(42, 59, 323 354)
Mannide distearate.....	51	Water: insoluble Ethanol, methanol: very soluble hot, very poorly soluble cold, crystallizes Ether: crystallizes Benzene, chloroform: soluble	Stearic acid: 84.8% $[\alpha]_D^{20} = +63.9°; 64.9°$ Molecular weight, 706 Density, above 1 Semi-translucent, brittle, white solid; conchoidal fracture	(58)
Isomannide stearate....	61.5	Ethanol: easily soluble hot, crystallizes Ether: easily soluble cold Benzene, chloroform: easily soluble cold	Volatile *in vacuo* $[\alpha]_D^{20} = +93.63°$ Molecular weight, 667 Amorphous, waxlike	(59)
Mannitol stearate......			Saponification value, 154.3 Molecular weight, 1766; theoretical, 1778	(53)
Mannitan dioleate (olive fatty acid)...........		Ether: easily soluble	Volatile *in vacuo* Structural formula: 3,6-dehydro-4,5-oleyl mannitol	(41, 319, 354)
Isomannide dioleate....			Oleic acid: 83.65%	(354)

TABLE 22—*Continued*

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
Mannitol oleate			Saponification value: 248.6, 182.5 Iodine value: 92.9, 76.4 Molecular weight: 727.3, 1625	(139)
Mannitol erucate			Saponification value, 162.4 Iodine value, 78.4 Molecular weight, 1215; theoretical, 2102	(53)
Mannitol ricinoleate			Saponification value: 172.2, 160.6 Iodine value: 69.8, 89.4 Molecular weight: 1407, 1866; theoretical, 1862	(139)
Mannitan monoester of coconut oil fatty acid	15–20 (setting point)	Ethanol: soluble Toluene: soluble Benzene, mineral oil: soluble Chlorinated solvents: soluble Ether-alcohols: soluble Ketones: soluble	Density, 1.02 Refractive index, 1.475 (25°C.)	(572)
Mannitan monoester of commercial stearic acid	45–55 (setting point)	Ethanol, ether-alcohols: soluble Esters: poorly soluble hot Chlorinated solvents, hydrocarbons: poorly soluble Castor oil: soluble Oils: soluble (hazy)	Density, 1.02	(572)

Mannitan monoester of commercial oleic acid	10–15 (setting point)	Ethanol: soluble Methanol: poorly soluble Hydrocarbons, chlorinated solvents: soluble Ketones, ether-alcohols: soluble Esters, oils: poorly soluble	Density, 1.02 Refractive index, 1.485 (25°C.)	(572)
Mannitol diester of linseed oil fatty acid			Molecular weight, 706 Refractive index, 1.4880	(370)
Mannitol tetraester of linseed oil fatty acid			Saponification value: 259, 227, 159.9, 181.5 Iodine value: 98.1, 91.8 Molecular weight: 1120, 1230 Refractive index, 1.4880	(139, 370)
Sorbitan monolaurate		Water: emulsifies	Waxlike	(274, 288, 487)
Sorbitan Monoester of coconut oil fatty acid	14–16 (setting point)	Ethanol: soluble Ether: moderately soluble Benzene: moderately soluble Chlorinated solvents: soluble Ether-alcohols: soluble Amines: soluble Ketones, esters, oils: moderately soluble	Saponification value, 160–170 pH (dispersion), 6–7 Density, 1.02 Refractive index, 1.472 (25°C.)	(572)

TABLE 22—*Concluded*

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C			
Monoester of commercial stearic acid....	45–55	Ethanol: soluble hot Ether: poorly soluble Benzene: soluble Petroleum ether: poorly soluble Chlorinated solvents: soluble Esters, ketones, ether-alcohols: poorly soluble	Density, 1.02	(572)
Monoester of commercial oleic acid......	5–6	Alcohol, ether, chlorinated solvents: soluble Esters: poorly soluble Oils: soluble	Saponification value, 135–140 pH (dispersion), 6–7 Surface tension (in 1 per cent aqueous solution), 27.5 dynes per cm^2.; (in 0.01 per cent), 31.2 dynes per cm.^{2} Density, 1.02	(572)
Dulcitol Hexapalmitate.......	74	Ethanol: poorly soluble Ether: moderately soluble hot Chloroform: easily soluble Benzene, pyridine, carbon disulfide: moderately soluble Acetic acid, ligroin: poorly soluble	Amorphous	(406)
Sorbitol hexahydroxyethyl ether Monolaurate..........		Water: soluble		(274, 288, 487)
Hexalaurate..........		Ethanol: easily soluble Acetone: soluble		(304)

J. VISCOSITY

The viscosity of a number of polyhydric alcohol esters has been determined. The values for certain monoglycerides are: monocaprylin, 0.0603; monocaprin, 0.0772; monolaurin, 0.0983; monomyristin, 0.1210; monopalmitin, 0.1472; monostearin, 0.1691 poises, at 97.3°C. (450). For certain ethylene glycol esters the values at 25°C. are: dioleate, 0.28; dilinoleate, 0.22; dilinolenate, 0.10 poises (414).

A number of viscosity determinations have been made for the esters of mixed fatty acids of certain oils (14, 73, 258, 499, 566, 572). Thus, for the glycol mono-, glycerol mono-, glycerol di-, and pentaerythritol esters of linseed oil fatty acids it is 0.5, 1.4, 0.6, 1.4 poises, respectively, at 25°C.; for the glycol monoester and the glycerol mono- and di-esters of tung oil fatty acids it is 2.25, 36.2, and 63.3 poises at 25°C.; for the glycerol monoester of dehydrated castor oil fatty acids it is 60 poises at 25°C. The sorbitan and mannitan monoesters of coconut oil fatty acids have viscosities of 40–60, and 20–40 poises, respectively, and mannitan monoleate a viscosity of 25–45 poises at 25°C.

K. THIN FILMS; STRUCTURAL DATA FROM SURFACE TENSION AND X-RAY MEASUREMENTS, ETC.

Films of polyhydric alcohol esters on distilled water have been studied by means of the surface-tension balance and by x-ray methods. Data for glycol esters (2, 103a, 370), the glycerides (5, 7, 25a, 370, 376, 377, 520), pentaerythritol (3), mannitol (370), and glucose esters (401) have been recorded.

The molecular length (film thickness) ranges from 10.2–12.8 Å. (cm. × 10^{-8}) for the linseed oil fatty acid esters of glycol (diester), diethylene glycol (diester), glycerol (monoester, diester), and mannitol (diester, tetraester), and for glycerol mono- and di-oleates. It is 24 Å. for dipalmitin, 20.6 Å. for monostearin, and 21.3 Å for distearin.

The molecular cross section is 22 Å. for glycol dipalmitate.

The molecular area has been measured when the film is "expanded", is under "no compression", and is at the "crumpling point" (all in square Ångström units or cm.^{2} × 10^{-16}):

ESTER	EXPANDED	NO COMPRESSION	CRUMPLING POINT
Glycol distearate		49.5; 51	
Glycol dilinseed		98	72
Glycol diricinoleate		253	
Diethylene glycol dilinseed		110	73
Glycerol monomyristate	70	26.3	
Glycerol monopalmitate	65; 70	26.3	
Glycerol dipalmitate		46; 46.4; 44.7	
Glycerol monostearate		27	20
Glycerol distearate		49	41
Glycerol monoöleate		47	25
Glycerol dioleate		86	63
Glycerol monolinseed		61	35
Glycerol dilinseed		103	73
Pentaerythritol tetrapalmitate		100	80
Mannitol dilinseed		105	75
Mannitol tetralinseed		176	147

TABLE 23

Sugar esters: physical and chemical data

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°C.			
Glucose monolaurate	110	Water: colloidally soluble Ethanol: easily soluble hot, poorly soluble cold Ether: easily soluble hot, poorly soluble cold	Specific rotation, 30° Reduces Fehling's solution	(60)
α-Glucose dilaurate	55	Water: colloidally soluble Ethanol: soluble hot, crystallizes on cooling Ether: poorly soluble cold	Specific rotation, 21.8° Reduces Fehling's solution	(60)
β-Glucose dilaurate	33	Water: colloidally soluble Ethanol: soluble hot, poorly soluble cold Ether: soluble cold	Specific rotation, 30° Reduces Fehling's solution	(60)
α-Glucose pentalaurate	52	Ethanol: poorly soluble cold Ether, petroleum ether, chloroform: easily soluble Acetone, ethyl acetate: easily soluble hot Benzene, carbon disulfide: easily soluble	$[\alpha]_D^{20}$ = 40.62° ($CHCl_3$)	(565)
β-Glucose pentalaurate	66	Ethanol: poorly soluble cold Ether, benzene, petroleum ether, chloroform, carbon disulfide: easily soluble Acetone, ethyl acetate: easily soluble hot	$[\alpha]_D^{20}$ = +3.9° ($CHCl_3$)	(565)
α-Glucose pentapalmitate	72–75	Ethanol: poorly soluble Ether, petroleum ether, chloroform: easily soluble Acetone, ethyl acetate: easily soluble hot	$[\alpha]_D^{20}$ = +29.7° ($CHCl_3$)	(565)

β-Glucose pentapalmitate	68–72	Ethanol: poorly soluble Ether, benzene, petroleum ether, chloroform, carbon disulfide: easily soluble	$[\alpha]_D^{20} = +4.6°$ (CHCl$_3$)	(565)
Glucose pentapalmitate	65–67; 62	Ethanol: gels on cooling Ether, benzene, chloroform, petroleum ether: easily soluble Ethyl acetate: crystallizes on cooling	$[\alpha]_D^{16} = +34.30°$	(256, 521)
Glucose				
Monostearate	110; 56.5–57	Water: colloidally soluble Ethanol, methanol: poorly soluble cold, crystallizes Ether: easily soluble, poorly soluble cold Mineral oil, acetone: soluble hot Benzene, chloroform: easily soluble	Specific rotation, 36.25° Reduces Fehling's solution	(60, 484)
Distearate	90–95	Water: colloidally soluble Ethanol: soluble hot, crystallizes, poorly soluble cold Ether: soluble hot, poorly soluble cold	Dextrorotatory Reduces Fehling's solution	(60)
Tristearate	60	Ethanol: soluble hot, poorly soluble cold Ether: soluble cold	Specific rotation, 12.00° Reduces Fehling's solution	(60)
Pentastearate	72–78; 70–71	Ethanol, methanol: poorly soluble cold Ether, petroleum ether, acetone, ethyl acetate: easily soluble hot, poorly soluble cold	$[\alpha]_D^{20} = +14.12°$ (CHCl$_3$) $[\alpha]_D^{16} = +34.17°$	(256, 565)
Stearate		Water: colloidally soluble Ethanol (absolute): soluble Ether: very soluble	Reduces Fehling's solution	(43)
Pentaoleate		"As for triolein"	$[\alpha]_D^{16} = +27.51°$	(256)

TABLE 23—*Concluded*

ESTER	MELTING POINT	SOLUBILITY	OTHER INFORMATION	REFERENCES
	°*C.*			
Glucose—(*Cont'd*)				
Ester of coconut oil fatty acid	41	Water: colloidally soluble Ether: soluble cold	Specific rotation, 21° Reduces Fehling's solution	(60)
Sucrose				
Octapalmitate	54–55	Ethanol: crystallizes Petroleum ether: crystallizes	$[\alpha]_D^{16} = +17.12°$	(256)
Octastearate	57	"As for tristearin"	$[\alpha]_D^{16} = +16.55°$	(256)
Linoleate		Benzene, turpentine, oils: soluble	Limpid viscous oil	(25, 265, 292, 465)
Eleostearate		Hydrocarbons, turpentine: soluble		(292)
Raffinose				
Hendecapalmitate	52–53; 43; 47	Alcohol, acetone: poorly soluble Ether: moderately soluble hot Benzene, chloroform, ethyl acetate: easily soluble	$[\alpha]_D^{20} = +31.8°; +4.2°; +27.2°$ ($CHCl_3$)	(256, 406)
Hendecastearate	63	Alcohol, acetone: poorly soluble Ether: moderately soluble hot Benzene, chloroform, ethyl acetate: easily soluble	$[\alpha]_D^{20} = +28.3°$ ($CHCl_3$)	(256, 406)

These, as well as other data, such as viscosity in solution (514, 515), have been used for the interpretation of the molecular structures of these esters (2, 3, 5, 7, 7a, 376, 377, 520). Ethylene glycol esters were unsuccessfully studied for anisotropical behavior under stress (555). The problem of forming multilayers on solid surfaces from monolayers on water has also been studied (4, 520).

Differences in adsorption on solids, such as alumina or silica gel, have been used to separate monolycerides from diglycerides (334).

L. CHEMICAL BEHAVIOR OF THIN FILMS

The rate of hydrolysis of certain glycerides under the influence of sodium hydroxide is proportional to their emulsifiability (383). The activation energy against sodium hydroxide was found to be 15,000 cal. for monopalmitin and 20,000 cal. for dipalmitin (7). The action of potassium permanganate–sulfuric acid on a monolaurin film was negative (4).

M. PHYSIOLOGICAL DATA

The formation of glycerides and other polyhydric alcohol esters by the action of certain enzymes has been studied (lipase from pancreas or the castor bean; adipose tissue; cytoplasma enzyme; bile salts), but could not be covered here. Certain glycol esters have been investigated as activators for the male sex hormone, testosterone, but only 1,3-propanediol palmitates were found effective (408, 409).

The question of the use of various polyhydric alcohol esters for foods has also been studied. Results on the value and permissibility of certain glycol esters in foods are controversial (121, 182, 357, 384, 466). Monoglycerides and diglycerides are harmless, and are utilized in the body as easily as fats of corresponding melting points (11, 76, 416, 464). Similarly, polyglycerol esters have been found harmless (62). There is also no objection against the use of mannitan and glucose esters in foods (59, 60, 61, 354).

III. Industrial Uses of Polyhydric Alcohol Esters

The extensive patent literature covering the preparation and use of polyhydric alcohol esters testifies to the considerable interest these materials have aroused in industry. Most applications of the polyhydric alcohol esters in various industries can be traced back to certain fundamental properties of these esters. It has been pointed out earlier that there are two basic types of polyhydric alcohol esters: namely, the completely and the partially esterified polyhydric alcohols. The partially esterified polyhydric alcohols are by far the more important group, because of their peculiar position between the hydrophilic and lyophilic materials. As a consequence, esters of this group have found definite use as interface modifiers. The wide variety of materials allows them to be "tailored" into an interface-modifying chemical or compound for almost any purpose. The inclusion of the group of ethers of polyhydric alcohol esters has extended this variety even further, and some of the most valuable interface modifiers are derived from it. It should be noted that certain completely esterified polyhydric alcohol ethers also are valuable as interface modifiers. In this case the hydrophilic character is due to ether linkages, not to hydroxyl groups.

The uses of the polyhydric alcohol esters will be surveyed below as a function of certain of their basic properties.

Some polyhydric alcohol esters may be used to replace the natural fats and oils because of their higher melting points or lower freezing points.

Monoesters and diesters of glycol or of glycerol derived from medium-chain-length fatty acids may serve as low-freezing low-viscosity lubricants for precision instruments (508).

On the other hand, hexitols or monosaccharides, fully esterified with cocoa butter fatty acids, were recommended to replace up to 25 per cent of chocolate fat (cocoa butter), in order to raise the melting point of the latter and to prevent the blooming of the chocolate (154).

Certain glycol esters, particularly of Montan wax, are recommended to replace Japan wax (174) and Carnauba wax (481), and as ingredients of wax polishes (313).

Certain esters of glycol (158), propylene glycol (49, 50), hexitol, and pentaerythritol (503) are stated to replace cocoa butter in suppositories. They have been suggested for this purpose also because they absorb water or disperse in it.

Glycol ricinoleates, as well as glycerol mono- or di-ricinoleates, may replace castor oil in the preparation of hydraulic fluid compositions of lower freezing point (19, 134, 135, 556, 558, 562). Glycerol or glycol polyricinoleates may replace castor oil in lubricating oils in order to lower their freezing point and viscosity index (542). Glycol distearate (417), as well as mannitan or sorbitan tetrastearates (418), are added to lower the pour point and to increase the viscosity index of lubricating oils.

Other applications for the polyhydric alcohol esters are based on their modified compatibility, solubility, or solvent power.

Glycol stearate has been suggested as an embedding material for microtome slicing, where it is superior to paraffin, as it is more compatible with alcohol and with water (413).

Diglycerides can dissolve 25 per cent to 30 per cent of phosphatides, such as lecithin (165, 166).

Polyhydric alcohol esters, such as the monoesters of glycerol, polyglycerol, or diethylene glycol, may be used as vehicles for water-soluble dyes. The dye then becomes effective on contact with moisture, as in lipstick (18, 233). Diethylene glycol laurate serves as a solvent for aniline dyes. Combined with mineral oil, it forms a non-volatile, non-hygroscopic liquid, suitable for reproduction of copies, e.g., with the Hectograph (107). Diethylene glycol laurate and tricresyl phosphate, containing an aniline dye in solution and a pigment, constitute a ribbon ink used in forming lithographic images on non-metallic plates (394).

Glycerol and glycol polyricinoleates are more compatible with mineral oil than is castor oil (542). Glycol ricinoleates, glycerol monoricinoleate, and glycerol diricinoleate find use in hydraulic fluids and lubricants, being more compatible with alcoholic solvents than is castor oil (19, 134, 135, 556, 558, 562).

Glycerol or other polyhydric alcohol monoricinoleates serve as solvents for aluminum stearate to form grease bases (180). Blends of glycol or glycerol esters of solid fatty acids with metal soaps are useful waxes (131, 392a).

Monoglycerides dissolve or blend with many resins such as natural resins (390, 391, 392, 499), shellac (46, 390, 392), alkyds (141), phenol–formaldehyde resins (380, 462), or aminotriazine–aldehyde resins (9), at elevated temperatures. In many cases they also react, forming modified products. Melamine–urea–formaldehyde resins may be plasticized by diglycol laurate (125). Hydroxy fatty acid esters of polyhydric alcohols dissolve acrylic resins, forming valuable blends (132).

Certain glycol or glycerol esters may serve as ingredients of polishes, owing to their high "solvent-fixing" power (solvent retention) (273, 286, 439, 481). Glycol or glycerol esters in conjunction with metallic soaps also are useful for this purpose (439). Emulsion polishes may be prepared with glycol esters (192, 496). A 3 per cent solution of glucose monostearate in white mineral oil will gel on cooling (484).

Diethylene glycol mono- and di-laurates have been suggested for perfume fixation (94).

Certain esters of glycol (258, 566) and of polyglycols, such as diethylene, triethylene, or dipropylene glycols (125, 158, 339), as well as polyhydric alcohol (glycol, glycerol, ether-glycols, mannitol, polyglycerol, pentaerythritol) esters of monohydroxy- or polyhydroxy-fatty acids (87), are described as plasticizers for nitrocellulose. Glycol ricinoleate (16), and esters of polyethylene glycol with fatty acids which are selected to give a product with a boiling point of 300–400°C. (369), may serve to plasticize cellulosic materials. Dioxanediol esters also may be used as plasticizers (510, 511).

Compositions containing diethylene glycol esters of fatty acids are suggested for use with zein (51).

Diethylene glycol esters may be used to soften or plasticize rubber and chlorinated rubber (29, 158). Glycerol monoricinoleate has possibilities as a softener for butadiene-type synthetic rubber (125).

Fatty acid esters of glycerol, pentaerythritol, sorbitol, glucose, sugars, inositol, or quebrachitol (145, 294), of dioxanediol (510, 511), the partial esters of glycol and glycerol (192), diethylene glycol (29), and water-soluble esters of polymerized polyhydric alcohols (34) are suggested as plasticizers.

Monoglycerides inhibit crystallization in fatty materials, such as saturated higher alcohols, waxes, hydrogenated oils, or solid fatty acids (15). Very small amounts (0.02–0.25 per cent) of completely esterified polyglycerols lower the pour test of salad oils on chilling (148).

Polyhydric alcohol esters may also serve for a variety of coating purposes.

Mono- and di-glycerides are used to form coatings on certain hygroscopic water-soluble solids, such as bile salts, liver concentrates, meat extracts, or powdered fertilizers, and may act to prevent caking of these materials when they are stored as powders (12, 337).

Certain monoglycerides or glycol esters may be used as casein-resisting coatings for milk bottle paper caps (507).

The softening, fulling, and sizing of rayon can be accomplished by dispersions of polyhydric alcohol esters, for instance, by ethylene, butylene, or amylene glycol monoesters (305, 341), glycerol mono- or di-esters (305), diethylene glycol esters (77), and monoesters of erythritol, arabitol, mannitol, etc. Textile sizing in general may be carried out with monoesters of ethylene glycol (192, 496), diethylene glycol (29, 130, 146, 403), polyglycols (275, 278), and glycerol (146, 412a), but also with esters of polyglycerols, pentaerythritol, erythritol, hexitols, sugars, and of the hydroxyalkyl ethers of polyhydric alcohols (96, 274, 276, 288, 307, 402, 412b, 487). Pile fabrics may be stiffened with glycol or diethylene glycol esters (136). Twisted cellulose yarns may be sized by soap–glyceride emulsions (505).

Water-soluble polyglycol esters of fatty acids may be used to disperse long-chain alkyl biguanidines, useful as textile softeners (280).

Water-soluble esters of polymerized polyhydric alcohols are stated to form useful films or coatings (34).

Certain polyhydric alcohol esters, mixed with oils and emulsified in water, may act as leather lubricants (29, 275, 302, 496). Mono- and di-glycerides are said to improve the consistency and lubricating action of lubricating oils (535). Esters of glycol (496), diethylene glycol, triethylene glycol, and polyethylene glycol (146, 365), polyglycol (275, 302, 488), glycerol (146), hydroxyalkyl ethers of polyhydric alcohol (274, 288, 487), esters of sorbitol (273, 286), of glycerol, erythritol, or mannitol (203), and polyglycerol-glycerol (236) have been recommended as textile lubricants. They are applied dispersed in water, either by themselves or with the aid of an emulsifying agent such as soap.

The introduction of polyhydric alcohols other than glycerol into drying oils, accomplished either by esterification of drying oil fatty acids, or by alcoholysis of drying oils followed by reësterification, has given some interesting results.

Glycol esters of drying oil fatty acids (73, 139, 142, 290, 386, 404, 414, 424), propylene glycol esters (73, 139), and the mono- and di-glycerides of drying oil fatty acids (73, 301, 309, 390, 499) are either slow drying or do not dry at all. Pentaerythritol esters (14, 53, 55, 139, 140, 142, 143, 144, 145, 273, 286, 290, 294, 504) and hexitol esters (14, 53, 139, 143, 144, 273, 286, 294, 504) are generally faster drying and more heat convertible than the corresponding glyceride oils. Special drying oils may be obtained from inositol (145), quebrachitol (145, 315), or from trimethylolmethane (290). Sugar esters (25, 145, 265, 292, 294, 465) are said to dry even more quickly and to be converted into insoluble and infusible resinous materials by heat.

Gelation of tung oil during heat treatment can be relieved by addition of monoglyceride (534).

The partial fatty esters of polyhydric alcohols and of their ethers, as well as certain completely esterified polyhydric alcohol ethers, are able to modify the surfaces of aqueous solutions and the interfaces between water and another liquid not soluble in water, that is, to act as emulsifying, dispersing, wetting, anti-spattering, foaming, suspending, or stabilizing agents. The esters are ordinarily not used alone, but in conjunction with other surface-active agents. An analysis of a commercial ester (381) shows such a combination with soap. However, a number of polyhydric alcohol esters have become known which, by themselves, are sufficiently well balanced in their affinities both for water and for non-aqueous materials so as not to require any stabilizers (200).

Within the large group of polyhydric alcohol esters there are compounds which are most suited for a particular purpose, such as wetting, anti-spattering, dispersing, or emulsifying action. Naturally, the variety of problems involving the modification of interfaces is very large and to date there is no reliable way of predicting which ester will be best suited for a certain task. The usually wide and sweeping claims of patents dealing with this matter have complicated the situation further.

The ability of polyhydric alcohol esters to disperse (form milks) in water had been observed by a number of early investigators, who first described this property, e.g., for the monoglycerides (75, 103, 548), diglycerol monostearate (264), mannitol esters (323), and the glucose esters (43, 60, 484).

There are numerous uses for polyhydric alcohol esters dispersed in water. Dispersions of certain diethylene glycol esters are said to be suited as lubricants for the stamping and drawing of nickel alloys, tin, aluminum, brass, and similar alloys (125). Such lubricant films are stated to be easily fired off in annealing, and also to permit the stamping of lacquered metal without fracture of the coating.

The use of dispersed polyhydric alcohol esters for textile sizing, softening, and for lubrication has already been mentioned.

Diethylene glycol stearate, blended with paraffin and amorphous petroleum wax and emulsified in water, may be applied (by spraying) to aluminum surfaces, e.g., in refrigerators, to dry there and act as a protective coating (125); similarly, this may be used to protect iron surfaces.

Glycol stearate, together with dimethyl cellulose, may be used as a thickener in dentifrices (440). Glycerol monostearate together with Irish moss will thicken and stabilize dairy products (326). Glycol and glycerol monostearates, stabilized by wetting agents (e.g., lauryl sulfate, oleyl methyl aminomethane sulfate) may be used to thicken aqueous hair dyes (525, 526). Glycol, diethylene glycol, and triethylene glycol esters have been claimed to be "edible" thickeners for use in custards, etc. (32).

Glycerol monolaurate (30), laurates of diethylene glycol, triethylene glycol, propylene glycol, mannitol, sorbitol, erythritol (184), and combinations of diethylene glycol or glycerol esters with lecithin (500) may be added to yeast to improve its wrapping and cutting quality, to reduce its crumbliness, and to improve its whiteness.

Mono- and di-glycerides are added to improve the whipping properties of cream (421). Glycol, diglycol, and particularly glycerol mono- and di-esters improve ice cream formulation by controlling "over-run", that is, the amount of air whipped in (226, 388, 468). They may also be added to frozen confections similar to ice cream (360).

Mono- and di-glycerides (243a, 249, 395, 397, 531), polyglycerol esters, glycol esters, hexitol, and sugar esters (241, 250, 397) are added to frozen or powdered dried egg materials, to prevent leakage of moisture upon thawing and to improve their emulsifying power.

Polyethylene glycol ricinoleate is said to be useful in the preparation of "completely soluble" antigens from microörganisms (311). Unsuccessful attempts were made to use glycerol and mannitol esters for a similar purpose (322, 323).

Polyhydric alcohol esters may also serve as dispersing agents in non-aqueous media.

Esters of polyhydric alcohol ethers, such as diethylene glycol stearate, will stabilize the suspension of iron and nickel carbonyls in liquid hydrocarbon fuels, used as anti-detonating agents (438).

Pigment dispersions in paint or varnish vehicles are said to be stabilized by glycol monostearate (496), by polyglycerol esters (236), by diethylene glycol stearate (29), and by a combination of glycol esters and metallic soaps (385). A diethylene glycol laurate was found to act as a true dispersing agent in pigment grinding in linseed oil, while diethylene glycol oleate and linseed oil monoglyceride had no effect (129, 501).

Monoglycerides (329) and polyglycerol and diethylene glycol monoesters (240) will reduce the viscosity of chocolates (i.e., cocoa powder–cocoa butter pastes); candy confections, such as enrobing materials, icings, etc. are similarly affected. An addition of 10 per cent of mono- or di-glyceride will stabilize peanut butter against gravitational settling of the suspended nut solids (86).

Diethylene glycol stearate aids pigment suspension in ink (29) and acts as a "stabilizer" in phosphorescent inks (485).

Polyglycerol monoesters may be used to stabilize pigment dispersions for the dulling or delustering of textiles (96). Mannitol or diethylene glycol stearates may be used to incorporate metallic powders into paper pulp, in order to manufacture a conductive paper (342).

Glycerol monostearate dispersions have been suggested for the stabilization of pigment dispersions in latex (125).

Esters of polyalkylene glycols (199, 275, 278, 280, 379, 488), glycerol (412a), polyglycerol (63, 160, 161, 228, 236, 238, 276, 412a, 412b), hydroxyalkyl ethers of polyhydric alcohols (274, 288, 295, 308, 412b, 486, 487), and of erythritol, pentitols, hexitols, or sugars (288) have been named as dispersing agents. However, it must be said that, as a rule, this term has been used rather loosely and often refers to emulsifying power (the ability to stabilize a dispersion of a water-insoluble liquid in water) and not dispersing action (the ability to stabilize and thin dispersions of solids by neutralizing the mutual attraction of the dispersed particles).

Polyhydric alcohol esters may be used as wetting, spreading, penetrating, and levelling agents.

Glycol and diethylene glycol monoesters and also mono- or di-glycerides are used as depressants of interfacial tension, by dissolving them in sub-emulsifying quantities in the oil of certain therapeutic compositions (399).

Glycerol monolaurate (69, 349), esters of hydroxyalkyl ethers of polyhydric alcohols (527), sorbitol monoesters (528), and polyglycerol monoesters (509) may be added to photographic emulsions to act as spreading agents in the preparation of multiple coatings.

Mannitan monolaurate (467, 519), polyglycerol laurate (461), and dioxanediol esters (510, 511) have been suggested as ingredients of insecticide compositions. Their function is to allow rapid spreading of insecticides without permitting penetration in depth. Mannitan monolaurate, by itself, has been stated to have insecticidal power. It reduces the inhibiting effect of greenhouse sprays on the photosynthesis of the plants thus treated (422).

Polyglycerol esters are suggested as additives to dry-cleaning solvents (456).

In general, the following materials have been described to act as wetting, levelling, penetrating agents or detergents: glycol (butylene, amylene glycol) esters of short-chain acids up to lauric acid (173, 192, 496); diethylene and triethylene glycol esters (192, 233, 237, 496); polyglycol esters (192, 199, 237, 275, 278, 279, 302, 305a, 355, 358a, 362a, 488); glycerol esters (69, 192, 233, 237, 289, 412a, 496); polyglycerol esters (160, 161, 192, 233, 236, 238, 276, 228); erythritol, pentitol, hexitol, and saccharide esters (63, 228, 467); esters of hydroxyalkyl ethers of polyhydric alcohols (274, 288, 295, 308, 412b, 486, 487).

A comparatively novel application for a surface-active agent is as an anti-spattering agent, that is, to reduce the spattering of shortenings or margarine during frying. This action is not common to all polyhydric alcohol esters and is said to be most marked with a specific group of esters described as "well-balanced" hydrophilic lipins. However, the recorded materials include propylene and ethylene glycol monoesters (91, 92), mono- and di-glycerides (91, 92, 159, 168, 374), diglycerol esters (91, 92), polyglycerol esters (160, 161, 168, 228, 229, 236, 238, 231, 232, 276), hexitol esters and sugar esters (105, 159, 163, 168, 228, 229, 231, 232).

Polyhydric alcohol esters, such as glucose, polyglycerol, sucrose, lactose, and mannitol esters (228), polyglycol esters (275, 278, 488), diglycerol, propylene glycol, and ethylene glycol monolaurate, glycerol monostearate, glycerol mono- and di-oleates (91, 92), and hydroxyalkyl glycerol esters (308) have been claimed as foaming agents. Glycerides, however, have also been stated to defoam yeast (30).

Polyhydric alcohol esters, added as such or after incorporation into shortening are said to improve pastries and other bakery products. Thus, glycerides may be added to the flour (110, 451) or to the shortening used (248, 433, 454, 455). Pastry of high sugar-to-flour ratio may be improved by the addition of glycerides (109, 111, 112, 113, 116, 117, 118, 119, 146, 186, 226, 246, 247, 430, 435, 436, 437, 446, 453, 454, 455, 529, 530). Other polyhydric alcohol esters suggested for the improvement of pastry are polyglycerol esters (110, 162, 186, 226, 247, 431, 451), sugar alcohol or sugar esters (110, 226, 431, 451), and even diethylene glycol esters (248). It should be noted that the addition of glycerol monostearate to cake was recently found to make little difference except for an increased volume index (126). Polyhydric alcohol esters will prevent dough from sticking to baking tins (146). Shortenings for baking and other purposes are said to be improved by the incorporation of mono- and di-glycerides (108, 109, 114, 115, 157, 167, 186, 246, 248, 372, 428, 429, 453, 471), polyglycerol esters (147, 432) and other polyhydric alcohol esters (248).

Among the most outstanding applications of partial fatty acid esters of polyhydric alcohols is their stabilizing action for certain water-in-oil emulsions, particularly margarine. For this, polyhydric alcohol esters are added to suitable mixtures of oils and hydrogenated oils, and milk is added with agitation until it is properly emulsified in the oils. Chiefly, two types of stabilizers for this purpose have been recommended: first, mono- and di-glycerides of fatty acids, which may be used as such or together with small amounts of soap or of free fatty acids (99, 100, 146, 160b, 163, 164, 226, 230, 234, 239, 335, 396, 398, 471, 496); polyglycerol esters (161, 163, 415, 489), glycol and diethylene glycol esters (160b, 248, 398, 496), sugar alcohol and sugar esters (160a, 160b, 245), and other polyhydric alcohol esters (192, 227, 398) have also been suggested. Monoglycerides may be used to help stabilize salad dressings (30, 471) or other water-in-oil emulsions (564). The second type of stabilizer is obtained by the esterification or reësterification of polymerized and (or) oxidized fatty acids or oils with polyhydric alcohols, such as glycerol, erythritol, hexitols, glycol, polyglycerol, or sugars (168, 373, 374, 489, 490, 491, 492, 493, 494, 495).

The use of diglycerides in conjunction with lecithin has also been described (166).

While polyhydric alcohol esters are useful water-in-oil emulsifiers under certain conditions, these same esters may also be used as oil-in-water emulsifiers. The conditions under which they are used determine the type of the resulting emulsion. In general, it appears that oil-in-water emulsions will result if the polyhydric alcohol esters are, by themselves, readily enough dispersible in water, or are used in conjunction with stabilizers more water soluble than they themselves. Such stabilizers are, in particular, alkali, ammonium, and amine soaps, or chemicals forming them *in situ*, but also wetting agents like the aryl alkyl sulfonates (199), sulfonated fatty alcohols (199, 498), sulfonated oils or sulfonated monoglycerides (237, 306), the cationic "Sapamines" (191b, 193, 194, 443, 444, 472), the non-ionic condensation products of decomposed proteins with fatty acids (198, 497), or the sulfosuccinates (199).

There are, of course, all kinds of emulsions, and their applications are very numerous. Certain specific uses, however, have been recorded in the literature, and may be briefly reviewed:

Petroleum-base insecticidal sprays are widely used in agriculture. They are usually emulsifiable oils which yield comparatively coarse and unstable milks with water. This instability is desirable as a means of protecting the foliage, and, in fact, emulsion breakers are suggested to insure quick breakdown. Examples of such materials are aluminum soaps. Other ingredients of these emulsions are amine soaps or mahogany soaps. Glycol esters (6, 344, 345, 346, 502), diethylene glycol esters (410, 411), triethylene or tetraethylene glycol esters (196, 412), mono- and di-glycerides (6, 343, 344, 345, 346, 347, 348, 502, 559), mannitan (467, 519), polyglycerol (461), and dioxanediol esters (510, 511) have been recommended as emulsifiers.

Detergent as well as lubricating (softening) action is required in washing wool. For this, glycol (496, 568) or polyglycol esters (275, 302, 488) may be used.

To get a one-bath waterproofing process, aluminum salt solutions are added to cold aqueous dispersions of glycol or diethylene glycol esters. Waterproofing results on hot-calendering of the treated cloth (106).

Kerosene or dichlorobenzene, emulsified by borax and diethylene glycol esters, serves as a radiator flush (340).

Linseed oil dispersed by polyethylene glycol esters may be used in the fat liquoring of leather (275).

Polyethylene glycol esters (277) serve as emulsifiers for resins dissolved in naphtha, for ink.

Diethylene glycol esters (567) or mono- and di-glycerides (506) give polishes when emulsified with soap, mineral oil or naphtha, and water.

Monoglycerides (102) have been suggested as stabilizers for heterogeneous reactions.

A very large percentage of all emulsions is used for creams, lotions, and other cosmetic products; hence it is not surprising that many emulsifiers have been suggested for this purpose. Glycol esters will disperse to form good creams, salves, or lotions (70, 71, 72, 101, 244, 251, 255, 356, 427, 434, 472, 524, 557, 560, 568, 571). Propylene glycol esters, particularly in conjunction with amine soaps, make good suppositories and other water-absorbing bases (49, 50, 91, 92). Pentanediol oleate has been recommended for shaving compositions (251). Diethylene glycol esters have been suggested for various cosmetic purposes (17, 18, 71, 242, 320, 325, 356, 570, 571). Polyethylene glycol esters are also suitable (199, 242). Diglycol stearate, together with sulfated hydrogenated castor oil, petrolatum, and water, will give a satisfactory base for ointments (175). Mono- and di-glycerides are widely recommended as cosmetic emulsifiers, such as for petrolatum ointments (389), for toothpastes (17), and for other purposes (27, 101, 188, 195, 244, 289, 320, 325, 328, 335, 356, 361, 387, 412a, 427, 434, 442, 445, 472, 475, 476, 496, 557, 569, 570, 571); polyglycerol esters are used similarly (243, 244, 361).

Textile sizing or lubrication may be accomplished with mineral or vegetable oils emulsified by diethylene glycol esters (125) or polyethylene glycol esters (275).

Vitamin-containing oils may be emulsified by polyglycerol monoesters (24), hexitol, or sugar esters (169).

In general, the majority of polyhydric alcohol esters have been recommended for emulsification. This includes the esters of glycol (31, 32, 91, 92, 146, 192, 197, 419, 496), glycol and glycerol (195, 404, 463), diethylene glycol (29, 31, 32, 71, 146, 196, 243, 257, 403, 496), polyglycols (34, 199, 200, 275, 302, 496), and glycerol (30, 33, 74, 75, 80, 91, 92, 99, 100, 103, 146, 191a, 192. 195, 197, 203, 257, 276, 289, 330, 332, 333, 335, 390, 403, 412a, 447, 457, 458, 478, 479, 496, 548), and also the esters of the polyglycerols (33, 34, 74, 91, 92, 147, 226, 236, 238, 242, 243, 264, 303, 305a, 393, 432), of hydroxyalkyl ethers of polyhydric alcohols (274, 288, 412b, 487), of pentaerythritol (33, 34), of erythritol (203), of hexitols such as mannitol or sorbitol (33, 34, 168, 203, 242, 243, 245, 323, 572), and of sugars, such as glucose or sucrose (60, 168, 245, 484).

Soaps blended with polyhydric alcohol esters are suitable as additions to hair-waving solutions (127). Glycol monoesters (496), diethylene glycol esters (29), and polyglycerol esters (236) may be used for the "superfatting" of soaps.

Polyhydric alcohol esters of higher aliphatic hydroxycarboxylic acids may be used as electric insulators (310) or to fill radio condensers (146). At the same time, glycol, glycerol, and other polyhydric alcohol partial esters, together with fatty acid alkylol amides, have been suggested for use in overcoming difficulties due to the static electricity of synthetic (cellulose ester or ether) yarns or films (137, 138).

Glycol, glycerol, or polyglycerol ricinoleates have been suggested for use in the breaking of crude petroleum emulsions (128, 423). Glycol oleate and glycerol monoricinoleate are suggested as ingredients of oil-well drilling fluids of low "gas cutting" tendencies (327).

Certain monoglycerides are said to prevent rancidity in shortenings (78, 79).

Glycol esters of the odd-numbered fatty acids have been suggested as food in certain diabetic diets (384). Palmitates of propylene glycol and trimethylene glycol activate the action of testosterone (261, 408, 409). Mono- and di-glycerides or glycol monoesters, emulsified with skimmed milk, have been suggested as a live-stock food in place of butter fat removed as cream (98).

Mono- and di-glycerides may be reacted with acidic unrefined oils to remove their free fatty acids. Advantages of this method over that of using glycerol are ready miscibility, quick reaction, and minimum formation of partial esters (67, 513).

Small amounts of glycerol monostearate are stated to eliminate "sun-checking" of butadiene synthetic rubbers (125). The sticking together of raw rubber sheets can be overcome by spraying wich a diethylene glycol stearate dispersion, which is absorbed in processing later on (125).

In closing this review, the attention of the reader is drawn to a recently published compilation of surface-active agents commercially available in the United States (26), which contains references to numerous polyhydric alcohol esters.

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