A Simplified Method for the Preparation of α- and β-Eleostearic Acids and a Revised Spectrophotometric Procedure for Their Determination[1]

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THE TUNG OIL utilization research program at the Southern Regional Research Laboratory required, for certain of its phases, preparations of pure eleostearic acids in quantity. With a high grade tung oil the preparation of the eleostearic acids should be simple. Domestic tung oil is produced exclusively from the *fordii* species of the genus *Aleurites*. *Fordii* oil normally contains some 78% eleostearic acid in glyceride form although some authentic samples exhibiting as high as 85% have been reported (3).

Two isomeric forms of eleostearic acid (9,11,13-octadecatrienoic acid) are recognized, and the *cis, trans* configurations of the double bonds in the triene systems for each have been established with certainty (1, 11). The tung tree elaborates only one of these isomers, the so-called α-form (9-*cis,* 11-*trans,* 13-*trans* octadecatrienoic acid (2). Consequently the eleostearic acid in fresh tung oil, pressed from normal, undamaged tung kernels, has the α-configuration exclusively. β-Eleostearic acid (9-*trans,* 11-*trans,* 13-*trans* octadecatrienoic acid) must be produced artificially by inducing the *cis* 9–10 double bond of the α-form of the acid to shift to a *trans* configuration.

Iodine, sulfur, selenium, and sunlight are variously reported to effect the α to β transformation. Certainly iodine and some forms of sulfur are efficient isomerization catalysts. Sunlight, of itself, is an unlikely cause of isomerization although light undeniably hastens the *cis* to *trans* shift whenever traces of iodine are present in the oil. In any event the transformation from α to β is easily accomplished whether the eleostearic acid is in the form of the free acid or the glyceride. It has been observed in this laboratory that this isomerization may be most readily accomplished by treatment of the tung oil (or eleostearic acid) with a small quantity of saturated potassium iodide solution, followed by exposure to diffuse daylight.

Numerous procedures have been reported in the literature for the preparation of pure α- and β-eleostearic acids (7, 8, 9, 10, 12, 13, 14, 15, 16). Varying in their degrees of complexity, some require special apparatus for excluding oxygen while filtering; others employ numerous washings and recrystallizations from various solvents while some, for β-eleostearic acid, even resort to recrystallization of the potassium salts. Such multiple operations are not only time-consuming but by their very nature afford ample opportunity for these highly unstable acids to undergo deterioration. On employing 95% ethanol as solvent, it has been found that acids of high purity can be obtained in good yields after a single recrystallization.

The purity of the α- and β-eleostearic acids was determined by spectrophotometric procedures as described by O'Connor *et al.* (10). The values found for the β-eleostearic acid preparations averaged 99.95% purity while those for the α-acid averaged 103.3%, based on calculations from the earlier absorptivities (10). As these values indicate an α-eleostearic acid of higher purity than heretofore available, the coefficients in the multicomponent spectrophotometric procedure have been revised.

Experimental

α Tung Oil. Domestic tung oil from the 1954 crop was used as the source of the eleostearic acids. Spectral analysis, by the method of O'Connor *et al.* (10), showed the oil to contain 78.2% α, 1.5% β, and 79.7% total eleostearic acids, calculated as free acids.

β Tung Oil. Isomerization of α tung oil was accomplished by blending 500 ml. of the oil and 1 ml. of saturated potassium iodide solution in a Waring Blender[3] for three or four minutes. The sample was then bottled and exposed to diffuse daylight. Separation of the solid glyceride was noted within a few hours. Three liters of oil were isomerized in this manner. Spectral analysis (10) of the solidified product after several days of exposure to daylight showed that it contained 58.0% β, 13.5% α, and 74.1% total eleostearic acids. Neither extended exposure of the sample to daylight for three weeks nor maintenance at 70°C. for 10 days appeared to produce any significant change in the extent of isomerization.

Preparation of α-Eleostearic Acid. Tung oil (200 g.) was saponified by refluxing with alcoholic potassium hydroxide (60 g. potassium hydroxide, 50 ml. water, and 500 ml. 95% ethanol). The flask and its contents were swirled occasionally during the 30-min. saponification period. After cooling, the soap was acidified in a separatory funnel with 725 ml. of 2 N hydrochloric acid. The liberated fatty acids were separated from the aqueous phase and dissolved without further treatment in 1,000 ml. of 95% ethanol. This solution was kept for 20–24 hrs. at −20°C. for formation of the first crop of acid crystals. The very light-colored crystals were filtered, then washed with about 75 ml. of cold 95% ethanol. In order to avoid air oxidation of the crystals during all filtrations, the rate of filtration was adjusted so that solvent or solvent vapors were always in contact with the crystals, *i.e.,* conscious efforts were made to avoid drawing air through the crystals being filtered. It was found experimentally that this precaution eliminated the necessity of performing filtrations, transfers, etc., under an inert atmosphere. Vacuum drying and subsequent ultraviolet analysis of an aliquot sample showed that the acid at this point in a typical preparation weighed approximately 142 g. and had the following composition: 100.9% α- and 1.85% β-eleostearic acids.

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[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.
[3] The mention of this and other commercial products does not imply endorsement or recommendation by the Department of Agriculture over others having similar properties but are mentioned as part of the exact experimental conditions used in the work being reported.

The moist crystals were dissolved in 500 ml. of 95% ethanol and allowed to recrystallize 20–24 hrs. at +5°C. After filtration and washing with 75 ml. of cold 95% ethanol, the crystals were rapidly transferred to a round-bottom flask and vacuum-pumped until no further loss in weight indicated them to be dry. Preparations of the pure α-eleostearic acid (58–62% yield) analyzed 0% β- and averaged 103.3% α-eleostearic acids. Cap. m.p. (corr.) = 49.2–49.4°C.

Preparation of β-Eleostearic Acid. β-Tung oil (200 g.) was saponified by refluxing with alcoholic potassium hydroxide solution (60 g. potassium hydroxide, 150 ml. water, and 500 ml. 95% ethanol). The flask and its contents were swirled occasionally during the 30-min. saponification period. Release of the free acids was accomplished by pouring the warm soap solution slowly and with much stirring into 725 ml. of 2 N hydrochloric acid. After cooling, the tan, oily crystals were filtered off with suction, washed with 100 ml. of water, and dissolved with slight warming in 1,500 ml. of 95% ethanol. This solution was held at—20°C. for 20–24 hrs. The light-colored crystals were vacuum-filtered and washed with about 100 ml. of cold 95% ethanol. Vacuum-drying and subsequent ultraviolet analysis of an aliquot sample showed that the acid at this step in a typical preparation weighed approximately 125 g. and had the following composition: 0% α- and 93.2% β-eleostearic acids.

The moist crystals were dissolved with slight warming in 750 ml. of 95% ethanol, and the solution was held at +5°C. for 20–24 hrs. The white, fluffy crystals were filtered off, washed with 100 ml. of cold 95% ethanol, then rapidly transferred to a round-bottom flask. The flask was held under vacuum until no further loss in weight indicated the crystals to be dry. Preparations of the pure β-eleostearic acid (92–98% yield, based on amount of β-acid present in original β-tung oil) analyzed 0% α- and averaged 99.95% β-eleostearic acids.

Storage of the Pure Acids. The pure eleostearic acids are quite unstable in the presence of air at room temperature (14). Also there is a marked tendency for pure α-eleostearic acid to isomerize to the β-acid under these conditions. However the acids may be successfully stored in sealed, evacuated ampoules at —20°C. Typical samples of α-eleostearic acid analyzed 95.1% α and 0% β after one month and 96.4% α and 1.2% β after six months of such storage. A typical sample of β-eleostearic acid analyzed 0% α and 99.1% β after one month under the same conditions.

Spectrophotometric Procedure for the Determination of α- and β-Eleostearic Acids

When samples of α-eleostearic acid, prepared from time to time by the older elaborate methods referred to, were measured spectrophotometrically for a check on their purity by the method of O'Connor *et al.* (10), absorptivities were found to be consistently higher than those published (Table I). Similarly the absorptivities measured from several preparations of the acid by the simplified procedure were also higher than those previously reported. Some consideration was given to the possibility that these higher values represent changes or modifications in the instrument used for the determinations. Eleostearic acids have rather sharp bands, the measurement of which can be affected by such factors as spectral band width.

TABLE I
Absorptivities for Pure α-Eleostearic Acid in Cyclohexane Solution

Sample	271.5 mμ			269.0 mμ		
	Min.	Max.	Av.	Min.	Max.	Av.
Published method (10)			168.6			149.5
From "earlier" preparations–See text (14 samples)	173.0	176.9	175.2	153.2	157.3	155.1
From "simplified" preparations (7 samples)	175.8	177.8	176.8	156.6	159.0	157.8
Reported by Paschke and Wheeler (12)			178.3			159.0
Averages—(excluding previously published values)–Used in revised procedure			176.7			157.3

In order to control this variable the original method was established with all measurements made at maximum sensitivity on a Beckman Model DU Spectrophotometer.[3] Investigations however have shown that the increase in the value of the absorptivities of the magnitude shown in Table I cannot be accounted for by such instrumental variables.

Paschke and Wheeler (12) have recently reported calculated purities of greater than 100% in the analysis of their preparations of α-eleostearic acid by use of the absorptivities and equations of O'Connor *et al.* (10). Their reported absorptivities agree rather well with the values more recently found in this laboratory (Table I).

It appears that somewhat better preparations of α-eleostearic acid than were used in 1945, when the original simultaneous equations were established, are now available and that modification of the spectrophotometric method to make use of these better values is necessary.

TABLE II
Absorptivities for Pure β-Eleostearic Acid in Cyclohexane Solution

Sample	271.5 mμ			269.0 mμ		
	Min.	Max.	Av.	Min.	Max.	Av.
Published method (10)			178.1			202.4
From "earlier" preparations–See text (5 samples)	168.5	170.9	169.7	200.3	203.8	202.2
From "simplified" preparations (5 samples)	167.9	171.2	169.0	200.8	206.2	202.3
Reported by Paschke and Wheeler (12)			165.4			201.0
Averages (excluding previously published values)–Used in revised procedure			168.0			201.8

In Table II the absorptivities for pure β-eleostearic acids are compared. It will be noted that there has been very little change in the absorptivity at 269.0 mμ, the position of the strongest maximum. The value at 271.5 mμ, the position of α-eleostearic acid maximum in the spectrum of β-eleostearic acid, has been revised downward. The value for this particular constant reported by Paschke and Wheeler is considerably lower than the original value used by O'Connor *et al.* The newer values obtained in this laboratory are intermediate between the older values and those reported by Paschke and Wheeler. It should be pointed out that, although the values for the β-isomer are not revised considerably, revision of the constants for α-eleostearic acid, particularly at 269.0 mμ (the position, in the spectrum of α-eleostearic acid, of the maximum for β-eleostearic acid) will, in the simultaneous equations to be used, affect the determination of the β-isomer. The ultraviolet spectra of pure α- and β-eleostearic acids, typical of those upon which the revised spectrophotometric procedure is based, are shown in Figure 1.

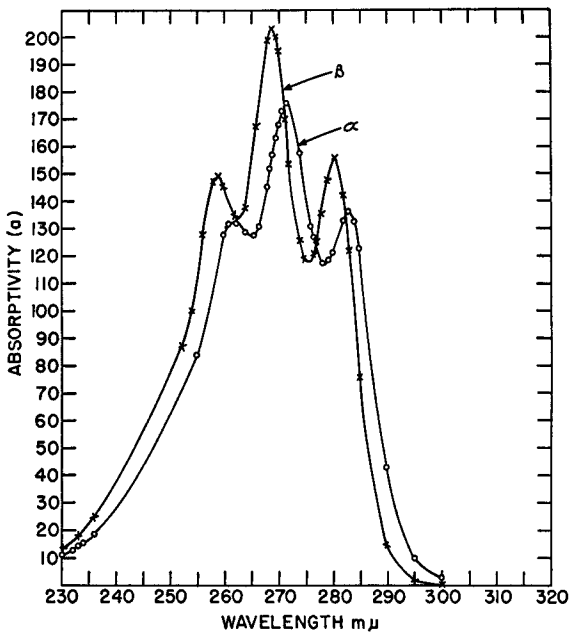

FIG. 1. Ultraviolet absorption spectra of cyclohexane solutions of α- and β-eleostearic acids.

In order to establish new simultaneous equations for the determination of α- and β-isomers, values of the absorptivities obtained from the older elaborate methods of preparation, from the simplified procedure, and from the work of Paschke and Wheeler *et al.* have been averaged, as shown in Tables I and II. This averaging gives a bit more weight statistically to the single values reported by Paschke and Wheeler *et al.* as compared to the average values obtained from 5 to 14 individual preparations in this laboratory. However use of values from two different laboratories should somewhat negate any undetected systematical error, and in any case the values reported are all in rather good agreement.

The revised simultaneous equations for α- and β-eleostearic acids in cyclohexane, found by O'Connor *et al.* (10) to be the solvent most suitable for the analysis of tung oils, are:

$$\% \text{ α-eleostearic acid} = 2.186\, a_{271.5} - 1.820\, a_{269.0}$$
$$\% \text{ β-eleostearic acid} = 1.914\, a_{269.0} - 1.704\, a_{271.5}$$

where a is the absorptivity at the specified wavelengths. The corresponding equation for total eleostearic acid concentration, using the isosbestic point 276.8 mμ, is:

$$\% \text{ total eleostearic acid} = a_{276.8} \times 100/123.8 = 0.8078\, a_{276.8}$$

The wavelength position of the isosbestic point is 0.3 mμ longer than that reported earlier (10). This wavelength position is very critical as it represents a portion of the curves where the slopes are very sharp. For accurate measurements of total eleostearic acids, a very careful wavelength calibration of the spectrophotometer at this region and very careful setting of the wavelength scale is required. When carefully performed, the measured total eleostearic acid content of a typical tung oil should check very closely with the sum of the α- and β-isomers. The absorptivity used in calculating the above equation was determined by careful measurements from spectrophotometric curves of the best samples, as determined from the α- and β-acid analyses.

While cyclohexane has been found to be an ideal solvent in the analysis of tung oils and various eleostearic acid preparations, it has not been suitable for measurement of the concentrations of several products resulting from reactions of either tung oils or pure eleostearic acids. In particular, products from Diels-Alder addition-type reactions are often insoluble or very difficultly soluble in cyclohexane. Therefore, as a number of highly purified acids were available, measurements of the absorption of the two isomers in 99% ethanol solutions were made. Absorptivities established from these measurements are:

α-eleostearic acid:

$$267.5\,m\mu = 160.4,\ 270.5\,m\mu = 183.7$$

β-eleostearic acid:

$$267.5\,m\mu = 210.4,\ 270.5\,m\mu = 171.5$$

The required simultaneous equations are:

$$\% \text{ α-eleostearic acid} = 1.888\, a_{270.5} - 1.539\, a_{267.5}$$
$$\% \text{ β-eleostearic acid} = 1.649\, a_{267.5} - 1.439\, a_{270.5}$$

The expression for total eleostearic acid, from measurements in ethanol, is:

$$\% \text{ total eleostearic acid} = a_{275.4} \times 100/131.0 = 0.7634\, a_{275.4}$$

These sets of equations are recommended for all measurements of either α- or β-eleostearic acid or total eleostearic acid content, and they should replace the earlier published equations (10). It should be re-emphasized that they are strictly applicable only to measurements on the Beckman Model DU Spectrophotometer [3] when operated at maximum sensitivity. Under such conditions the entrance-slit widths should be very close to 0.3 to 0.4 mm. at the three wave lengths involved.

When in any analysis the concentration of one of the eleostearic acid isomers is found to be zero, a more accurate determination of the single isomer present can be made by a direct calculation, abandoning the simultaneous equations.

In cyclohexane:

$$\% \text{ α-eleostearic acid} = a_{271.5} \times 100/176.7 = 0.566\, a_{271.5}$$
$$\% \text{ β-eleostearic acid} = a_{269.0} \times 100/201.8 = 0.496\, a_{269.0}$$

In 99% ethanol:

$$\% \text{ α-eleostearic acid} = a_{270.5} \times 100/183.7 = 0.544\, a_{270.5}$$
$$\% \text{ β-eleostearic acid} = a_{267.5} \times 100/210.4 = 0.475\, a_{267.5}$$

These simultaneous equations were established originally for the determination of α- and β-eleostearic acids in tung oils. In such samples absorption at the selected wavelengths from constituents other than the eleostearic acids is negligible. If the procedure is extended to the analysis of other products containing α- and β-eleostearic acids, an investigation must be made to ascertain that none of the components in such a sample contribute to the measured absorptivities. If interfering absorption is detected, inde-

pendent methods for correcting for it must be incorporated into the procedure.

Infrared Absorption Spectra

The pure samples of α- and β-eleostearic acids were further characterized by means of infrared absorption spectra. The spectra of typical preparations of the two acids were obtained from potassium bromide discs and, as shown in Figure 2, are characteristic of solid state spectra rather than solution spectra.

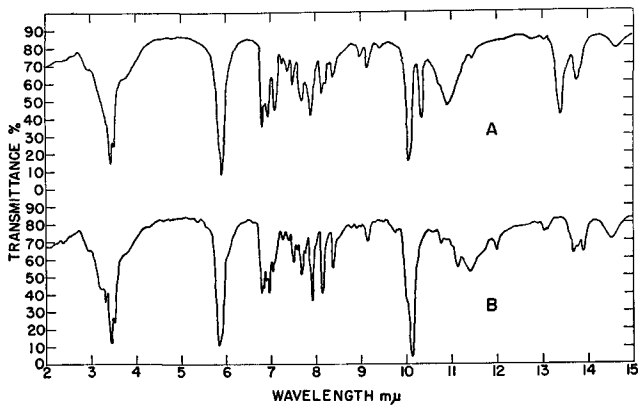

FIG. 2. Infrared absorption spectra of potassium bromide discs of α-eleostearic acid (A) and β-eleostearic acid (B).

Differences in the solid state or crystalline spectra of long-chain fatty acids were first pointed out by Jones and co-workers (5) and have been discussed in considerably more detail by Meyer and Schuette (6).

The most prominent bands in the spectra of the eleostearic acids are the C-H stretchings at about 3.3–3.4 μ; the C = O stretching of the acid group at 5.9 μ; the C-H bending at about 6.95 μ; and the C-O stretchings at 7.2 and 8.9 μ. The α-acid can be most readily distinguished from its β-isomer by the appearance of a band in the infrared spectra with a maximum at 10.4 μ, one of the pair of bands characteristic of the *cis-trans* conjugated system (4). This group is found in α-eleostearic acid but not in the β-isomer (1, 11). The presence of eleostearic acid can be established qualitatively, and its appearance or disappearance during reaction followed most easily, by observation of the strong band at about 10.1 μ, characteristic of the *trans-trans* conjugated double bonds (4), which are found in both isomers (1, 11). In a completely unknown material this identification would not be valid without ultraviolet absorption evidence for the triene conjugated system.

In the region between about 7.5 and 8.5 μ spectra of crystalline fatty acids exhibit a series or progression of sharp bands, which, as originally pointed out by Jones *et al.* (5) are proportional to the number of carbons in a straight-chain, saturated fatty acid. These bands are believed to be caused by twistings or waggings of methylene groups, a band appearing for every two such groups (5). The chain length of a saturated fatty acid can be determined from the empirical equation:

I. (No. of observed bands in progression) $\times$ 2 + 2 = No. of carbon atoms in a straight chain.

This relation is illustrated in the spectra of saturated fatty acids in Figure 3. Caprylic acid exhibits only

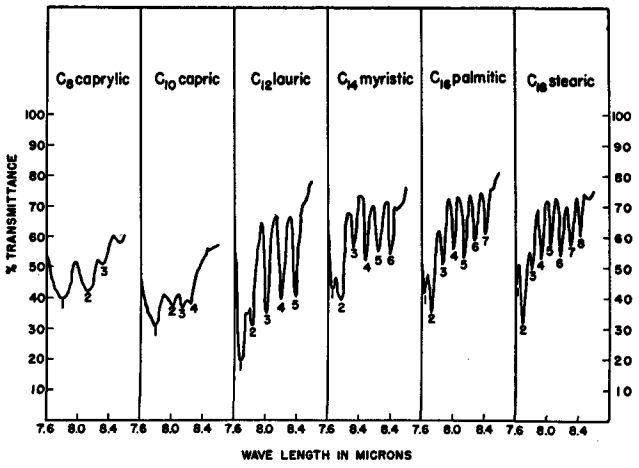

FIG. 3. Infrared absorption spectra of potassium bromide discs of the saturated fatty acids of even carbon atom content from caprylic (C_8) through stearic (C_{18}), in the region 7.5 to 8.5 microns, showing the progression bands by means of which chain length can be calculated.

three bands in this region, and application of the empirical relation gives the correct number of carbon atoms, eight. The relation holds exactly for all the members of the homologous series included in Figure 3, from caprylic with eight carbon atoms to stearic with 18. For example, stearic acid with 18 carbon atoms exhibits eight bands in its spectrum.

In the spectra of unsaturated fatty acids each double bond replaces two methylene groups, and the equation must be revised:

II. (No. of observed bands in progression + No. of double bonds) $\times$ 2 + 2 = No. of carbon atoms in straight chain.

When the number of double bonds becomes zero, *i.e.*, a saturated fatty acid, equation II reduces to I. As seen in Figure 2, the eleostearic acids exhibit five bands in this region, and application of the revised relation gives 18, the correct number of carbon atoms in the eleostearic acid chain.

Summary

Simplified methods for the preparation of pure α- and β-eleostearic acids are described. These procedures involve saponification of α- and β-tung oils under mild conditions, followed by direct crystallization of the liberated acids at $-20°$ C. from ethanolic solution. Only one recrystallization from ethanolic solution at $+5°$C. was required to produce the pure acids.

Absorptivities obtained from measurements of the ultraviolet absorption revealed α-eleostearic acids of from 3–4% higher purity than those used in obtaining the equations previously recommended for the simultaneous determination of α- and β-eleostearic acids. This has necessitated a revision of these equations. Equations for the determination of each isomer from both cyclohexane and ethanol are reported. Equations are also given for an independent determination of total eleostearic acid, and for the determination of one isomer in the absence of the other.

Infrared absorption spectra in the rock salt region from 2-15 microns have been measured from potassium bromide discs. These solid-state or crystalline

spectra reveal, in addition to the prominent bands assigned to characteristic groupings of the eleostearic acid molecule, the progression bands by means of which carbon chain length can be computed.

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Analysis of Polyethylene Glycol Esters

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FATTY ACID MONOESTERS of polyethylene glycols are widely useful surface-active substances. As prepared industrially, these products usually contain not only the monoester but also appreciable amounts of the diester and unreacted polyethylene glycol as well. This result is unavoidable when one mole of fatty acid is esterified with one mole of polyethylene glycol, and it is also encountered in the base-catalyzed reaction of ethylene oxide with a fatty acid:

$$3RCOH + 3n\ C_2H_4O \rightarrow RCO(CH_2CH_2O)_nH + RCO(CH_2CH_2O)_nCR + HO(CH_2CH_2O)_nH$$

In an investigation of the latter reaction in this laboratory it was of interest to know approximately the relative amounts of the three products obtained under various reaction conditions. The nature of the mixture precludes estimating the composition by means of the hydroxyl and saponification numbers. Attempts to find a colorimetric or a precipitation method specific for the polyethylene glycol were unsuccessful (1, 2, 5). Chromatography as a means of separation also did not appear to be promising.

The characteristic high solubility of the polyethylene glycols in water suggested that this component of the mixture might be selectively extracted. This would permit analysis by means of hydroxyl and saponification numbers. However, when the ester is derived from a fatty acid having 9–20 carbon atoms and a polyethylene glycol having 9–20 oxyethylene units, the monoester will also be appreciably, if not completely, soluble in water at room temperature. If water is added to a mixture containing such a monoester, a solution or an emulsion is generally obtained. Advantage must be taken of the knowledge that the monoester will follow an inverse solubility-temperature relationship in water and will also be less soluble in salt solutions. This behavior is typical of the nonionic surfactants. Accordingly the fatty acid monoester is found to be substantially insoluble in hot salt solution while the polyethylene glycol dissolves and consequently can be separated.

Several tests were carried out to determine the effectiveness of extraction of polyethylene glycol in the manner contemplated. Sodium chloride was used to prepare a saturated salt solution at room temperature. Typically 25 g. of sample were extracted with 50 ml. of salt solution at 95–100°C. The procedure used in carrying out the extraction and in recovering the extracted sample is described in detail in the following section. Typical lauric acid-ethylene oxide condensation products, known to contain free polyethylene glycol along with monoester and diester, were extracted successively three times, and the change in hydroxyl and saponification numbers was noted after each extraction. From the data obtained (Table I) it was concluded that three extractions would insure complete removal of the polyethylene glycol.

TABLE I
Effect of Successive Extractions on Polyglycol Removal

	Hydroxyl number [a]		Saponification number [a]	
	Sample 1	Sample 2	Sample 1	Sample 2
Original material	100.9	80.0	95.3	75.7
After one extraction	61.9	53.2	108.3	85.3
After two extractions	56.5	47.3	107.8	85.8
After three extractions	56.3	46.7	109.8	87.5

[a] mgKOH/g.

As a further check on the removal of polyethylene glycol, relatively pure polyethylene glycol-600 monolaurate and dilaurate were used to prepare a blend which contained about 30% monoester, 35% diester, and 35% free polyethylene glycol-600. A sample of this blend was extracted, using the standard procedure, and the hydroxyl and saponification numbers were determined after extraction. Polyethylene gly-

TABLE II
Completeness of Removal of Polyglycol by Extraction

	Original material	After extraction	With 10% polyglycol added	After re-extraction
Hydroxyl No.[a]	81.7	32.2	49.0	32.1
Saponification No.[a]	58.1	91.3	83.8	93.5

[a] mgKOH/g.