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Preparation and Some Properties of Tung Oil Monoglycerides

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IN CONNECTION with a program of research at the Southern Utilization Research Branch on extending the utilization of tung oil, it appeared of importance to investigate methods for the preparation of tung oil monoglycerides and to examine some of their chemical and physical properties. It was anticipated that tung oil monoglycerides would have potential value as fugitive emulsifiers and sticking agents, for example, for use with agricultural sprays and in the preparation of alkyds and other surface coatings.

The tung oil used in all the experiments was a domestic commercial pressed tung oil (1954 crop), containing 0.44% free fatty acid (as eleostearic acid). Analysis for triene conjugation by the spectrophotometric method of O'Connor, Heinzelman, McKinney, and Pack (9) indicated the presence of 82.6% *alpha*-eleostearic acid, 0.3% *beta*-eleostearic acid, and 81.8% total eleostearic acid.

Quite early in the course of the investigation it became evident that commonly accepted methods (5, 10, 11) for the determination of monoglycerides were not applicable, possibly owing to the unusually high degree of triene conjugation and unsaturation present in these materials. In some cases values in excess of 100% were obtained for the monoglyceride content, and in others the experimentally determined monoglyceride content was clearly not consistent with values to be expected on the basis of other analytical data such as percentage by hydroxyl. However modification of one of the published methods gave reproducible results for monoglyceride content in reasonably good agreement with those to be expected on the basis of other experimental factors.

Experimental and Discussion

Glycerolysis with Sodium Hydroxide. Feuge and Bailey (4) have shown that about 40% by weight of the monoglycerides of hydrogenated cottonseed oil is formed at equilibrium conditions, which are obtained by heating the fat with 16.7% glycerol for three hours at 200°C., using 0.1% sodium hydroxide as a catalyst. Tung oil monoglycerides were prepared by this procedure. These crude monoglycerides, freed of glycerol and dried, contained 5.6% hydroxyl when analyzed by the method of West, Hoagland, and Curtis (13) but gave abnormally high values of about 90% for monoglyceride content when analyzed by the periodic acid methods of Pohle, Mehlenbacher, and Cook (10) and by the method of Handschumaker and Linteris (5). A value of 42.4% monoglycerides was obtained when the periodic acid method of Pohle and Mehlenbacher (11) was used with one-half hour reaction time. This value is in reasonably good agreement with that to be expected from the hydroxyl content and from the results obtained by Feuge and Bailey with hydrogenated cottonseed oil. However these monoglycerides were found to contain only 42% triene conjugation (as eleostearic acid) when analyzed by the spectrophotometric method of O'Connor *et al.* (9), indicating that about half of the triene conjugation originally present in the tung oil (81.8% eleostearic acid) had been destroyed. Because of the extensive loss of eleostearic acid at the high temperatures employed with sodium hydroxide as a catalyst, glycerolysis using sodium methoxide at lower temperatures was investigated.

Glycerolysis Using Sodium Methoxide. Tung oil monoglycerides richer in eleostearate content could be obtained by heating dry tung oil with anhydrous glycerol, using sodium methoxide as catalyst. The tung oil was dried by treating it with anhydrous sodium sulfate. Anhydrous glycerol was prepared by distilling 95% glycerol, A.C.S. grade, at low pressures until all the water was removed and then distilling the glycerol at reduced pressure. A suspension of sodium ethoxide in xylene (11%) was prepared by Eckey's modification (3) of the method of Bruhl (2).

In reactions carried out at 65°C. it was found that increasing the amount of added glycerol from 10 to 30% and the amount of sodium methoxide from 0.5 to 1.0% and increasing the reaction time from one-half to two hours all tended to increase the yield of monoglyceride, but increasing the catalyst from 1 to 2% and increasing the reaction time from two to four hours did not significantly affect the yield. Employment of 30% added glycerol and 1% sodium methoxide with a reaction time of two hours at 65°C. resulted in a product containing 32.2% monoglycerides after removal of excess glycerol. These crude monoglycerides were tested for eleostearate content (9). They showed no *beta*-eleostearate and between 77.0 and 78.4% total eleostearic acid, indicating that no appreciable amount of conjugated triene had been destroyed in this procedure by using lower temperatures and sodium methoxide as catalyst.

A method which proved to be still more effective for producing relatively higher concentrations of monoglycerides was an adaptation of the method of Mattil and Sims (8). Dry tung oil and anhydrous glycerol were heated with five parts of pyridine for 5 min. at 80°C., using 2% sodium methoxide as catalyst. The crude tung oil monoglycerides, after washing with an excess of dilute hydrochloric acid and with a hot solution of sodium chloride and drying,

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TABLE I

Interfacial Tension (Against Water)
Dynes per cm. at 25°C.

Tung oil monoglycerides (% added)	Cottonseed oil	Tung oil	Linseed oil
0	20.8	14.6	10.0
0.1	4.8	5.0	—
0.5	3.4	3.8	—
1.0	3.3	3.1	2.9
2.0	2.1	2.3	2.6
3.0	1.8	2.0	2.4

were found to contain 78.2% monoglycerides (when analyzed by the method of Pohle and Mehlenbacher, using one-half hour of reaction time), 7.57% hydroxyl, and 63.0% triene conjugation as eleostearic acid.

Concentration of Monoglycerides. Various methods were employed in an attempt to concentrate the tung oil monoglycerides but without significant success. Use of 60% isopropanol, 60% isopropanol-hexane, 70% isopropanol-hexane, 65% ethanol, 65% ethanol-hexane, and 80% acetone all failed to give products high in both monoglyceride and eleostearate content. In those cases in which the monoglyceride content was substantially increased the eleostearate content was greatly decreased and, on the other hand, if the eleostearate content were increased, the monoglyceride content decreased. There was some indication of preferential glycerolysis of the less unsaturated acids, leaving a preponderance of eleostearate in the diglyceride and triglyceride portions rather than in the monoglyceride portion. Attempted purification by means of urea segregation (12) was also ineffective. These methods having failed to yield a product rich in both monoglycerides and conjugated triene, an attempt was made to prepare pure glyceryl monoeleostearate. *Alpha*-eleostearic acid (99.8%) was converted to the acyl chloride (1) and treated with acetone glycerol according to the method of Jackson and King (6). Although preparations rich in both monoglyceride and eleostearate were obtained, attempted isolation of the pure compound was not successful, partly because of the ease of hydrolysis of the monoglyceride and partly because of the instability of the eleostearate moiety.

Surface and Interfacial Tension. It is known that monoglycerides tend to decrease the interfacial tension between water and various oils. It is also known that tung oil when used in surface coatings imparts exceptionally high resistance to moisture. It was of interest therefore to determine the surface and interfacial tension of tung oil, to compare the values obtained with the values for other oils, and to observe the effect of adding tung oil monoglycerides on the interfacial tension of these oils. The surface tension and interfacial tension of tung oil (which does not appear to have been determined before) were measused, using a Du Nouy tensiometer which was standardized against water and benzene. The surface tension, at 25°C., for tung oil, linseed oil, and cottonseed oil was found to be 33.1, 31.3, and 30.9 dynes per cm., respectively.

Tung oil monoglycerides proved to be quite effective in lowering the surface tension of water and its interfacial tension with various oils. As little as 0.006% crude tung oil monoglycerides (containing 82% monoglycerides) lowered the surface tension of water from 70.4 to 34.7 dynes per cm., and 0.1% of these crude tung oil monoglycerides lowered the interfacial tension of the cottonseed oil from 20.8 to 4.8 dynes per cm. Additional data showing the effect of tung oil monoglycerides on interfacial tension are given in Table I.

Fugitive Emulsifiers. Fugitive emulsifiers, that is, materials which can exert a temporary emulsifying action, are useful for many purposes.

The potentialities of tung oil monoglycerides as fugitive emulsifiers which might result by virtue of polymerization due to the triene conjugation were tested, using a suspension of lead arsenate, and the results indicated that they are effective. Filter papers (24 cm. in diameter) were suspended in an air-conditioned room until they attained constant weight and were then sprayed with 10 ml. of a suspension of lead arsenate. Typically the suspension was prepared by mixing 1 g. of lead arsenate and 0.1 g. of the emulsifier with 50 ml. of distilled water; the mixture was made slightly alkaline to phenolphthalein. This mixture was continuously agitated while being sprayed from a spray gun onto the filter paper, which was then allowed to dry to constant weight (over-night). The papers were then washed by spraying with 100 ml. of distilled water and again allowed to dry to constant weight in the air-conditioned room. The differences in weights before and after spraying with insecticide and after washing with water indicated the amount and proportion of lead arsenate retained. This was occasionally checked by determination of the amount of lead on the filter papers before and after washing, and reasonably satisfactory agreement between the two determinations was generally obtained.

The following are illustrative of results typically obtained. The water spray washed away only 12% of the dried residue when 0.2% crude tung oil monoglycerides was used as the emulsifier for the 2% suspension of lead arsenate while 33% was washed away when an equal amount of cottonseed oil monoglycerides was used as the emulsifier. In this case 67.2 mgms. of lead were found on the paper, after washing, when the tung oil monoglycerides were used as against only 34.6 mgms. of lead on the filter paper when the cottonseed oil monoglycerides were used. Similarly use of 0.04% crude tung oil monoglycerides with a 2% aqueous suspension of lead arsenate resulted in a loss of 35% of the dried residue after spray washing while use of the same amount of a commercial spreader-adhesive allowed 41% to be washed away. In this case 32.2 mgms. of lead were found on the filter paper after washing when the tung oil monoglycerides were used as emulsifier and 28.7 mgms. of lead were found when the commercial product was used.

For comparative purposes the ammonium soap of tung oil fatty acids was prepared, and it also proved to be an effective fugitive emulsifier. The ammonium soap was prepared according to the method of Kench and Malkin (7) by the action of concentrated aqueous ammonia on an alcoholic solution of tung oil fatty acids. The addition of 2% of this ammonium soap to a suspension of lead arsenate (2%) allowed only 1% of the insecticide to be washed from the filter paper, after drying over-night, and 83.1 mgms. of lead were found on the filter paper whereas the addition of the same amount of a commercial fish oil soap allowed 25% of the insecticide to be removed by washing under similar conditions and only 54.6 mgms. of lead to remain on the paper.

Summary

Several methods for the preparation of tung oil monoglycerides were investigated. Products richest in both monoglyceride (78%) and triene conjugation (63% as eleostearic acid) were obtained by glycerolysis with sodium methoxide in pyridine solution. Attempts to increase the content of monoglyceride and triene conjugation by selective solvents were unsuccessful. The monoglycerides were effective in lowering the surface tension of water as well as the interfacial tension of several oils, including tung oil, against water. The tung oil monoglycerides behaved as fugitive emulsifiers and, after drying, retarded the removal of spray residue (lead arsenate) by washing with a water spray more than did other emulsifiers, such as cottonseed oil monoglycerides. The ammonium soap of tung oil fatty acids also acted as a fugitive emulsifier.

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Glycerolysis of Coconut, Sesame, and Linseed Oils. Fractionation of the Products with Alcohol and Urea

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DIRECT ESTERIFICATIONS of raw peanut and mustard oils with excess glycerol have been studied by Mehta, Rao, Laxmikanthan, and Shah (1), who reported that the composition of the reaction product is dependent upon various factors such as temperature, time, amount and nature of the catalyst, the proportion of glycerol, and nature of oil or fat.

Choudhury and Mukherji (2) studied the interesterification of various vegetable oils with ethanol and showed that coconut oil, which has a low molecular weight and iodine value, and castor oil, which has a high hydroxyl value, interesterified most rapidly. Among the oils of nearly the same molecular weight those with lower iodine values reacted more rapidly than those possessing higher iodine values, *i.e.,* the rate of ethanolysis was inversely proportional to unsaturation. Haller (3), using an acid catalyst, also observed the same phenomenon and ascribed the behavior of coconut oil to the presence of low-molecular-weight fatty acids. Pore (4) also showed that simple saturated (stearic) triglycerides transesterified more easily with methanol than did the unsaturated (oleic) glycerides. But in contradiction to the observations of Haller, Choudhury and Mukherji, Pore found that the length of the saturated chain had no effect on the rate of methanolysis.

The reaction of glycerol with olive, coconut, and linseed oils at 220°C. in the presence of 0.1% potassium hydroxide (based on the oil) was studied by Rossi, Bottazi, and Croce (5). Although the durations of the induction periods varied, all reactions eventually proceeded at the same rate. Addition of 10 and 20% monoglycerides shortened or eliminated the induction period. The effect of chain length and unsaturation of fatty acids on the rate of glycerolysis and compositions of the products were investigated in the present work with coconut oil because of its lower molecular weight, and with linseed and sesame oils because of their varying degree of unsaturation.

Pure mono- or diglycerides are better raw materials for the manufacture of detergents, special surface-active agents, and oil-modified resins than are technical monoglycerides. Consequently an investigation was undertaken to develop relatively simple methods for the fractionation of technical monoglycerides. Feuge and Gros (6) tried to purify the commercial monoglycerides from hydrogenated cottonseed oil by distribution between hexane and methanol or ethanol. They obtained from ethanol layer monoglycerides of 80% purity in a yield of 70%. Basu-Roy-Choudhury *et al.* (7) used a low-temperature crystallization method for the purification of crude monoglycerides of olive oil and oleic acid. Crystallization from methanol at 45°C. yielded in each case a fraction containing 80–85% monoglycerides.

The principle of urea-adduct formation should also apply to the otherwise rather cumbersome separation of mono-, di-, and triglycerides. It has been cited by Holman *et al.* (8) that preliminary experiments on fractionation with urea of crude monoglycerides carried out by Roncero, Fiestas, Mazuelos, and Moreno (9) gave unsatisfactory and unexpected results. In order to study the mode of separation of mono- and diglycerides by urea, experiments were conducted in this laboratory with the technical monoglycerides of sesame oil and of lauric acid. While this work was in progress Bradley, Mueller, and Shokal (10) reported that urea forms complexes more easily with diglycerides than with monoglycerides. Contrary to this observation, Heckles and Dunlap (11) showed that urea forms adducts with monoglycerides more easily than with diglycerides. They also showed