a procedure for estimating the phenolic hydroxyl groups present in a partially hydrogenated *p-tert*-butylphenol-formaldehyde resin. The projected procedure involved the determination of the aliphatic secondary hydroxyl groups by esterification with higher fatty acids. This value subtracted from the total hydroxyl content, determined by the acetic anhydride method, should have provided an indication of the quantity of phenolic hydroxyl groups present. It was indeed surprising to discover that both the aliphatic and the phenolic hydroxyl groups of the partially hydrogenated polymer were esterified by higher fatty acids with relative ease at 220-250°C.

To test the general applicability of this reaction, fatty acid esters of many monohydric and dihydric phenols were prepared by direct esterification. Since in this investigation the reaction was of greater interest than the actual products obtained, much of the work was carried out with commercially available fatty acids and mixtures thereof. The phenols used included: phenol, *p-tert*-butylphenol, *p*-chlorophenol, *p*-phenylphenol, *o*-phenylphenol, cardanol, β-naphthol, 2,2-bis-*p*-hydroxyphenylpropane, *p,p'*-dihydroxydiphenyl, and 2,5-di-*tert*-butyl hydroquinone. Among the fatty acids used were: stearic acid, lauric acid, caprylic acid, oleic acid, and soya bean oil fatty acids. The methods of preparation yields and properties are given in Table I.

The esterification was accelerated by catalysts such as sulfuric acid, phosphoric acid, zinc stearate, lead stearate, and triphenyl phosphite. Of these, sulfuric acid was the most effective although its use was limited to distillable products since it caused the reaction mixture to darken. Zinc and lead stearate were equal to each other in activity but exerted less catalytic effect than sulfuric acid.

The esters were prepared azeotropically, using xylene or benzene to remove the water of esterification. The reaction temperature was controlled by the quantity of xylene or benzene present in the reaction mixture as well as by the amount of heat applied externally. Reaction times varied from 6 to 117 hrs. whereas temperatures varied from 115-290°C. The volatile esters were fractionally distilled whereas the unreacted fatty acids were removed from the nonvolatile esters by heating the products at 250°C. below 0.1 mm. No attempt was made to obtain maximum yields.

Experimental

o-Phenylphenyl Stearate. A mixture of *o*-phenylphenol (85 g.), stearic acid (141 g.), xylene (110 cc.), and conc. sulfuric acid (2 g.) was heated at 173-8° with agitation for 22 hrs. The reaction vessel was equipped with a water-trap of the Dean-Stark type, which allows the removal of the water formed during esterification azeotropically. After six hours of reaction 90% of the theoretical quantity of water had collected. The theoretical amount of water was not obtained until the reaction mixture was heated for 22 hrs. The product was diluted with xylene, washed with water, and dried over anhydrous sodium sulfate. The solution was filtered and concentrated, and the residue was fractionally distilled through a 1-ft. Vigreux column. A fraction (14 g.) was collected, which distilled below 215°/0.05 mm. The main fraction, 177 g., b50μ 230°, was a low-melting solid. The yield was 81%. The product was recrystallized from Solax and acetone. Melting point 42-3°; % carbon found 82.86, 82.61 (th 82.57); % hydrogen found 10.18, 10.24 (th 10.55).

This is a general procedure. Preparations, yields, physical properties, and analyses of esters are given in Table I.

Acknowledgment

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Solubility of 1-Monostearin in Various Solvents[1]

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IN THE COURSE of research on acetostearins and other synthetic fats, large quantities of 1-monostearin were needed. These were prepared satisfactorily from technical grade products by fractional crystallization from solvents according to conditions described in earlier publications (4, 10). To prepare products of high purity however, repeated crystallization from solvents was necessary; and it became desirable to know more exactly the solubility of 1-monostearin in a number of common solvents. The solubility determinations which were made are described in the present paper.

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Materials

Monostearin. The 1-monostearin used in the solubility determinations was prepared as described by Singleton and Vicknair (10). Purified stearic acid and 36.2% of U.S.P. glycerol were reacted at 200°C. for 3 hrs., using 0.1% of sodium hydroxide as catalyst. The reaction product was acidified to destroy the soap and then washed repeatedly with hot water, followed by fractional crystallization from an isopropanol-water solution (70% isopropanol). Final purification consisted of repeated crystallization from commercial hexane.

Purity of the product was 99.2%, according to the periodic acid method of analysis (5), and the melting point was 81.8°C. by the capillary tube method, which

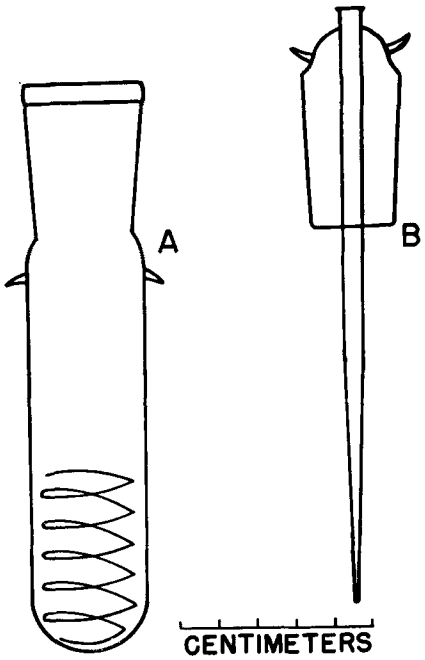

FIG. 1. Solubility cell.

agrees closely with the 81.5°C. reported by Lutton and Jackson (7) for pure 1-monostearin in the highest melting form.

Solvents. The solvents used in the solubility determinations were commercial hexane, acetone, purified by the method of Werner (12), absolute ethanol, absolute isopropyl alcohol, and absolute methanol. The four last-mentioned solvents were of C.P.-analyzed grade. Before use each of the solvents was dried over anhydrous sodium sulphate and then filtered.

Apparatus and Method

The solubility of the monostearin in the various solvents was determined by the synthetic method, in which the temperature of a known quantity of solvent and solute is slowly decreased until that temperature is reached at which crystallization of the solute begins. The technique used by the present investigators included certain details of procedure first described by Andrews and his coworkers (1).

Andrews *et al.* employed the synthetic method in studying the solubility of isomeric organic compounds but refined the usual mode of experimentation to attain higher accuracy. They placed the solution to be studied in a solubility cell containing a thermocouple and a stirring device. The solubility cell was in turn placed in a cooling bath, the temperature of which was decreased at a slow, constant rate. When crystallization began, which on occasion was initiated by seeding, stirring was stopped and the rise in temperature within the cell was noted. After several runs at different cooling rates the true equilibrium temperature at which crystallization commenced was determined graphically, either from a plot of heat loss *vs.* temperatures or a plot of the maximum temperatures reached after crystallization commenced *vs.* a specific portion of the area between the time-temperature curves for the bath and solution.

The solubility cell used in the present experiment was adapted from previously developed solubility apparatus (2) and is shown in Figure 1. The cell proper, *A*, was made of Pyrex glass and had sealed to it the outer part of a 24/40 standard taper joint. The inner part of this joint, *B*, which was used as a closure, had sealed to it a tapering, thin-walled thermocouple well. To insure an air-tight seal, the two parts of the joint were polished with jewelers' rouge before being used.

The contents of the solubility cell were stirred by means of a free-moving spiral of iron wire (B&S No. 18), tin-tipped to make it rust-proof, which is shown in place in *A*. The spiral was moved up and down by a magnetic field supplied by an electromagnet.

The temperature of the sample-solvent system was measured with a calibrated, single-element thermocouple constructed from B&S No. 40 copper wire and No. 30 constantan wire. The voltage of the thermocouple was measured with a White double potentiometer (range 100,000 microvolts) used in conjunction with a high-sensitivity galvanometer and a reflected scale and telescope arrangement. To convert microvolts to temperature the Southard and Andrews reference tables (11) were used up to 310°K. For higher temperatures these tables were extended, assuming that the rate at which voltage changed with temperature was the same as that given in the International Critical Tables. The apparatus is believed capable of detecting a temperature change of 0.001°C. or the presence of 0.01 to 0.02% of crystals in the solution.

A typical equilibrium point determination was made as follows. Weighed portions of sample and solvent were placed in the solubility cell, which was then tightly capped. The assembled apparatus was clamped in a controlled-temperature bath in such a manner that the solvent level was well below the liquid level of the bath, and the electromagnet was then set in place. Stirring was begun, and the bath temperature was raised until the sample was completely in solution. The bath temperature was then allowed to drop at a constant, known rate (0.1° to 0.3°C./min.) as measured by a second thermocouple. The temperatures of both the solution and the bath were recorded at 1-min. intervals. At the point of solute crystallization the temperature of the sample rose sufficiently to mark the uncorrected limit of complete solubility of the sample in the particular solvent used. Time-temperature curves were plotted for both the sample and the bath, which were cooled at several different rates. For each cooling rate the area under the curve for the sample and above the curve for the bath was determined for the time-interval during which the temperature of the solution first dropped below and then regained the maximum temperature recorded during crystallization. This area then was plotted against the highest temperature the solution attained during crystallization. Extrapolation to zero area gave the temperature at which the sample would have crystallized had there been no supercooling or heat exchange with the bath. This temperature was the corrected equilibrium point for the particular solute to solvent ratio used. Several such determinations with different solute to solvent ratios yielded the necessary equilibrium-point temperatures to define the solubility curve of the sample in a particular solvent.

Results and Discussion

As a check on the reliability of the present method the solubility of purified stearic acid in acetone was determined and compared with the published data of

Ralston and Hoerr (8). As shown in Figure 2, there is very close agreement between the two sets of solubility values.

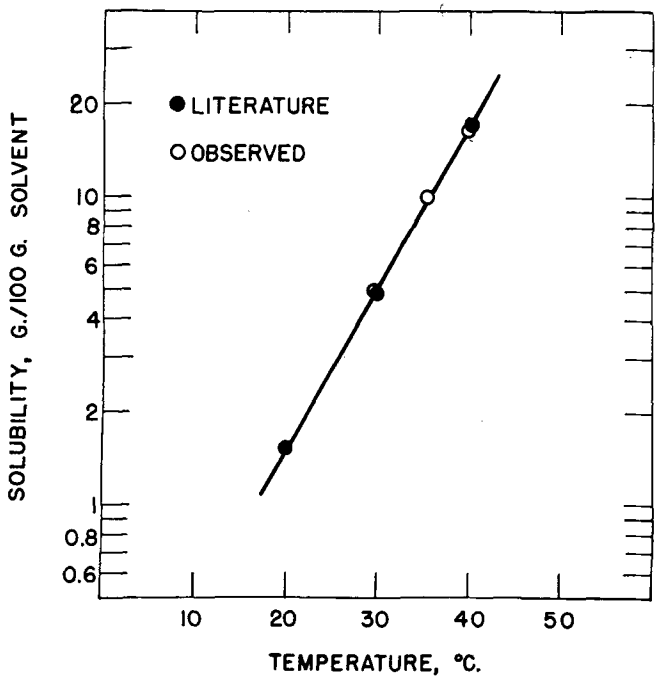

FIG. 2. Solubility of stearic acid in acetone as determined by the present method and compared with published results.

The equilibrium point temperatures of monostearin in each of the five solvents at various solvent ratios, as determined experimentally, are shown in Table I. These data were recalculated to express the solubility of monostearin in terms of mole fractions, and plotted on semilogarithmic coordinates as functions of the reciprocal of the absolute temperature, as shown in Figure 3.

Curve 2 of Figure 3 illustrates the three points of the general solubility curve. The shape of this curve can be explained as follows. At low concentrations

TABLE I

Solubility of Monostearin in Various Solvents

Solvent	Temperature, °C.	Solubillity, g./100 g. solvent
Acetone	8.83	0.482
	17.20	0.990
	24.08	1.957
	31.33	4.070
	41.19	9.883
Isopropyl alcohol	11.40	1.002
	18.23	1.973
	22.99	3.215
	27.25	4.953
	34.94	9.999
	43.30	24.779
	47.22	40.009
	49.01	50.000
Methyl alcohol	19.65	0.999
	25.46	2.002
	34.23	4.960
	39.49	9.809
	44.82	25.000
Ethyl alcohol	29.35	5.000
	36.72	9.960
	45.339	19.802
	45.66	29.965
	49.31	49.770
Hexane	44.28	0.227
	53.19	0.783

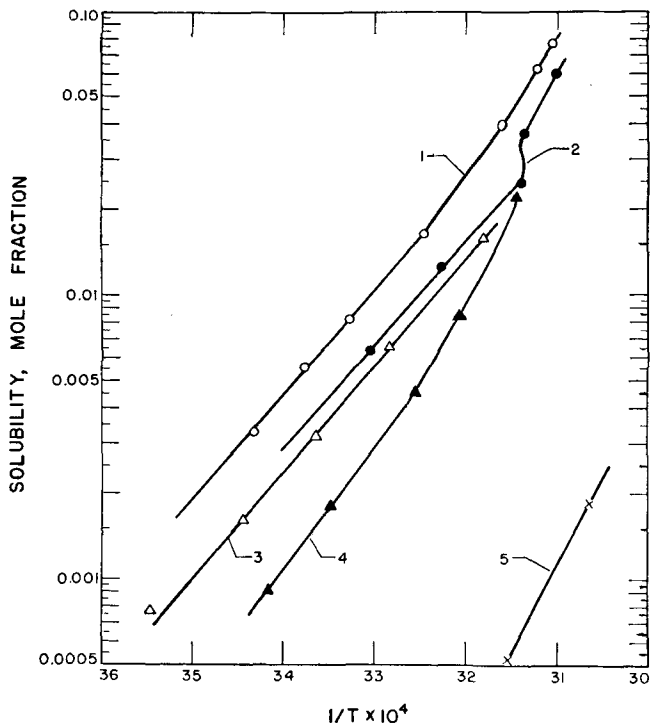

FIG. 3. The solubility of monostearin in 1) isopropyl alcohol; 2)ethanol; 3) acetone; 4) methanol; and 5) hexane.

the solute particles are widely separated, and their escaping tendency is influenced mostly by the solvent molecules. As the concentration of the solute molecules increases, their escaping tendency is influenced more and more by attraction for each other. At the sigmoid portion of the curve the ruling attraction changes from solute-solvent to solute-solute. At higher concentrations the escaping tendency is influenced mostly by the concentration of solute molecules and the curve comes closer to that for ideal solubility. Curves 1 and 4 show two sections of the general curve while curves 3 and 5 show but one.

A comparison of the solubility of monostearin in the various solvents at a given temperature and below 0.01 mole fraction of monostearin (Figure 3) shows that on a mole fraction basis the solubility is greatest in isopropyl alcohol and decreases in the order ethanol, acetone, methanol, and hexane. Since there is no great difference in the molecular weights of these solvents, this same order prevails when the solubility of monostearin is expressed as grams of material dissolved per unit weight of solvent.

1-Monostearin apparently forms dilute solutions in isopropanol, ethanol, and methanol with solubilities lower than ideal. The actual amount of 1-monostearin soluble closely parallels that of stearic acid, which has a solubility also lower than ideal. The order of the solubility of 1-monostearin in each of the various solvents tested is the same as that of stearic acid.

The solubility of 1-monostearin in the alcohols increases, with an increase in the similarity of the molecular structure of the alcohol to that of 1-monostearin, *i.e.*, the solubility appears to increase with the increasing chain length of the alcohol.

1-Monostearin is a polar compound and shows greater solubility in polar than in non-polar solvents. There is no direct relationship between the magni-

tude of the dipole moment of the solvent and the solubility of 1-monostearin in it.

Available data on the solubility of tristearin (6), which is non-polar, show that it is relatively insoluble in the alcohols, which are polar. Because the reverse is true for 1-monostearin, this difference in solubility can be used to advantage in the fractional crystallization of the monoglycerides from the triglycerides concomitantly formed in the normal preparation of monoglycerides. Daubert and King (3) found this same relationship with mono- and tripalmitin in the alcohols.

Summary

The practical limits of the solubility of pure monostearin in various solvents at different temperatures has been determined for isopropyl alcohol, ethanol, acetone, methanol, and commercial hexane. The synthetic method was employed, in which the temperature of known quantities of solvent and solute was decreased until crystallization of the solute began. This temperature, corrected for supercooling and heat loss to the surrounding bath, was taken as the equilibrium temperature between the known weight of solute and the known weight of solvent.

The solubility-temperature data of monostearin in each of the various solvents are presented both graphically and in tabular form.

A comparison of the solubility of monostearin in the various solvents at comparative temperatures indicates that its solubility is greatest in isopropyl alcohol and decreases in the order ethanol, acetone, methanol, and hexane.

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Tocopherol Retention in Oils Aerated in Glass and Iron Tubes

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VEGETABLE SEED FATS normally contain a natural "built-in" phenolic type of antioxidant. This is not true of animal fats. Hence the two types of fat require different protective supplementation. Vegetable seed fats with their normal content of tocopherols seldom require added phenolic type of antioxidants but do require a) getting the most use possible out of the tocopherols present and b) protection against metals which act as pro-oxidant catalysts.

In a preceding paper (1) a modification of the conventional A.O.M. test for evaluating the keeping qualities of fats and oils was presented. This method involves the substitution of an iron tube for the glass tube normally used in the A.O.M. test. The greater susceptibility of oils to oxidative deterioration in iron tubes was found to be due not to the pro-oxidant effects of dissolved iron but primarily to contact metal catalysis. Isopropyl citrate esters, predominantly monoisopropyl citrate, minimize the deleterious effects due to both dissolved iron and contact metal catalysis.

In reporting the results previously obtained, it was postulated that a) the tocopherols (very weak acids) in the oils are either adsorbed by the metal wall and rendered ineffective or are destroyed during the period of aeration, and b) the competition for metal between tocopherols and the monoisopropyl citrate (a very much stronger acid) is in favor of the latter. Regardless of which mechanism is involved, the tocopherols were expected to remain in the oil as effective antioxidants for longer periods of time when monoisopropyl citrate is also present. That acid synergists inhibit tocopherol destruction has been reported (2-4).

In the present study the fate of the tocopherols in the aerated oils was investigated. The experimental design called for tests conducted on the oils aerated in both glass and iron tubes and in the absence and in the presence of added monoisopropyl citrate. In addition, the influence on tocopherol retention of iron in solution, as the only source of the pro-oxidant catalyst, was evaluated.

Experimental

The aeration methods of test have been described in the previous publication (1). Tocopherol analyses were conducted according to the Rawlings' (5, 6) modification of the Emmerie-Engel (7) colorimetric method. In order to liberate tocopherols, possibly adsorbed to the walls of the iron tubes, the tubes were drained of the test oil and then filled to the same 20-ml. volume with coconut oil containing 0.08% of isopropyl citrate esters, predominantly monoisopropyl citrate. The oils were heated to 98°C. in the tubes and then tested for increased tocopherol content on the assumption that the presence of the more acid monocitrate would displace adsorbed tocopherols. The tocopherol analyses of the test oils were conducted serially on each oil as it was progressively oxidized during the period of aeration. The tocopherol analyses on the coconut oil with added monoisopropyl citrate were conducted on the wash-outs of different tubes, following specific periods of aeration.