palladium catalyst. The product obtained had an iodine value of 4, a hydroxy value of 145, and acid value of 1.8, and a capillary melting point of 86°.

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# Preparation of Pure Palmitic Acid and a By-Product Plasticizer from Cottonseed Oil[1]

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IN THE COURSE of investigating methods for fatty acid purification it was observed that very pure fatty acids could be obtained by recrystallization of their amine salts from organic solvents. The cyclohexylamine salts of the higher fatty acids were found to be particularly amenable to this procedure because of their excellent filtration characteristics and high temperature coefficients of solubility. While this method had never been applied to such a complex mixture as the cottonseed acids, where the acid to be recovered was not in the predominant concentration, it nevertheless appeared promising because of the unique composition of the cottonseed acids. Although palmitic acid accounts for only about 22–24% of the total acids, the major constituents of which are linoleic and oleic acids, it is the dominant saturated acid in a ratio of at least 10 to 1.

Application of the amine salt method to the cottonseed acids proved to be very effective when cyclohexylamine was the amine used. From the point of view of the by-products formed however, it was found advantageous to use a mixture of cyclohexylamine and morpholine. The residual unsaturated fatty acids can thus be recovered as the morpholine salts, which can be converted to useful morpholide plasticizers (2).

## Experimental and Results

*Materials and General Procedure.* The cottonseed acids were obtained by saponification and subsequent acidulation of a refined and bleached cottonseed oil with an iodine value of 108.8 and a thiocyanogen value of 69.9. The hydrogenated cottonseed acids were similarly derived from the same oil after selective hydrogenation to an iodine value of 63.1 and a thiocyanogen value of 62.9. The cyclohexylamine and morpholine were White Label Eastman Kodak products. Drum C. P. acetone was employed as the solvent.

In general, one part by weight of cottonseed acids was dissolved in about four parts by weight of acetone containing a slight excess (0.5%) of the amine as calculated from the neutralization equivalent of the acids. The heat of solution was usually sufficient to cause complete solution, but in some instances it was necessary to warm to 40–45°C. The crude amine salt of palmitic acid was separated on a Buchner funnel at the crystallization temperature and washed *in situ* with a small volume of cold solvent. The moist filter cake was then redissolved in acetone and subjected to a number of recrystallizations in a centrifugal filtration tube (4). There were no intervening crystal washings in these operations. All concentrations were reported in terms of the dry amine salt, taking into account the residual solvent in the filter or centrifuge cake, as determined on an aliquot. The acid was regenerated from the amine salt by exhaustive extraction with warm hydrochloric acid solution by a modified Soxhlet-type liquid-liquid extraction. Unless otherwise mentioned, all freezing points were determined by the sealed tube thermostatic method (3).

*Cyclohexylamine Method.* A 100-g. portion of the cottonseed acids and 35.8 g. of cyclohexylamine were dissolved in 500 ml. of acetone. Crystallization and filtration of the crude cyclohexylamine salt of palmitic acid from this solution were carried out at room temperature (about 27°C.). An aliquot of the filter cake was taken from this and subsequent recrystallizations for iodine value and freezing point determinations on the regenerated acid in order to follow the improvement in purity. The regenerated acid at this point had an I.V. of 42 and a f.p. of 51.8°C. The remainder of the moist filter cake, consisting of 47 g. of the dry amine salt and 66 g. of residual solvent, was dissolved in 34 g. of additional acetone and recrystallized at room temperature in a centrifugal filtration tube. The regenerated acid now had an I.V. of 10.2 and a f.p. of 59.6°C. The centrifuged cake, amounting to 25.6 g. (dry basis), was redissolved in 95 g. of acetone, allowed to crystallize at room temperature, and centrifuged. Analysis of the filter cake then indicated an I.V. and f.p. for the regenerated acid of 1.2 and 62.3°C., respectively. The last recrystallization was carried out from 48 g. of acetone (7.6 g. of cake, dry basis) and the mother

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liquor again removed by centrifugation. The final product, amounting to 5.6 g. (dry basis), gave a regenerated palmitic acid having a neutralization value of 256.2 (theory 256.4), an I. V. of 0.2, and f.p. of 62.5°C. As previously explained (1), this can be identified by f.p. comparisons with palmitic acid of established purity as a very pure palmitic acid and represents an over-all recovery, allowing for the aliquots removed, of 45% of the palmitic acid content in the original mixed acids.

The mother liquor from the primary crystallization consists essentially of the amine salts of linoleic and oleic acids in a ratio of about 2 to 1. Since this amine salt mixture is a by-product constituting about 75% of the original cottonseed acids, it would be desirable to use an amine the salts of which have a known utility.

*Morpholine Method.* It has already been reported (2) that the morpholine salts made from an oleic acid which contains only limited amounts of saturated and polyunsaturated acids can readily be converted to the morpholide, a good primary plasticizer for vinyl resins. It was also found that the morpholide formed from the unsaturated fraction of cottonseed acids had equally good plasticizing characteristics if the polyunsaturation was reduced either by partial epoxidation of the morpholides or by selective hydrogenation of the original cottonseed oil. This suggests the use of morpholine instead of cyclohexylamine in the preparation of pure palmitic acid since the unsaturated acids would then be recovered as the morpholine salts.

Cottonseed acids, morpholine, and acetone were mixed in the same stoichiometric proportions as in the cyclohexylamine method. Crystallization and filtration were carried out at 3°C. The three subsequent recrystallizations, involving centrifugal filtration, were also conducted at 3°C. at concentrations employing 0.9, 1.3, and 1.2 g. of dry solids, respectively, per gram of acetone. The final regenerated palmitic acid still contained considerable impurity as shown by its iodine value, 3.2, and its freezing point 60.2°C. Thus, though the morpholine method results in a more valuable by-product than does the cyclohexylamine method, it is relatively ineffective for isolating pure palmitic acid, probably because of the unfavorable crystalline and filtration characteristics of its salts.

*Mixed Amine Method.* The solid-liquid phase diagram for the ternary reciprocal salt system, involving the cyclohexylamine and morpholine salts of stearic and palmitic acids (5), indicated that it should be possible, by using an appropriate mixture of cyclohexylamine and morpholine, to isolate the cyclohexylamine salts of the saturated acids from cottonseed acids by solvent crystallization and to recover the unsaturated fatty acid fraction as morpholine salts in the mother liquor.

Using the same proportions as before, an acetone solution was made of the cottonseed acids and an amine mixture containing an amount of cyclohexylamine and morpholine in equivalence to the saturated and unsaturated acids, respectively. The first crystallization was conducted at 3°C. The crude cyclohexylamine salt of palmitic acid was recrystallized twice, using the same procedure as described for the cyclohexylamine method. The purity of the regenerated palmitic acid (I.V., 0.2; f.p., 62.3°C.) is comparable to that obtained by the cyclohexylamine method after the same number of recrystallizations. The mother liquor consisting essentially of morpholine salts of the unsaturated fatty acids can be converted directly to morpholides and epoxidized to yield a primary plasticizer for vinyl resins (2).

The mixed amine method was also applied to the hydrogenated cottonseed acids to see if this alternative method of obtaining a more profitable by-product would interfere with the isolation of a pure palmitic acid. The fatty acids obtained from the selectively hydrogenated cottonseed oil were treated with the mixed amines in the same proportions and under the same conditions as described above. The regenerated palmitic acid even after five crystallizations was still far from pure. It had a low freezing point, 58.7°C., and a high iodine value, 8.2, indicating the presence of considerable unsaturated contaminants. The *cis* and *trans* isooleic acids, resulting from isomerization during hydrogenation, evidently interfered with the isolation of the palmitic acid by this method.

The morpholine salts of the unsaturated fatty acids in the first mother liquor were converted to the morpholides as before, omitting the epoxidation step. This morpholide mixture proved to be an efficient primary plasticizer for vinyl resins with better low-temperature characteristics than the epoxidized morpholides obtained from the unhydrogenated cottonseed oil.

Table I shows the properties of the palmitic acid samples obtained by the different methods. Sample 5 was the product obtained from the hydrogenated cottonseed acids, using morpholine only. Sample 6 resulted from repeated recrystallization of the unhydrogenated cottonseed acids from acetone.

TABLE I

Iodine Value (Wijs) and Freezing Point of Palmitic Acid Recovered from Cottonseed Acids by Various Methods

| Sample | Cottonseed acids | Amine[a] | Times crystallized | Recovered palmitic acid | |
|---|---|---|---|---|---|
| | | | | I.V. | f.p., °C. |
| 1 | Original | C | 4 | 0.2 | 62.5 |
| 2 | Original | M | 4 | 3.2 | 60.2 |
| 3 | Original | C + M | 3 | 0.2 | 62.3 |
| 4 | Hydrogenated | C + M | 5 | 8.2 | 58.7 |
| 5 | Hydrogenated | M | 5 | 22.2 | 51.4 |
| 6 | Original | None | 4 | 4.0 | 60.3 |

[a] C = cyclohexylamine; M = morpholine.

It is apparent that the cyclohexylamine and mixed amine methods are equally effective in producing a palmitic acid of high purity from cottonseed acids and that they are superior to either the morpholine method or direct acetone recrystallization. In addition, the mixed amine method has the advantage of yielding a by-product which can be converted to a good plasticizer. While none of the methods are adequate when applied to the fatty acids from selectively hydrogenated cottonseed oil, the best results are still obtained by the mixed amine method.

It can be concluded that the complete process would be applicable to fatty acids from any natural glyceridic oil, such as palm oil, in which palmitic acid constitutes a very large proportion of the saturated acids. For fatty acid mixtures obtained from other glyceridic oils the process can still be used to separate the saturated from the unsaturated acids.

## Summary

A laboratory process has been developed which permits the isolation of a highly purified palmitic acid from cottonseed acids through the recrystallization of its cyclohexylamine salt from acetone and subsequent regeneration of the acid. The by-product, predominantly cyclohexylamine salts of the unsaturated fatty acids, can be modified and converted to morpholides which have shown promise as vinyl plasticizers. The morpholine salts can be obtained as a direct by-product by the use of an appropriate mixture of cyclohexylamine and morpholine with the composite acid. By using an amount of cyclohexylamine closely equivalent to the saturated fatty acid content and sufficient morpholine to make up the residual neutralization equivalent of the composite cottonseed acids, the saturated acids can be isolated as cyclohexylamine salts. The stripped mother liquor will consist essentially of the morpholine salts of the unsaturated acids. Pure palmitic acid is obtained by recrystallization of the cyclohexylamine salts. The complete process is applicable to fatty acids from other natural glyceridic oils in which the dominant saturated acid bears a ratio to the other saturated acids closely paralleling that in cottonseed oil. The process is not operable with partially hydrogenated oils.

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# Vapor Pressure Equilibrium of Stearic Acid in Triglyceride and in High Paraffin Solutions

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NO VAPOR PRESSURE DATA on solutions of fatty acids are available which would indicate their behavior with respect to Raoult's law. In the literature it is therefore frequently assumed that solutions and mixtures of fatty acids, at least at higher temperatures, are ideal solutions (1, 2). On the other hand, numerous works give evidence of the molecular association of fatty acids in the vapor phase and in solution (3). Recently the degree of association of fatty acids has been determined in the pure state and in high-paraffin solutions at various temperatures by an infrared spectrometric method (4). In view of the association, deviation from ideality may be predicted.

In the present investigation the vapor-pressure equilibrium of stearic acid has been measured at 180°C. in peanut oil and high-paraffin solutions. It has been found that both systems show a positive deviation from Raoult's law. Quantitative relationship could be established between the degree of association of stearic acid and its partial vapor pressure. Evidence of association between triglycerides and fatty acids has been obtained.

## Experimental

*Vapor Pressure Equilibrium of Stearic Acid in Peanut Oil Solutions.* The isothermic deodorizer, which has been described in a previous article (5) and, at moderate rates of flow of steam, has a vaporization efficiency of 1, has been found to be eminently suitable for the measurement of vapor pressures within the desired range of 1 micron to 10 mm. Hg. This deodorizer is essentially an entrainment-distillation apparatus, in which, for the present purposes, water vapor and iso-octane vapor were used as carrier gases. Since the vapor pressure of mercury is known exactly throughout a wide temperature range, it was used to test the apparatus.

The substances distilled over were determined; stearic acid, titrimetrically; mercury, gravimetrically. The pressure was maintained between 100 and 300 mm. by means of a manostat; lower pressures were avoided to prevent evaporation during the heating and cooling periods.

The vapor pressure values found for mercury at 180°C. are recorded in Table I. Their agreement with the literature values of 8.76 (6) and 8.79 (7) is satisfactory as the difference between the mean values is less than 1%. The method of measurement may thus be considered as suitable.

TABLE I
Vapor Pressure Determinations of Mercury at 180°C.

| | | | | |
|---|---|---|---|---|
| Steam flow rate........ | 1/h. | 93 | 93 | 31 |
| Vapor pressure........ | mm. Hg. | 8.76 | 8.73 | 8.65 mean: 8.71 mm. |

The vapor pressure of the stearic acid (m.p. 69.9° C.) was determined with steam and also with iso-octane (2,2,4-trimethylpentane) as carrier gas as the latter is indifferent to triglycerides (see later measurements from the point of view of hydrolysis). Practically no difference was found between the two series of measurements, as may be seen from Table II.

The mean value of 0.796 mm. is in good agreement with the recent value of 0.80 mm. found by Pool and Ralston (8). This agreement has more importance because the latter value was obtained from boiling point measurements. Consequently it indicates that stearic acid vapors are not associated at 180°C. in the vapor phase. This conclusion however may not be extended to low fatty acids, which at this temperature have substantially higher vapor pressures and are therefore associated, as pointed out by Jantzen (9).

The vapor pressure of stearic acid in stearic acid/peanut oil solutions was determined under the same conditions as used in the above experiments, with iso-octane vapor as carrier gas. For the calculation the following equation, based upon Raoult's law (10), was used:

$$P'_v = P\frac{(M_o - M) + A \ln (M_o/M)}{(M_o - M) + S}$$