has a lower order dependence on hydrogen than hydrogenation. The greater the hydrogen depletion at the catalyst surface, the more isomerization will be favored relative to hydrogenation. Excessive *trans* formation with very active catalysts can be overcome therefore by adequate agitation.

Agitation must be increased with increasing concentration of metal in oil if the *trans* content is to be held constant. Increasing the catalyst concentration merely divides the available hydrogen so that the concentration at the surface of the catalyst is less and *trans* formation is consequently favored.

By proper choice of conditions a shortening stock of good stability and plastic properties may be obtained from hydrogenation with palladium catalysts. The dilation figures obtained for the products from Experiments 4, 7, 10, and 11 show these all to have good plastic properties. These products were obtained with mild operating conditions that would be commercially attractive. The amount of catalysts used in most laboratory experiments was very small so it was difficult to recover them quantitatively and examine their behavior on repeated re-use.

In pilot plant experiments, undertaken to demonstrate that palladium could be used successfully with larger amounts of oil, the amount of catalyst used was larger, allowing it to be recovered and re-used. The results of this work will be reported later, but it may be said now that the products of the laboratory could be duplicated with amounts of catalyst that would be economically attractive.

Summary

Palladium-on-carbon catalysts are exceedingly active for the hydrogenation of natural unsaturated oils when very mild conditions are used. Selectivity is usually good, and *trans* content can be adequately controlled by the proper choice of conditions. In the range of operating variables used in this work, *trans* formation is lessened with increased agitation and pressure, decreased catalyst activity, decreased concentration of metal in oil and on carrier, and with decreased temperature. Some shortening stocks were obtained which have good physical properties, as expressed by their dilatometric curves.

Acknowledgment

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Isolation of an Hydroxy Acid Concentrate from Wool Wax Acids[1]

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THE PRESENCE of hydroxy acids in the saponifiable fraction of wool wax has been reported by a number of investigators (1, 5, 6, 7, 8, 9, 10, 13). Kuwata (8) used a combination of extraction and distillation to isolate 2-hydroxyhexadecanoic acid. Weitkamp (13) obtained the same acid and 2-hydroxytetradecanoic acid by an amplified distillation of their methyl esters. Horn and coworkers (6, 10), using a countercurrent distribution technique, obtained a 2-hydroxy acid fraction consisting of 27% of the total saponifiable fraction. The latter authors isolated 2-hydroxydodecanoic, 2-hydroxyoctadecanoic, and 2-hydroxy-16-methyl heptadecanoic as well as those acids previously reported.

Other positional isomers of the 2-hydroxy acids that have been isolated are 30-hydroxytriacontanoic acid and 32-hydroxydotriacontanoic acid (7).

In order to study the chemical and physical properties of the hydroxy and unhydroxylated acids, particu-

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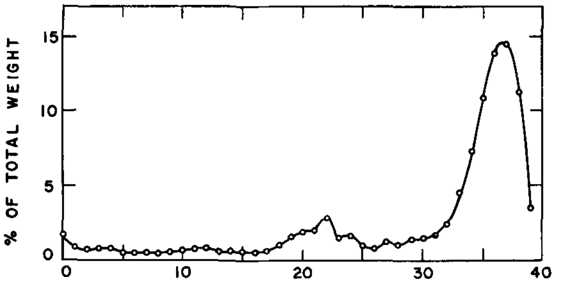

FIG. 1. Distribution of methyl esters in a Craig apparatus, using the 45% ethanol-45% methanol-10% water-heptane system.

larly as their heavy metal soaps, a larger quantity of acids was required than that obtained by the techniques used in earlier work. The present paper describes a method for obtaining an hydroxy acid concentrate on a large scale. Also included are additional studies on the countercurrent solvent distribution of both the wool wax acids and their methyl esters.

Preparation of Wool Wax Acids. USP lanolin was saponified according to the procedure of Barnes, Curtis, and Hatt (2), and the unsaponifiable material was removed by repeated extraction with commercial heptane. The wool wax acids were liberated by hot acidification of the sodium soap solution with sulfuric acid. The acids obtained in this manner had an appreciable ester number, presumably on account of such compounds as estolides, lactides, and lactones. The tendency for wool wax acids to esterify in this manner is so great that acid numbers decreased with increasing storage-time even at room temperature in the solid state. A corresponding increase in the ester number was also noted. The change in ester number was studied by periodically analyzing samples stored at room temperature. Over a seven-month period the ester number of one sample increased from 7.5 to 23.9. A control stored at 0°C. showed no change in ester number.

In order to reduce the ester number, the acids were resaponified with 100% excess potassium hydroxide, and the resulting soap solution was added slowly to a stirred ice-water mixture containing hydrochloric acid no more than 5% in excess over that required for neutralization of the potassium hydroxide. By using a minimum amount of mineral acid and a low temperature, the tendency of wool wax acids to undergo esterification is effectively inhibited. The acids obtained by this procedure analyzed as follows: acid number, 160.4; saponification number, 163.6; ester number, 3.2; percentage of hydroxyl 2.48.

Fractionation of Wool Wax Acids. An attempt was made to fractionate wool wax acids between aqueous alcohol mixtures and commercial heptane (3). In one experiment 90% aqueous ethanol was used as the lower phase, in another an aqueous alcohol mixture 45% ethanol–45% methanol–10% water). In both experiments the hydroxyl content of the residual material remaining in the heptane layers was greater than the hydroxyl content of the material removed in the alcohol layers. Since the hydroxy acids were not concentrated in the more polar alcohol layers to any appreciable extent, it appeared that partition of wool wax acids between these two immiscible solvents was not a feasible fractionation scheme.

Countercurrent Distribution of Methyl Esters of Wool Wax Acids in a Craig Apparatus. Methyl esters of wool wax acids (acid number, 1; saponification number, 159.9; percentage of hydroxyl, 2.2) were partitioned in a 40-Tube Craig countercurrent distribution apparatus in order to determine partition coefficients for the hydroxy and unhydroxylated esters. Each tube of the apparatus accommodated 40 ml. of solvents (20 ml. of each layer). The solvent layers chosen were commercial heptane and the mixture of methanol-ethanol-water previously mentioned. At the completion of the distribution the entire contents of each tube was poured into a tared beaker and the solvents were evaporated. The curve shown in Figure 1 was obtained by plotting tube number against the total amount of solute contained in each tube expressed as a percentage of the total weight of solute recovered. In this curve the position of the peaks are reversed, compared to the other figures, since the heptane layer rather than the alcohol layer is the mobile layer in the Craig apparatus. The unhydroxylated ester peak lies to the right of Figure 1 while the hydroxy ester peak lies to the left. Partition coefficients may be derived from the experimental curve by the following trial-and-error process. Using the application of the binomial theorem to countercurrent distribution (4, 14), an assumed value for the partition coefficient is used to calculate the amount of solute in the tubes corresponding to the peak in question. If the calculated curve does not fit, then the process is repeated until a fit with the experimental curve is obtained. No exact values for partition coefficients could be obtained in the present instance since none of the calculated curves could be fitted to the experimental curve. However useful information could be obtained from inspection of the experimental curve. The unhydroxylated ester peak is skewed away from the hydroxy ester peak. In a separation in which the lower layer is moved (the Craig apparatus moves the upper layer), substantially all of the unhydroxylated material will remain in the apparatus while the hydroxy material is removed by a single withdrawal technique of lower layers. Increasing the concentration should skew the unhydroxylated ester peak further and help keep the bulk of this material in a few tubes or bottles (12).

Large-Scale Partitions of Methyl Esters. Thirty grams of the methyl esters were split into three equal portions. Each portion was dissolved in 100 ml. of equilibrated heptane and added to a separatory funnel. Three additional separatory funnels, each containing 100 ml. of the heptane layer, completed the extraction train. The heptane solution in each funnel, starting

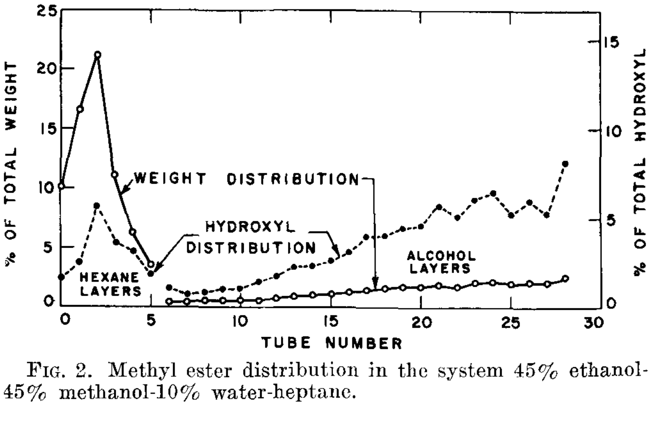

FIG. 2. Methyl ester distribution in the system 45% ethanol-45% methanol-10% water-heptane.

with the first and continuing through the extraction train in order, was extracted with 100-ml. portions of the alcohol layer (45% ethanol-45% methanol-10% water). Twenty-three extracts were withdrawn from the extraction train. The results are shown graphically in Figure 2; the last fraction withdrawn is plotted next to the last fraction remaining in the apparatus (11). The combined withdrawn fractions, having a percentage of hydroxyl of 5.07, constituted 31.3% of the charge. The combined residual fractions, having a percentage hydroxyl of 0.46, constituted 68.7% of the charge.

These results clearly indicate the superiority of methyl esters over free fatty acids in these partitions since a higher average percentage of hydroxyl is obtained for the withdrawn fractions and a lower average percentage of hydroxyl is obtained for the fractions remaining in the apparatus.

For production work a much larger quantity of methyl esters (354 g.) was fractionated by using 1-gal. Pyrex bottles and 1200-ml. portions of both layers. As in the previous case, the charge was divided into three equal portions in the first three bottles. However seven bottles rather than three completed the extraction train. Thirty extracts were withdrawn from the train. Fractions 10 to 34 of the withdrawn material, amounting to 84 g., were combined. The percentage of hydroxyl of the combined fractions was 5.5; the saponification number was 163.0; the acid number was 0.7. Fractions 35 to 38 of the withdrawn material, amounting to 18.2 g., were hard, transparent, and highly colored. They were not combined with the hydroxy esters. The residual material amounted to 240.4 g. with an hydroxyl content of 0.9%.

Summary

The fractionation of the methyl esters of wool wax acids by partitioning between two immiscible solvent layers has been described. Three fractions were obtained: a fraction rich in hydroxyl content, a fraction low in hydroxyl content, and a small amount of hard, transparent, highly colored material. The same procedure when applied to the free wool wax acids did not yield a satisfactory hydroxy acid concentrate.

The preparation of wool wax acids with an essentially zero ester number, that is, in a form free of estolides, lactides, and lactones has also been described.

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The Isomerization of Fats During Hydrogenation and the Metabolism of the Component Fatty Acids[1]

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IT HAS LONG BEEN KNOWN that catalytic hydrogenation of an unsaturated fat produces isomeric unsaturated fats. As early as 1919 Moore (1) isolated solid unsaturated fatty acids from hydrogenated ethyl oleate, and in 1929 Hilditch and Vidyarthi (2) showed that these isomers had resulted from both geometrical and positional isomerization. It is however only in the past few years that improved methods have given impetus to research on the mechanisms involved in the isomerization caused by hydrogenation of oils. Furthermore, since the nutritional effects of fatty acid isomers have been questioned (3), a number of studies on this subject have appeared in the recent literature.

The extent of both geometrical and positional isomerization during hydrogenations has been shown by studies on purified fatty acids and their esters. Boelhouwer *et al.* (4) demonstrated the extensive migration of double bonds which took place during the catalytic hydrogenation of methyl oleate. Their data indicated a preference for a shift of the double bonds away from the carboxyl group. However Allen and Kiess (5) showed the migration of the double bonds to be equal in either direction, and their results were later confirmed by Knegtel *et al.* (6).

The hydrogenation and isomerization of linoleic acid are perhaps more important to commercial operations since the hydrogenation of vegetable oils to form shortening or margarine stocks results in the saturation of the linoleic acid to a mono-ene without extensive reduction of the oleate.

The methylene-interrupted diene system in linoleic acid complicates the study of the positional isomerism since either of the two double bonds may be saturated with hydrogen in addition to their migration along the chain. Allen and Kiess (7) found the migration to be confined to one pentadiene system in contrast to the report by Cousins *et al.* (8), who found double bonds in all positions from 6 through 14. Chahine *et al.* (9) studied the effect of operating conditions on the hydrogenation of cottonseed oil; these workers also found a wide distribution of the remaining double bonds. Cousins *et al.* (8) showed that, after partial hydrogenation of methyl linoleate, the greatest con-

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