The Role of Solidification Points in the Identification and Determination of Saturated Fatty Acids[1]

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If the several theories which have been proposed in explanation of the biogenesis of the saturated fatty acids are sound, one should expect to find no gaps in this homologous series when it comprises one of the two major fractions of an oil. No extensive search of the literature on the composition of the fatty oils is necessary, however, in order to uncover instances, particularly with respect to acids above C_{18}, in which the conclusions of the investigator do not fit into such a picture in that a broken series of saturated acids has been reported. For this reason there exists a need for an analytical tool which, when used in conjunction with the newer techniques and improved apparatus of the present day, will serve not only qualitatively in the characterization of acids, but also quantitatively in their determination. Because binary mixtures of highly purified fatty acids have a constant temperature of solidification—it is easily reproducible within 0.05° C. for any composition—the solidification point forms the basis for such a procedure. The practical application of this technique to analytical problems requires a series of curves showing the relationship between solidification temperature and mol-percentage composition of neighboring pairs of acids. The series for the acids C_8 to C_{26}, inclusive, has been completed (1). It has been published, in part (2), together with other pertinent information.

For the reason above stated, plus a desire to eliminate certain assumptions, and with them the attendant errors with which the analyst in the fatty oil field must contend, the technique in question has been developed in this laboratory.

Fractional distillation of their methyl esters is deemed to be the most efficient method for separating the constituents of the solid acid fraction of a fatty oil. Residual unsaturated acids—the separation of the saturated from the unsaturated acids is never quantitative in the sense of a zero iodine number—are retained in the distillation flask by taking advantage of the fact that their brominated esters are relatively non-volatile. Complete separation of the saturated acids from the unsaturated, and their segregation into a number of fractions, can then be effected if distillation is carried out at reduced pressures, preferably below 2 mm. Hg.

The skill of the operator and the equipment used for fractional distillation will determine the efficiency of this separation of a saturated acid from its nearest homologue. In most instances the mean molecular weight, as derived from the saponification equivalent, has been used as a basis for calculating the composition of the individual fraction. In doing so, two assumptions were made, viz., each fraction contains only that pair of fatty acids which is nearest in molecular weight to the mean molecular weight of the fraction itself, and the mean molecular weight so obtained is, indeed, the correct one. The first assumption is valid if the fractionating column in question is manipulated by an experienced operator, and then only in those instances where an almost ideal fractionation has been obtained, for even if fractions are cut at the point of change from one composition to another, one is never certain that they do not contain three neighboring fatty acid esters. Hence, a calculation which is based only on mean molecular weight is erroneous. As for the second assumption, a simple calculation involving, for example, palmitic and stearic acids will show that an increase of one unit in mean molecular weight is equivalent to a decrease of approximately four per cent of the former. It is apparent, therefore, that an accuracy of ±0.5 unit in mean molecular weight is essential for arriving at a calculated composition which, even at best, will be somewhat in error.

It has been found that the composition of a known mixture of two acids can be determined with an accuracy of 0.5 per cent by simply reading off from the pertinent curve the values indicated by the solidification point experimentally determined. In those cases where the shape of the curve, because of its three segments, indicates a choice of two compositions, the correct one is selected in the light of the results of a rough molecular weight determination.

A preliminary molecular weight determination is desirable for the added reason that it serves as a confirmation of the binary nature of the mixture, because if the mean molecular weight as determined by titration and that calculated from the extrapolated composition do not agree, it is evident that a third component is present in the fraction under analysis. If the values obtained by these two methods agree within reasonable limits of error — experience has shown that two units is the permissible discrepancy —the evidence is conclusive that two, *and only two*, acids are present in the mixture in question. This fact can be further confirmed by first adding to the mixture a small, but known, amount of either of the pure fatty acids involved and then re-determining the solidification point of the whole. In this manner the original mixture can be made to follow the curve for the binary system in question.

For the successful use of these curves it is essential that the fractions under examination be binary mixtures and that the acids themselves be regenerated from their esters. In order to obtain these binary mixtures during the course of the distillation, fractions should be separated from each other by making the "cut" while the still is delivering material at constant composition. In this way the "cut" will have been made so that each fraction receives the first pure ester distilling over followed by increasing amounts of the next higher ester. Collection of the succeeding fraction is begun as soon as the ester of

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the next higher acid is being distilled at constant temperature in virtually a pure state. Failure to obtain a successful "cutting" is immediately brought to light by the fact that the solidification point of the regenerated acids of the several fractions cannot be made to fall upon a curve for any of the binary systems.

This application of a fundamental principle of phase rule chemistry to the analytical problems of fatty oil and wax investigations has met with much success in demonstrating that the so-called margaric acid (C_{17}) of alfalfa seed oil is in reality a mixture of palmitic and stearic acids (3). It was also used in the identification of the previously unreported myristic acid in alfalfa seed oil (4), and in demonstrating the existence of behenic acid to the extent of 1.3% in peanut oil as well as in establishing the identity of the C_{24} (2.2%) acid therein as *n*-tetracosanic (1). The saturated acids of carnauba wax from C_{18} to C_{26}, inclusive, have been identified by others (5) in another application of this method.

At present the method is being applied to a study of the saturated fatty acids of various oils with the twofold objective of obtaining revised data on the composition of the former and of demonstrating the probable existence of still unreported individuals therein. Because of the academic interest involved, this study has been made to include also the acids of odd number carbon atom content, alone and in admixture with those of even number. Solidification point diagrams of the acids higher than C_{26} are contemplated that these curves may find application in the examination and identification of the higher fatty acids of the waxes.

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Foaming Properties of Rosin Soap and Their Comparison With Those of Fatty Acid Soaps

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Questions have frequently been asked about the foaming or sudsing properties of rosin soaps. Tests in the Naval Stores Research Division laboratory gave only qualitative data on the foaming properties of rosin soaps. Therefore, after Ross and Miles (2) described a method for comparing the foaming properties of soaps, it was decided to employ this procedure for evaluating the foaming properties of soaps made from gum rosin, modified rosin, and rosin acids and at the same time compare them with soaps made from individual fatty acids.

Experimental

Preparation of Soaps. The soaps for the foaming tests were prepared as follows:

A five-gm. sample of rosin or fatty acid was dissolved in 100 to 200 c.c. of 95 per cent alcohol. Using phenolphthalein as indicator, the alcoholic solution was almost neutralized with five N. NaOH and the neutralization was completed with 0.5 N. NaOH. The alcohol was evaporated and the sample dried in a vacuum oven at 100° C. The soap was powdered and stored in a vacuum desiccator.

Method. The solutions for the foaming tests were prepared by placing a weighed amount of the anhydrous soap in a 250-c.c. volumetric flask and then dissolving the soap in about 125 c.c. of hot distilled water, after which distilled water was added to make the volume of the solution 250 c.c. at 45° C. The solution was brought to this temperature by placing the flask in a constant temperature bath maintained at 45° C. and leaving it there for 10 to 15 minutes. The same routine was followed in preparing and testing all of the soap solutions.

The dimensions of the apparatus and conditions of test using the apparatus described by Ross and Miles (2) were: The inside diameter of the tube in which the foam formed was 48 mm. The orifice of the 200-c.c. pipette was 2.8 mm. The height of fall was 92 cm. The tests were conducted at 45° C.

Soaps made by the above procedure from the following products were tested for foaming properties: Rosin (color grade WW) made from longleaf pine gum; rosin (color grade WW) made from slash pine gum; oxidized rosin[1]; dehydroabietic acid (m.p. 170° C. $[\alpha]^{20}_{D}$ + 60°); abietic acid ($[\alpha]^{20}_{D}$ — 87°); dihydroabietic (m.p. 129°-130° C. $[\alpha]^{20}_{D}$ — 3°) acid; tetrahydroabietic acid (negative to tetranitromethane test for unsaturation); pyroabietic acid[2]; hydrogenated rosin[3]; commercial stabilized rosins; two series of commercial individual fatty acids; and one series of pure individual fatty acids.

Results

The rosin soaps made from slash-pine rosin and longleaf-pine rosin had the same foam producing properties. The curves in Figure 1 show that the oxidation of the unstable rosin acids in rosin tends to make the relation between foam production and

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[1] Rosin (color grade WW) powdered and exposed in a thin layer to air at room temperature for over two months.

[2] Samples prepared at 200° C. and 275° C. as described by Fleck and Palkin (1).

[3] Rosin hydrogenated at 170° C. under a hydrogen pressure of 1,900 lbs. per sq. in.