mondsia chinensis. Sex definitely influences lipide metabolism, but these effects apparently vary with each species. In an earlier study (5) sex was found to exert a greater effect on plant waxes than plant maturity.

Acacia vernicosa has been combined with *A. constricta* by some taxonomists, and their waxes are remarkably similar. In fact, the waxes of all members of the Leguminosae that were studied are quite similar. The waxes of the two species of *Heteropogon* are similar to each other, as are also the waxes from three species of *Quercus*.

The bark of *Fouquieria splendens* is reported by Lewkowitsch (6) to contain 9% wax. In the present study the yield of acetone-insolubles of the petroleum ether extract of the bark of *F. splendens* was only 0.007% of the dry bark. There was 1.3% of a nonwax fraction. However an acetone extraction of the bark, following the petroleum ether extraction, yielded 11.3% of an orange-brown, semi-solid, tacky, resinous substance. This material was not further characterized, but it appears that the bark of *F. splendens* contains a high proportion of an acetone-soluble resin rather than wax. The ephemeral leaves are not very waxy either because they contained only 0.33% wax on a dry leaf weight basis.

As previously mentioned, it is often stated in textbooks that plants native to arid regions possess thick waxy cuticles. Table I shows that a few species do produce considerable wax (*Asclepias subulata, A. albicans, Larrea tridentata, Juniperus deppeana, Prosopis juliflora* var. *velutina*), but the majority of xerophytes and succulents in this survey contain only small amounts of wax (*Agave parryi* var. *huachucensis, Croton texensis, Trianthema portulacastrum, Atriplex canescens, Eriogonum deflexum, Fouquieria splendens, Beloperone californica, Cowania mexicana* var. *stansburiana, Olneya tesota, Acacia constricta, A. greggii, A. vernicosa*, and *Opuntia fulgida* var. *mammillata*). Apparently the thick cuticles of many desert plants, such as *Agave, Opuntia*, and even *Asclepias albicans*, are composed mainly of substances that are not waxes.

Summary

The yield and characteristics of the waxes from 42 species of plants native to southern Arizona were determined. Although a few have high yields of wax when expressed on the basis of amount of wax per unit area of plant surface, the majority of species contains only a small amount of wax. It was concluded that the often quoted statement, "plants indigenous to arid and hot regions have waxy cuticles," is untenable and should be modified to read " . . . waxlike cuticles." Some taxonomic relationships and some effects of sex on plant waxes were discussed.

Acknowledgments

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Crystallization of Indian Beef Tallow Fatty Acids from Aqueous Ethanols

V. V. R. SUBRAHMANYAM and K. T. ACHAYA, Regional Research Laboratory, Hyderabad, India

THE EMERSOL continuous process (1) for commercial crystallization of beef tallow fatty acids into unsaturated (mainly oleic) and saturated (usually a 45:55 eutectic of palmitic and stearic) acids employs 90% methanol as solvent, a crystallization temperature of −12°C., and a solvent/acid ratio of 4. The choice of a polar solvent is based on the formation of needle-like crystals with good filtering and washing characteristics, the absence of the need for low crystallization temperatures, and the added advantage of miscibility with water by which further reduction of fatty acid solubility can easily be attained. In India, unlike industrially-advanced countries, methanol is scarce, but ethanol is comparatively cheap and abundant. Indigenous beef tallows, and indeed most Indian vegetable, animal, and fish fats, are considerably more saturated than their American or European counterparts (2, 3) so that crystallization conditions may well differ.

Emery Industries state that 95% ethanol can be used for solvent crystallization by the Emersol process, but details, to our knowledge, are unpublished and other dilutions have not been mentioned. Kane and Patel (4) have studied the crystallization of the mixed fatty acids of several fats, not including tallow, from aqueous 80% ethanol at 0°C. at a solvent/acid ratio of 10. Their choice of conditions was based on theoretical solubility considerations. Their aim was to replace the Twitchell lead-salt separation of saturated from unsaturated acids as an analytical procedure. Earlier studies on the use of ethanol for fatty acid crystallization include those of Raymond (5) and of Wolff (6). Ku (7) and Ralston and Hoerr (8) determined the solubilities of pure fatty acids in various dilutions of ethanol. Intersolubility effects limit the application of these values to a complex mixture. A study of the behavior of Indian beef tallow fatty acids on single-stage crystallization from ethanol in various aqueous dilutions is reported in this paper.

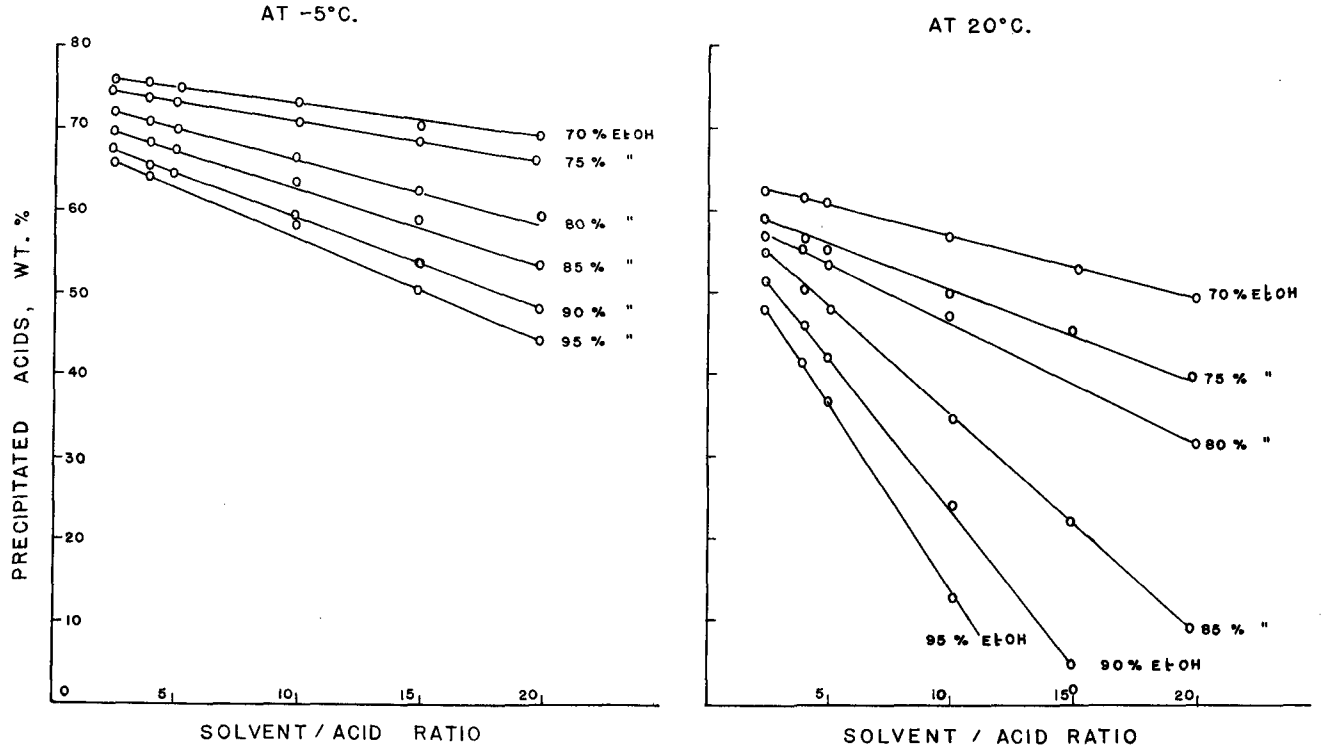

FIG. 1. Variation of precipitated acids with solvent/acid ratio on crystallization of Indian beef tallow fatty acid from aqueous ethanols at −5°C. and 20°C.

Experimental

Beef Tallow. The Indian beef tallow (I.V. 33.9, I.V. of mixed fatty acids 35.9), obtained from a young animal in the local slaughter-house, was rendered in the laboratory and analyzed for component fatty acids by the usual lead salt-ester fractionation technique. The following results were obtained as wt. % of fatty acids, excluding unsaponifiable matter: myristic 1.3, palmitic 39.7, stearic 23.1, arachidic 0.2, tetradecenoic 0.8, hexadecenoic 3.4, oleic 27.6, linoleic 3.9, total saturated 64.3. The high degree of saturation is evident. Western beef tallows have I.V. *ca.* 45 and a total saturated acid content of *ca.* 55%. The various Indian specimens studied (2, 3) show an I.V. between 30 and 35 and a total saturated acid content of *ca.* 65.

Crystallization from Aqueous Ethanols. Appropriate dilutions of absolute ethanol were made, the densities determined, and the compositions read off from tables in Perry's Handbook (9). The addition of small calculated amounts of either water or alcohol gave 70, 75, 80, 85, 90, and 95% ethanols by wt., corresponding to 77.0, 81.4, 85.4, 89.5, 93.3, and 96.8% ethanols by volume. Crystallizations using each of these six dilutions of ethanol were conducted at six solvent/acid ratios (S/A), *viz.* 2.5, 4, 5, 10, 15, and 20 (by wt.), and at four temperatures within the bounds of industrial feasibility, *viz.* 20°, 10°, 6°, and −5°C. Based on conclusions drawn from these data, selected trials were also made at −12.5°C., using 85, 90, and 95% ethanols at S/A ratios of 2.5, 4, 5, and 10.

About 4 g. of the weighed mixed fatty acids were dissolved in the required weight of solvent. The crystallization bath consisted of a cylindrical copper bath containing waste alcohol, surrounded by another metal vessel placed in a lagged wooden box. The temperature of the cooling mixture of ice water or ice salt in the outer metal vessel was regulated to maintain the desired temperature in the inner bath. Fine compensation for temperature fluctuations was obtained by immersing a coil in the bath, through which cold or warm water could be passed at any rate required. The crystallization flasks were allowed to cool to about 5°C. below the actual temperature of crystallization, then immersed in the bath liquid at the correct temperature, and maintained there for 3 hrs.

For each ethanol concentration, experiments at all the six S/A ratios were conducted simultaneously. Rapid filtration on a sintered glass funnel and washing with 10 ml. of the solvent at the right temperature were followed by isolation of the soluble and insoluble fatty acids. Weights and I.V.s were then determined. From the large mass of data the best crystallizations out of the 36 performed at each temperature are shown in Table I. The calculated I.V. for an oleic-linoleic mixture in the percentages present in the tallow is 101.4. This I.V. was used to deduce the percentages of unsaturated acids (Ol.) present in the precipitate P and of saturated acids (St.) present in the solubles S. The total saturated acid content of the tallow is of course given by P − Ol. + St., and was remarkably close to the experimental value of 64.3% in every case. The results at the extreme temperatures, 20° and −5° C., are shown in part graphically in Figure 1. The pattern was intermediate at the other temperatures.

Results and Discussion

Conclusions. With the increase in S/A ratio the linear variation in the precipitated acids for any particular ethanol concentration (Figure 1) indicates that any differential in the solubilities of palmitic and stearic acids is not pointed up by increasing the proportion of solvent, and the saturated mixture behaves

TABLE I

Best Crystallizations of Indian Beef Tallow Fatty Acids from Aqueous Ethanols at Various Temperatures

Temp., °C.	Ethanol concn., % wt.	S/A ratio	Precipitated acids P			Soluble acids S		
			%	I.V.	% unsatd. acids present, Ol.	%	I.V.	% satd. acids present, St.
20	70	2.5[a]	63.6	14.5	9.1	36.4	75.7	9.2
10	75	4[a]	65.8	11.9	7.8	34.2	85.9	5.2
6	80	5	65.8	10.4	6.8	34.2	85.2	5.5
−5	80	5	70.3	10.9	7.6	29.7	95.1	1.8
	85	5	67.9	10.5	7.0	32.1	88.6	4.0
−12.5	85	10	69.7	11.0	7.6	30.3	93.5	2.3
	90	5	68.7	10.3	7.0	31.3	88.5	4.0

[a] External solvent needed for filtration.

as an entity. There is a wider graphical spread of the descending lines at higher temperatures. Hence the lowering of solubility of the precipitated acids is more marked at higher temperatures and for stronger ethanols as the S/A ratio increases. Solubilities of saturated acids are affected more strongly by aqueous dilution than those of unsaturated acids. As ethanol is diluted, higher S/A ratios are necessary to obtain discrete filterable crystals.

Optimum separations are judged by a maximum yield of precipitated acids of minimum I.V. and a concurrent maximum of soluble acids of maximum I.V. In practice, the sum of unsaturated acids in the precipitate and saturated acids in the solubles, *i.e.*, Ol. + St., should be a minimum. From Table I the separation at −5°C. with 80% ethanol and S/A ratio 5 is very similar to that at −12.5°C. with 85% ethanol and S/A ratio 10. The possibility of filtration difficulties in the first set of conditions would make the second the optimum conditions of choice.

Assessment. Ethanol crystallization can yield from Indian tallows products similar in purity (but varying in relative proportions) from those obtained from American tallows by the Emersol process, using 90% methanol, −12°C., and an S/A ratio of 4, *viz.*, precipitated acids of I.V. 7–15 and soluble acids of I.V. *ca.* 104. The higher solubility of fatty acids in ethanol necessitates the use of a more dilute solvent. The higher total saturated acid content of Indian tallows requires a higher S/A ratio and yields soluble acids lower in I.V. by *ca.* 10 units. The temperature of crystallization is the same in both systems. Toxic hazards involved in the use of methanol are eliminated with ethanol.

Practical Considerations. The actual choice of commercial conditions will, of course, be governed by economic considerations, for which pilot-plant work is necessary. Since the crystallization is single-stage, it is adaptable to continuous operation. Aqueous ethanol corrodes steel equipment, and metallic contamination discolors fatty acids by salt formation, hence stainless steel equipment would be necessary. Ester formation during ethanol removal can be overcome by proper equipment design. Indian tallow, lacking a parent meat-packing industry, is not yet an industrial commodity. Until it is, imported tallows will have to be used. Alternately the controlled hydrogenation of suitable vegetable oils to yield mainly palmitic-stearic-oleic mixtures can be considered. Such work is in progress.

Summary

Crystallization of Indian beef tallow fatty acids (total saturated acid content 64.3% by wt.) from six dilutions of ethanol (95 to 70%) at five temperatures (20° to −12.5°C.) and at six solvent/acid ratios (2.5 to 20) was systematically studied. Optimum conditions of choice would use 85% ethanol at −12.5°C. at a solvent/acid ratio to 10 to give 69.7% precipitated acids, I.V. 11.0, and 30.3% soluble acids, I.V. 93.5. Other conditions of a similar order are possible. The comparatively saturated character of Indian beef tallows and the use of ethanol cause a departure from the Emersol process operating conditions using methanol, which is designed for American tallows. Considerations bearing on large-scale application are discussed.

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Epoxidized Jojoba Oil as a Stabilizer for Vinyl Chloride Containing Plastics

SARA P. FORE, FRANK C. MAGNE, and W. G. BICKFORD, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

JOJOBA *(Simmondsia chinensis)* may become of economic significance as a crop for the southwestern area of the United States. The seed of the plant contains about 50% of an oil having potential industrial importance. Jojoba oil can serve not only as a direct replacement for sperm whale oil but also as a raw material for chemical modification. Sulfurization of the oil produces a superior high pressure lubricant additive, and the hard wax obtained on hydrogenation of the oil can serve well in polishing wax formulations (1).

Jojoba oil is unusual among vegetable oils in that

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.