The Sodium Reduction of Wool Wax[1]

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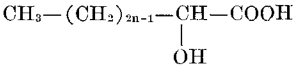
WOOL WAX alcohols or lanolin alcohols have been used extensively in cosmetics and medical ointments. They are usually obtained by the saponification of wool grease followed by the extraction of the alcohols from the soaps. The yield of alcohols by this method is, at best, about 50% of the raw material. The acids, which are recovered from the saponification reaction as soaps, may be classified into four series (5, 12, 16) as follows:

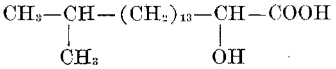
I. The normal series; straight chain fatty acids,
$CH_3—(CH_2)_{2n}—COOH$ (n = 4 to 12 inclusive).

II. The hydroxy series; straight chain hydroxy acids,

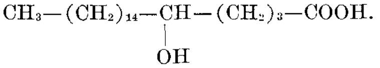


$CH_3—(CH_2)_{2n-1}—\underset{OH}{\underset{|}{CH}}—COOH$ (n = 5 to 8 inclusive), and

one branched chain isomer

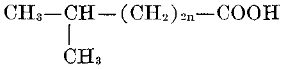


$CH_3—\underset{CH_3}{\underset{|}{CH}}—(CH_2)_{13}—\underset{OH}{\underset{|}{CH}}—COOH$ and possibly



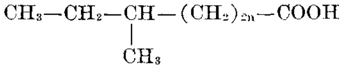
$CH_3—(CH_2)_{14}—\underset{OH}{\underset{|}{CH}}—(CH_2)_3—COOH.$

III. The iso series; iso acids,



$CH_3—\underset{CH_3}{\underset{|}{CH}}—(CH_2)_{2n}—COOH$ (n = 3 to 12 inclusive).

IV. The ante-iso series; ante-iso acids



$CH_3—CH_2—\underset{CH_3}{\underset{|}{CH}}—(CH_2)_{2n}—COOH$
(n = 2 to 13 inclusive).

Each of these series has its structural counterpart in the aliphatic alcohol portion of the unsaponifiable fraction (4, 7, 10). These acids, in the form of esters, on reduction by sodium and methylisobutyl carbinol are converted to alcohols similar to the aliphatic alcohols obtained by saponification. The sterols and triterpenoid-sterols are not in any way affected by this treatment. Thus, when sodium reduction is applied to wool grease or lanolin as an alternative to saponification for alcohol production, all of the raw material is utilized in making the product. The reduced lanolin recovered is in the form of a useful mixture of alcohols which differs from the wool wax alcohols obtained by saponification only in its increased aliphatic alcohol content.

The hydrogenolysis of lanolin which has been reported in the patent literature (6, 9) and described by Fayaud and Rivera (2) results in similar reduction of the esters present. It appears however from the analysis of the product obtained by Fayaud and Rivera that other more drastic changes take place with hydrogenation. Furthermore the presence of sulfur, which is a contaminant of many wool greases, hinders the hydrogenation process. The sodium reduction process can be applied to all grades of wool grease. Even acid cracked grease yielded a good product in our experiments.

Experimental

The reduction procedure employed was essentially the same as that described by Hansley (3) except that it was found necessary to increase the quantity of solvent xylene to prevent gelling of the reaction mixture.

a) *Sodium Reduction of U.S.P. Lanolin.* In a reaction flask equipped with an addition funnel, reflux condenser, stirrer, and gas inlet tube were placed 23.3 g. of sodium metal and 300 ml. of xylene. The air was flushed from the flask, and an inert atmosphere was maintained during the reduction by feeding a constant stream of nitrogen to the system. The flask and its contents were heated to a point just short of reflux temperature, and the molten sodium was dispersed in the solvent by rapid stirring. A mixture of 100 g. of U.S.P. lanolin, 100 g. of xylene, and 44.4 g. of methylisobutyl carbinol was fed into the reaction flask at a rate just sufficient to maintain good reflux. The amounts of sodium and methylisobutyl carbinol employed were in 25% stoichiometric excess of that calculated, based upon analytical determinations of the ester and acid numbers and hydroxyl content of the sample. After the addition of the lanolin-xylene-reducing alcohol mixture was completed (about 1 hr.), an additional 15 ml. of methylisobutyl carbinol were added, and the resulting reaction mixture was refluxed with stirring for an additional hour.

The alkoxide mixture was hydrolyzed by adding the hot solution slowly, with stirring, to 150 ml. of hot water. The hydrolysis was also carried out in a nitrogen atmosphere. The rate of addition of the reduced mixture to the hydrolysis flask was controlled so as not to exceed the capacity of the reflux condenser. Heating and stirring were continued for about ½ hr. to insure complete hydrolysis. The resulting emulsion was treated with enough ethanol to break it. The aqueous layer was discarded. The organic layer was then washed with 2 separate portions of hot barium chloride solution (5 g. of $BaCl_2$ in 175 ml. of water). Washing was continued with hot water until the pH of the washings was down to 8. The organic layer was then distilled to remove water, solvent, and excess reducing alcohol. The residue consisting of product alcohols and barium soaps was well extracted with acetone. Evaporation of the acetone extract yielded 79.7 g. of reduced lanolin.

b) *Sodium Reduction of Acid-Cracked Wool Grease.* Water present in acid-cracked wool grease was removed by azeotropic distillation with xylene prior to the reduction operation. A boiling flask, equipped with a reflux condenser attached to a water trap, was charged with the grease sample and xylene. The mixture was refluxed until no more water was collected in the trap. Additional solvent xylene was added to the flask so that the weight ratio of grease to solvent was 1:1. The proper amount of reducing alcohol was then added to complete the feed mixture. The reduction was then carried out as described above.

Discussion and Results

When the sodium reduction process is applied to glycerides, little difficulty is experienced during the

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TABLE I

Sodium Reduction of Lanolin and Other Waes

Substance Reduced				Product			
	Ester No.	Acid No.	% OH	Ester No.	Acid No.	% OH	Yield %[c]
U.S.P. Lanolin	95.4	1.2	1.22	3.9	0.5	4.93	79.7
Technical Lanolin	84.8	0.9	1.11	6.2	0.5	4.65	80.2
Neutral Wool Grease[a]	92.5	4.0	1.63	9.2	1.0	5.05	......
Acid Cracked Grease	78.2	28.2	1.42	11.7	0.5	4.32	65.0
Sperm Oil[b]	136.5	0.45	0.2	3.7	0.0	6.27	85.2
Beeswax	72.3	20.6	1.83	5.7	0.3	5.06	76.0

[a] Product from this reduction was not recovered via the barium soap precipitation procedure.
[b] Iodine number before reduction 90.6, after reduction 84.9.
[c] Based on total weight of substance reduced.

step of washing out the excess alkali and sodium soaps. The alcohols resulting from the sodium reduction of wool wax differ in character from those obtained when glycerides are reduced in that no water-soluble glycerol is present. Moreover the alcohols obtained are a more complex mixture; they include long chain aliphatic alcohols, some of which are diols, sterols, and triterpenoid-sterols. This mixture includes some efficient emulsifying agents, and any unreduced fatty acids are present as sodium soaps, which act as emulsion stabilizers. When water-washing is attempted, extremely stable emulsions result. These emulsions make the removal of the excess alkali and the recovery of the reduced wool grease very difficult. Addition of acid decomposes the sodium soaps and breaks the emulsions but contaminates the product with the liberated fatty acids. It also promotes reesterification of the alcohols with the contaminating fatty acids.

It was found that if the sodium soaps present were converted to water-insoluble soaps, such as the barium soaps, a pronounced reduction in the emulsifying power of the mixture occurred. The change in the stability of the emulsions produced in the washing operation after rendering the soluble soaps ineffective was very noticeable. Before the treatment with barium chloride, emulsions were formed which were stable for days. After forming the insoluble barium soaps, the emulsions broke in 5 min. and the excess alkali could readily be removed by water-washing.

Because of the nature of the materials involved, distillation as a means of recovery of the product is not feasible. The product alcohols were effectively extracted from the barium soaps by acetone, provided that all water and most of the xylene were removed prior to the extraction. There was a tendency toward gelling if much xylene were present.

The procedure can also be applied to other waxes.

The results of experiments on beeswax and sperm oil are given in Table I. There are no glycerides present in any of these substances except sperm oil, and the amount of alcohols present in the aqueous layers which were discarded was considered negligible.

The results obtained in the reduction experiments on varying grades of wool grease are also recorded in Table I. Regardless of the quality of the grease a product of low ester and acid number was obtained by this procedure.

In Table II a comparison is made of some analytical data on the product obtained by the sodium reduction of a lanolin sample with the constants reported (2) for a product obtained by the hydrogenolysis of lanolin. Also included in this comparison are the data on the alcohols obtained by the saponification (1) of lanolin.

The data given by Fayaud and Rivera for the lanolin used in their hydrogenolysis experiments indicate that it is comparable in composition to the lanolin used in our sodium reduction process. But when the two reduction products are compared, wide differences are apparent in the hydroxyl content and refractive indexes. From the lower hydroxyl content of the hydrogenated lanolin it may be inferred that, under the conditions employed, the reduction proceeded past the alcohol stage. Some hydrocarbons may have been formed, and it is estimated that the hydroxyl content of the hydrogenated product is about 70% of what is should be.

In general, the product obtained from the sodium reduction of wool wax is a semi-soft solid, wax-like in appearance and slightly sticky to the touch. Its melting point (42°C.) lies between those of lanolin and the wool wax alcohols. The lanolin alcohols obtained from the reduction of the lanolins were cream-colored, those obtained from the technical greases were light brown. The unpleasant odor sometimes noticeable in wool grease and lanolin is missing from these reduction products. The reduced lanolin has an advantage in solubility over that possessed by wool wax alcohols. For example, 10 parts of reduced lanolin will dissolve quite readily in 100 parts of mineral oil. This offers advantages in preparing many formulations.

TABLE II

Comparison of Lanolin with Reduction Products

	U.S.P. Lanolin	Sodium Reduced Lanolin	Alcohols from Wool Wax Saponification	Untreated Lanolin[a]	Hydrogenated Lanolin[a]
Refractive Index	1.475 at 60°C.	1.474 at 60°C.	1.498 at 60°C.	1.47 at 60°C.	1.572 at 60°C.
Acid Number	1.2	0.5	1.0	0.51	0.3
Ester Number	95.4	3.9	2.4	94.0	3.2
Percent Hydroxyl	1.22	4.93	4.57	0.59[b]	3.51[b]
Cholesterol, %[c]	19.4	25.4	39.1	......	......
Lanosterol, %[c]	13.3	19.9	27.1	......	......

[a] As reported by Fayaud and Rivera (2).
[b] Calculated from acetyl values.
[c] Determined by the method of Luddy, Turner, and Scanlan (8).

According to Peel (11), the advantages of wool wax are concentrated in the alcoholic portion and the most important single constituent is cholesterol. It is apparent, from the data given in Table II, that the sterols are not affected by the reduction procedure. The amounts of cholesterol and lanosterol in the reduced lanolin is in fair agreement with what would be expected. Tiedt and Truter (14) have shown that the esters of wool wax were devoid of emulsifying power and that the ability of lanolin to hold water in water-in-oil emulsions was due almost entirely to the free alcohol content. They also claim that of the constituents of lanolin the most powerful emulsifying agents are the 1,2-diols. The hydroxyl content of the reduced lanolin is at least equal to if not greater than that of the saponification alcohols. About 5% of the alcohol fraction are diols (4, 15). Hydroxy acids have been reported (5) to comprise about 30% of the acid fraction, and these compounds upon reduction would yield 1,2-diols. It is logical to assume that the emulsifying properties of wool wax alcohols would be enhanced by the addition of the glycols formed by the reduction of the hydroxy acids of wool grease. It was found, on testing the reduced lanolin for its emulsifying properties (13) according to a procedure by Schulman and Cockbain, that they were equal to or better than those of wool wax alcohols obtained by saponification.

Summary

The sodium reduction technique has been modified for application to various grades of lanolin and wool grease. The improved process gives good yields of alcohols with low ester and acid numbers. The sterols present in the grease are not affected by the reduction. A recovery procedure is described which avoids the difficulties with extremely stable emulsions. The essential features of this procedure are the elimination of emulsion-stabilizing sodium soaps by precipitation with barium chloride prior to the washing of the reduction mixture and acetone extraction of the alcohols from the insoluble barium soaps.

Acknowledgment

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Some Effects of Semolina Lipoxidase Activity on Macaroni Quality[1]

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THE PROBLEM of assessing the macaroni-making quality of a sample of durum wheat or durum semolina is largely one of predicting the color of the macaroni which the sample will produce. The most reliable way of doing this is to process macaroni from the sample and to measure the color of the product, either visually or by using some type of instrument. This requires too long a time for some commercial applications and is not convenient in dealing with new varieties at early stages of development because of the small amount of wheat that can be spared for testing. Accordingly it is necessary to seek useful indirect methods of predicting macaroni color.

The desirable color for macaroni is a clear bright yellow. This results from the presence in the semolina of certain yellow carotenoid pigments. The problem, then, should be simply one of determining the amount of pigment in the semolina from which the macaroni is made. However when quality testing of durum wheats was first begun about 20 years ago, it was noted (1) that certain semolinas appeared to bleach badly during processing while others retained their color. For this reason no useful correlation between semolina pigment and macaroni color was found.

In seeking an answer to this problem some years ago, a study was made (5) of the rate at which semolina pigment was destroyed during mixing of macaroni doughs. As a result of this work it was postulated that durum wheats contained the enzyme lipoxidase and that it was the presence of this enzyme, in varying amounts, that gave rise to the variations in pigment loss during macaroni processing. In this brief review I will discuss the application of this hypothesis to the development of a simple prediction test which allows one to estimate the macaroni color of a sample of wheat or semolina of about 20 g.

The data in Figure 1 are taken from some of our earlier work and show that the rate of pigment oxidation during mixing for two samples of semolina which contain the same amount of pigment initially but which vary widely in macaroni-making quality; The methods have previously been described (5). The upper curve, showing rapid oxidation of pigment, is for a semolina yielding a pale macaroni; the lower curve, showing slow oxidation of pigment, is for a semolina yielding a yellow macaroni. Following this investigation we began working with a Warburg apparatus to find out if crude aqueous extracts of durum wheat or semolina showed any lipoxidase activity. Enzyme extracts were prepared by grinding the material with sand and water, followed by centrifuging (3); preparation of a suitable linoleic acid emulsion was eventually solved by using a non-ionic surface-active agent, Triton X-100 supplied by Rohm and Haas (3). The pH optimum for this enzyme-substrate system was found to be 6.5 in phosphate buffer. We found that these wheats did contain significant amounts of this enzyme and obtained the sort of results shown in Figure 2. These curves show the rate of oxygen uptake for aqueous extracts of semolinas, using the linoleic acid emulsion as substrate, at pH 6.5; they represent the same two types of semolina as those shown in Figure 1. The close corre-

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