TECHNOLOGICAL ASPECTS OF LANOLIN*

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Lanolin is refined wool grease which is a by-product of the wool-scouring industry. Three methods are in use for recovering wool grease from the raw wool. In the solvent extraction method the grease is leeched out by percolating a suitable solvent through the raw wool. The other two methods have this in common, that the wool is first scoured with soap and alkali. The scouring liquor containing the wool grease is then treated in either of two ways: (1) it is passed through centrifuges producing the grease known as centrifugal grease, or (2) the scouring liquor is "acid-cracked." The grease which is pressed and collected is known as degras.

The solvent-extracted wool grease is dark in color, has a free fatty acid content of 7–11 per cent, and has a good physical body. Solvent wool grease is the purest form of crude material available. Very little solvent wool grease is used in the production of lanolin.

The centrifugal wool grease is light in color, has a free fatty acid content of 1–2 per cent, and has a soft physical body. In the recovery process the heavier wool grease fractions are thrown out by centrifugal force and the softer bodies are recovered. Most of the lanolin produced is manufactured from centrifugal wool grease.

The acid-cracked wool grease or degras is dark in color, has a free fatty acid content of 12–18 per cent, and the physical body is dependent on the original soap used to scour the wool. The fatty acid liberated from the scouring soap is collected with the wool grease and remains mixed with the grease. A fair amount of degras is used in lanolin production.

Pure wool grease is excreted by the sheep from the sebaceous glands through its hair follicles adhering to the wool fiber to protect it from the elements, (1), soil conditions, and its own waste. Hence, wool grease has excellent adhesive properties and for that reason lanolin is used in protective oils, ointments, and cosmetics to provide the necessary adhesion for assimilation, emolliency or protection.

Wool grease must be purified, alkali-refined, bleached, and de-

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odorized to conform to the requirements for lanolin in the U. S. Pharmacopœia (2).

One of the synonyms for lanolin is wool fat (2). Chemically, lanolin is not a fat but a wax. Approximately 7 per cent of lanolin is free alcohols and the balance is essentially esters of high molecular weight sterols, combined with straight chain fatty acids. There are no glycerides present. In the crude form wool grease contains free fatty acids which are reduced to 0.56 per cent maximum to meet the U.S.P. requirements for lanolin.

The literature has many references to lanolin and its component parts. No conclusions were found to indicate what individual esters exist in lanolin. The esters of lanolin may be a combination of any one alcohol with any number of the fatty acids present or, conversely, any one acid may be combined with any number of the alcohols present. As there is a possibility for a tremendous number of combinations, we may have a long wait for any definite knowledge of the chemical entities present. However, it is possible to split the ester by complete saponification and to study the individual acid and alcohol fractions liberated.

The most complete study of the acid fraction is that of Weitkamp (3). He reports that the acidic constituents of lanolin are divided into four groups. The first group is of the even normal series consisting of the acids from C_{10} to C_{26}. The second group consists of two even acids in the alpha hydroxy series. The third group consists of 10 even acids from C_{10} to C_{21} in the iso-series. The fourth group consists of 11 odd acids from C_9 to C_{27} and C_{31} in what Weitkamp calls the anteiso series. The individual acids are present in very small percentages and the maximum content of any one acid is 7 per cent. Weitkamp found that the fatty acids are saturated. Lanolin has an iodine value of 18–36 showing some unsaturation, but this is present in the alcohol group.

For a product to turn rancid there must be some unsaturation in the fatty acid molecule (4) for oxidation to take place at the unsaturated carbon-to-carbon linkage. As there is no unsaturation in the fatty acids of lanolin, pure lanolin will not turn rancid. Some lanolins may develop a rancid odor which is often traced to small amounts of added scouring soap which may not have been removed in alkali refining. The rancidity develops in the unsaturated fatty acids of the contaminating soap. Other odors may be present in lanolin due to the chemicals used as well as to differences in refining techniques.

No comparable study of the alcohol fraction has been made. More work has been done on the alcohol fraction but the results obtained are not as definite as those of Weitkamp in his study of the acid fraction. The early literature (5) states that the unsaponifiable part of wool grease or the wool grease alcohols consist of cholesterol, "Isocholesterol," and inactive alcohols.

Only two true sterols have been found, namely, cholesterol and dihydrocholesterol. Windaus and Tschesche (6) reported that the so-called "Isocholesterol" consisted of 92 per cent lanosterol and 8 per cent agnosterol and these are triterpene-like alcohols rather than sterols. However, Ruzicka, *et al.*, (7, 8, 9) found two more alcohols, dihydrolanosterol and dihydro-agnosterol. Furthermore, Ruzicka proved that lanosterol and dihydrolanosterol are identical with kryptosterol and dihydrokryptosterol. These four alcohols obtained from the so-called Isocholesterol fraction each have 30 C atoms. They have the same C skeleton, the hydroxyl group in the same position, but differ in the number and position of the double bonds.

	Double Bonds	Melting Point, °C.
Lanosterol ($C_{30}H_{50}O$)	2	140.5–141.5
Dihydrolanosterol ($C_{30}H_{52}O$)	1	144.5–145.5
Agnosterol ($C_{30}H_{48}O$)	3	163.5–164.5
Dihydroagnosterol ($C_{30}H_{50}O$)	2	156–157

The two double bonds of lanosterol are not conjugated. The one that is easily reduced is found in the side chain. Agnosterol has three double bonds. Two are found in different rings but are conjugated while the third double bond is in the side chain and it is this one that is easily reduced. Since it is a known fact that pure lanolin does not develop rancidity, it must mean that even when these double bonds are oxidized no odor develops.

Despite the extensive literature relating to lanolin and its use in water-in-oil emulsions, there is no agreement as to the particular property which is responsible for its ability to absorb water. Many have attributed the power to the cholesterol content. Powers, *et al.* (10), found that the emulsifying efficiency of cholesterol is much less than the emulsifying efficiency of mixtures of cholesterol and cholesterol esters when used with petrolatum for the purpose of emulsifying water.

Most of the literature relating to emulsification of lanolin or of its liberated fractions reports results obtained after dilution with mineral products. Therefore, an investigation was undertaken to determine, if possible, the effect of cholesterol in free and combined form on the water absorption of lanolin.

Commercial samples of lanolin were obtained which were refined in various ways from each one of the methods described for the recovery of wool grease. It was felt that the method of recovery might have an effect on the water absorption power and that all types of lanolin should be investigated. The free, combined, and total cholesterol contents were determined (11). The alcohol fraction for the determination of the total cholesterol content was obtained (12) through pressure saponification with alcoholic alkali for sixteen hours.

The British Pharmacopœia

method of determining the cholesterol content must not be taken as the actual cholesterol content but as the percentage of alcohols which will be precipitated with digitonin and calculated as cholesterol. Gardner, *et al.* (13), tabulate some of the alcohols which also give precipitates with digitonin and which may be present in the free or combined alcohols of lanolin. Windaus (14) also tabulates the relative solubilities of digitonides. Anderson (15) states that if cholesterol is formed from plant sterols, a number of different as well as isomeric cholesterols might be expected to occur in animal fats and waxes, corresponding to the various phytosterols contained in the plant material which serves as food. Therefore, the results listed are only relative in relation to the cholesterol content.

From the results obtained there is no indication that the free, combined, or total cholesterol has any effect on the water absorption power of lanolin.

Contrary to popular belief the benefits derived from lanolin are not centered about the properties of the individual fatty acids or alcohols present. The water absorption and emollient properties of lanolin are due to the composition of the mixture. This mixture, which we call lanolin, is essentially a chemical combination of fatty acids and alcohols in ester form. No evidence has been published to show that any chemical individual contained in the mixture is entirely or partly responsible for the properties of lanolin.

Table 1

Anhydrous Lanolin, U.S.P. Sample No.	Free Cholesterol, %	Unsaponifiable or Total Alcohols, %	Cholesterol of Total Alcohols, %	Calculated Total Cholesterol, %	Combined Cholesterol by Difference, %	Water Absorption, %
1	2.0	43.8	26.1	11.4	9.4	350
2	2.4	42.1	26.8	11.3	8.9	370
3	1.8	43.1	32.1	13.8	12.0	460
4	1.4	43.1	26.8	11.6	10.2	460
5	2.6	45.3	27.8	12.6	10.0	470
6	1.9	47.0	37.5	17.6	15.7	480
7	1.9	45.9	30.1	13.8	11.9	490
8	1.8	46.9	28.4	13.3	11.5	500
9	2.8	48.7	30.0	14.6	11.8	520
10	5.5	46.0	31.4	14.4	8.9	530
11	2.5	44.3	30.5	13.5	11.0	540
12	1.7	40.7	27.2	11.1	9.4	560

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