Lanolin and Its Derivatives[1]

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ABSTRACT

Lanolin, which is extensively used in pharmaceuticals and cosmetics, is generally considered to consist of a mixture of naturally formed esters derived from higher alcohols and higher fatty acids. This paper encompasses the chemical description of lanolin; the composition of its esters, acids, and alcohols; the chemical and physical modifications of lanolin; the refining of lanolin; and some of its applications in pharmaceutical and cosmetic formulations. Some new developments in lanolin chemistry will also be highlighted.

PREPARATION OF LANOLIN

Lanolin is derived from wool grease which is the "fat-like" substances exuded by the sebaceous glands of sheep. This natural lubricant protects the wool of the sheep from the effects of weathering (sun, wind, rain, etc.) and constitutes from 10-25% of the weight of the sheared greasy wool. The wool also contains substantial quantities of soil, salts, water, and foreign organic matter.

Basically, three methods are in use to recover 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 and subsequently evaporating the solvent. The other two methods involve the scouring of the wool with soap and alkali and recovering the wool grease by either centrifuging or "acid cracking."

Wool grease, sometimes referred to as degras, must be purified, alkali refined, bleached, and deodorized to conform to the requirements for lanolin in the "U.S. Pharmacopoeia" (1). Allowable impurities in anhydrous lanolin sold in conformity with the maximum U.S.P. specifications are as follows: 0.56% free fatty acid (as oleic), 0.25% moisture, 0.1% ash, and a trace of chloride. There should be none of the following present: free alkali, ammonia, glycerine, petrolatum, or soluble oxidizable impurities. A good lanolin, however, will usually test better than U.S.P. specifications.

CHEMICAL COMPOSITION OF LANOLIN

Lanolin is an amber-yellow, tenaceous, unctuous mass, with pronounced emollient (or soothing) properties and slight, characteristic odor.

Although it appears to be a fat or a grease, chemically lanolin is classified as a wax. It melts at 36 C to 42 C, is insoluble in water, but mixes without separation with twice its weight of water, sparingly soluble in cold alcohol, more soluble in hot alcohol, and freely soluble in ether and chloroform.

Chemically, lanolin consists of a complex mixture of esters and polyesters of high molecular weight alcohols and fatty acids. Approximately 4% of lanolin is a mixture of free alcohols, and the remaining portion consists of traces of free acids and hydrocarbons.

Though there are many literature references pertaining to lanolin and its component parts, no conclusions were found that identify the individual esters which exist in lanolin.

Upon saponification of the lanolin esters with alcoholic alkali, the alkaline soaps of lanolin acids are separated from the unsaponifiable portion containing the lanolin alcohols. The resultant mixture is composed of ca. 50% acids and 50% alcohols by weight. Individual components can then be identified in the acid and alcohol fractions.

The various acids have been identified by one researcher (2) who breaks the thirty or so individual acids into four groups – normal, hydroxy, iso, and anteiso acids. Because lanolin is a natural product, the percentages of the constituents vary considerably. Hydroxy acid content of lanolin fatty acids have been reported to be as low as 5% and as high as 40-45% of the total acids. This fraction of the acids is very important in understanding the chemistry of lanolin as the free hydroxyl group allows for the formation of polyesters as well as many of the other chemical modifications of lanolin which are covered below.

The alcohol fraction of lanolin has been investigated (3) and shown to be composed mostly of monohydric alcohols with a small portion of dihydric alcohols which also lend to the formation of polyesters in whole lanolin. The largest portion of the alcohol fraction consists of sterols with cholesterol being the dominant entity.

Lanolin has strong emulsifying and penetrating properties and because of these, blends and combines well with practically all other materials used in cosmetics and pharmaceuticals. In addition to its water-binding and emulsifying qualities, it owes its importance in pharmaceuticals and cosmetics to the ease with which it is absorbed onto human skin and hair. Its adhesive and tackifying properties make it as excellent candidate for use as a plasticizer in adhesives and resins.

Uses of lanolin can be divided into two areas – (a) dermatological and cosmetic, and (b) industrial.

Industrially, lanolin is used as a lubricant and rust preventative. It can be found in leather-treating processes, fabric treatment, and as an ingredient in printing inks.

In the form of crude wool wax, the uses of lanolin in the field of dermatology and cosmetics probably go back beyond the dawn of recorded history. Evidence (4) has been found of the use of wool wax by the early Egyptians as an important ingredient in their beauty aids, ointments, salves, lotions, and the like. Modern doctors, dermatologists, and cosmetic scientists have long been familiar with the unusual cleansing, soothing, and lubricating values of lanolin. Because of these properties, lanolin's uses in the dermatology field include the following: as a base (or vehicle) in the formulation of ointments, salves, creams, lotions, etc.; in adhesives bandages, surgical dressings, anti-dermatitis preparations.

In the cosmetic field, specific uses for lanolin include absorption bases, hair lotion, hand creams, cold creams, makeup, nail polish removers, lipsticks, deodorants, antiperspirants, after-shave preparations, and many others.

LANOLIN DERIVATIVES

Physical Modifications

As the consumer became more sophisticated, improvements such as attractive appearance, pleasant feel, and appealing odor were expected. Tackiness, poor spreadability, malodor, and poor color were some of the deficiencies of lanolin that were corrected by making derivatives.

As lanolin technology evolved and a better understanding was gathered about the chemistry of lanolin, it was discovered that the properties of lanolin could be altered

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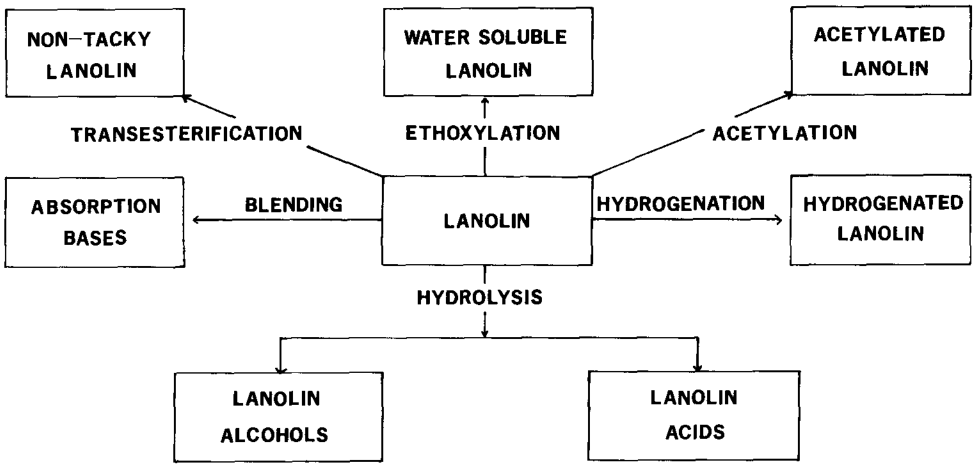

FIG. 1. Chemical modification of lanolin.

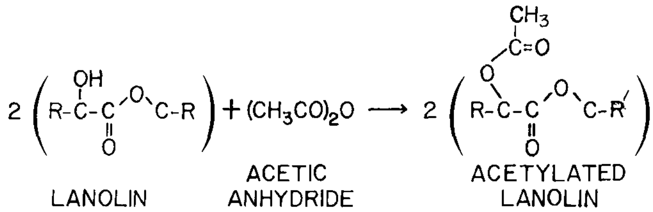

FIG. 2. Acetylation. R = hydroxy lanolin acids; R' = lanolin alcohols.

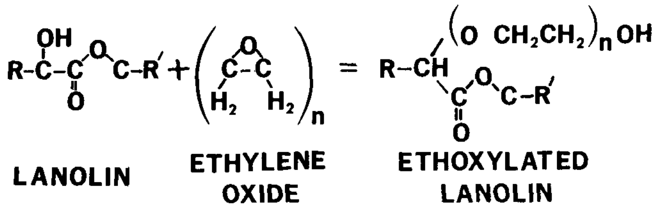

FIG. 3. Ethoxylation. R = hydroxy lanolin acids; R' = lanolin alcohols.

through various chemical and physical processes.

Solvent fractionation of lanolin via vacuum distillation and solvent crystallization separates lanolin into liquid lanolin and lanolin wax (5). Liquid lanolin has less drag and tackiness, but retains the emollient properties of lanolin. Liquid lanolin is soluble in mineral oil, while U.S.P. lanolin is not. It has a high spreading coefficient, making it useful in bath oils. It also improves drug release and penetration, and acts as a skin moisturizer, plasticizer, and pigment dispersant. Liquid lanolin is nonirritating or sensitizing, and is virtually odorless and tasteless.

Modern cosmetics employ the attributes of liquid lanolin in creams, lotions, bath products, makup, and such. Basically, it finds its use for any application in which whole lanolin would be used, but where a less-tacky, more emollient feel or better oil solubility is desirous.

Lanolin wax is a better w/o emulsifier than lanolin and is used extensively as a bodying agent and emulsifier. Lanolin wax has been shown to improve the homogeneity of wax mixtures and creams. Like its liquid counterpart, it is nonirritating or sensitizing and virtually odorless and tasteless. Being wax-like in nature, and possessing the adhering properties of lanolin, lanolin wax is finding its greatest uses in the preparation of modern lipsticks and lip glossers where it plays an important role in keeping the pigments, lakes, and dyes on the lips.

Chemical Modifications

Both the liquid and wax portions of lanolin, as well as lanolin itself, can be further modified to produce a wide variety of properties. (A summary is shown in Fig. 1.) Through these modifications, which will be described below in more detail, the main goal is to improve one or more of the attributes of lanolin while eliminating one or more of its disadvantages. In this way, a particular derivative will suit a particular application better than the whole lanolin would, or it can provide the means for the employment of the beneficial properties of lanolin in an application where previously (because of solubility, odor, or other reasons) one could not use lanolin.

HYDROGENATION

Hydrogenation of lanolin improves its stability and increases water absorption and mineral oil solubility. The hydrogenation of lanolin is not merely a saturation of double bonds, but the reaction carries on well beyond this point. There are practically no esters in hydrogenated lanolin, as is indicated by the decrease in saponification value from 95 to to approximately 3 to 4. The esters of lanolin are split into acids and alcohols, fatty acids are converted to alcohols, and a portion of the alcohols are further reduced to simple hydrocarbons. Although the exact composition of hydrogenated lanolin is not known, the presence of a high hydroxyl value indicates a large percentage of hydrogenated free alcohols, sterols, and small quantities of hydrocarbon. Hydrogenated lanolin retains the adhering and emollient properties of lanolin without the tackiness, color, odor, and taste of whole lanolin. It is employed in lip products, delicately scented preparations, and emulsion formulas because its increased hydrophilic nature contributes to the stability of creams and lotions.

ACETYLATION

When lanolin is reacted with acetic anhydride, the hydroxyl groups on the hydroxy esters are capped with an acetate linkage, as is shown in Figure 2. The acetylated lanolin becomes more hydrophobic as is indicated by its failure to form w/o emulsions and its solubility in cold mineral oil. Lanolin treated in this manner has a higher ester content and a slightly lower melting point. Functionally, acetylated lanolin is useful in forming water resistant films for applications in sunscreen preparations or baby products. Even in the usual hand and body creams, the water resistant film of acetylated lanolin is useful to slow down transepi-

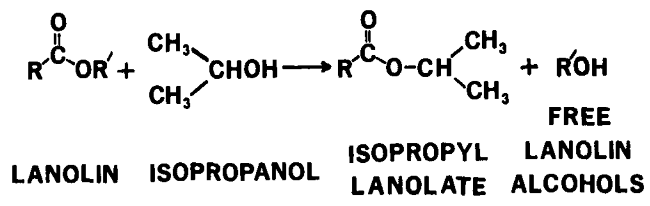

FIG. 4. Transesterification. R = lanolin acids, R′ = lanolin alcohols.

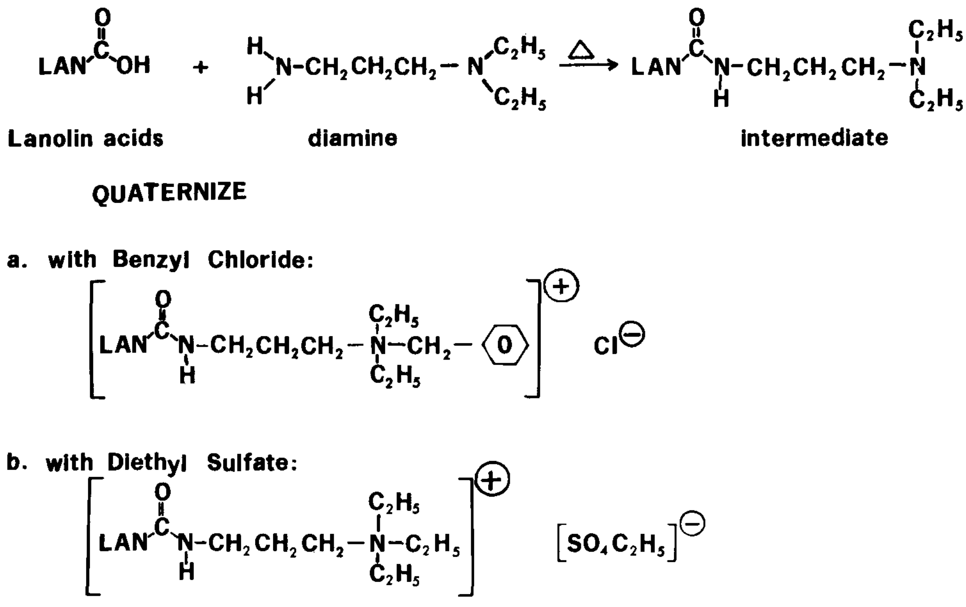

FIG. 5. Lanolin quaterniums.

dermal water loss. This retains moisture in skin and enhances skin softening and protection from defatting effects of the outside environment.

ETHOXYLATION

Another interesting chemical modification of lanolin, shown in Figure 3, is ethoxylation onto the free hydroxy group of lanolin esters, acids, and alcohols. As the E-O chain length increases, water solubility and surface activity also increase, while emulsification decreases. Alcohol solubility also increases without loss of emolliency. Ethoxylated lanolin derivatives are used to solubilize sunscreens, perfumes, and medicaments, and as emollients in hair products. Most common types contain 6-75 moles of E-O.

Because of their water solubility, ethoxylated lanolins enjoy their greatest usage in detergent solutions where they help to combat the defatting action of detergents on the skin and hair without significantly affecting the cleansing properties of the detergents. Typical uses include shampoos, soaps, and dishwashing detergents. This property also allows formulators to take advantage of the lubricating and emollient aspects of lanolin in applications where its uses were limited because of insolubilities. After-shave lotions, pre-shaves, astringent lotions, and colognes are a few such examples.

TRANSESTERIFICATION

In transesterification of lanolin, shown in Figure 4, controlled partial saponification is obtained to produce a mixture of lanolin alcohols, isopropyl esters, and free lanolin. This modification retains the emollient properties of the lanolin or liquid lanolin, and improves solubility and spreading.

In the case of lanolin, the melting point is depressed, and the tackiness associated with lanolin is virtually eliminated. It is a functional derivative used in the creation of delicate, velvety-feeling emulsions where the beneficial properties of lanolin are desirous.

In the case of liquid lanolin, this partial transesterification results in a lighter feeling, less viscous product. This derivative is particularly suited for applications where a minimum of greasiness is desirous.

HYDROLYSIS

The alcohol and acid fractions of lanolin as described above also serve as useful cosmetic ingredients.

To the cosmetic formulator, lanolin alcohols represent one of the most powerful w/o emulsifiers known. The vast variety of chemical structures which comprise this product enable it to absorb up to 2000% its own weight of water. Being a hard, brittle, wax-like substance, formulators also take advantage of its properties to contribute stability and emolliency to stick preparations.

Lanolin alcohols have been subjected to many processes, including fractionation, adsorption, and extraction. They can be processed further to form multi-sterol extracts and absorption bases for w/o products, ointments, suppositories, and makeup bases. By ethoxylation of the alcohols, derivatives with the hydroalcoholic solubility may be obtained. The alcohol fraction may also be esterified with acetic, ricinoleic, and linoleic acids, which may in turn be further ethoxylated. All of these modifications and reactions represent individual derivatives designed to accomplish a particular function in cosmetics. Emulsification, solubilization, providing emollience, reducing greasiness, are just a few of the many applciations of lanolin alcohol derivatives.

Lanolin acids are composed of many complex individual members. Being a fatty acid, or more correctly stated, a mixture of fatty acids, they are useful to the cosmetic chemist as a means of forming emulsifying soaps. One patent (6) describes the metal soaps of lanolin fatty acids as a very useful w/o type emulsifier. They also find great use as a superfatting agent in formulas for soap bars and the like. These fatty acids also lend themselves to esterification, amine neutralization, and ethoxylation, to produce derivatives with unique properties.

Quaternization (7) has also resulted in interesting products with unusual substantivity when applied to hair and skin. This is accomplished through acidification of the alkaline soaps of lanolin to yield crude lanolin acids, which are refined through a distillation and deodorization process, and then bleached or deodorized. These refined acids are then reacted with a diamine to form an amido-amine structure. Subsequent quaternization yields the structures shown in Figure 5. These (8) new products have shown to be compatible with anionic surfactants, to be substantive to hair and skin, as evidenced by SEM studies, to possess low toxicity when compared to stearalkonium chloride, and to be microbiologically effective against both gram negative and gram positive organisms. A wide range of cosmetic and pharmaceutical preparations may be prepared from this unique material.

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