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Wool Wax Alcohols: A Review

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ABSTRACT

Wool wax alcohols consist of aliphatic monoalcohols and alkane 1,2 diols, cholesterol, triterpene alcohols, and small amounts of hydrocarbons and autoxidation products. The monoalcohols and the diols consist of normal, iso and anteiso series. The average composition of the wool wax alcohols is based on data which were published during the past 25 years.

INTRODUCTION

Wool wax alcohol is a material which derives from the saponification of wool wax. The composition of this material has been extensively studied for the past 100 years by using a variety of fractionation techniques and analytical methods. This review is an attempt to summarize the work and results of various investigators as well as the average composition of wool wax alcohols.

EARLY INVESTIGATIONS

Lanolin was launched as a commercial product in Germany during 1885 by Jaffe and Darmstadter. What was known around that time about the composition of wool wax alcohols is as follows.

1. Chevreul was able to establish in 1856 that wool wax does not contain glycerides. This finding was confirmed by Hartman (1) and Schulze (2).
2. Hartman (1) identified cholesterol as a component of wool wax alcohols during 1868. The identification was made solely on the basis of cholesterol's physical properties.
3. Schulze (2) published three articles during 1870-1873 in which he confirmed the presence of cholesterol in wool wax alcohols. Schulze saponified the wool wax with NaOH, extracted the wool wax alcohols with ether and recrystallized the extract from alcohol plus ether. He thus collected a large amount of cholesterol which he identified by its melting point, color reactions and elemental analysis.

It should be noted that both Hartman and Schulze had available to them substantial information concerning the physical and chemical properties of cholesterol. Prior to 1816, when Chevreul (3) coined the term "cholesterine" (chole-bile, steros -solid), it was known that this material is present in gallstones and that it can be crystallized from alcohol as white platelets. It was also Chevreul (4) who established in 1815 that cholesterine is an unsaponifiable. The term "cholesterine" was changed to "cholesterol" when Berthelot (5) demonstrated the presence of a hydroxyl group in this material. Shortly afterwards, Wislecenus and Moldenauer (6) reported a dibromide of cholesterol, thus establishing the presence of a double bond.

While attempting to separate cholesterol from wool wax alcohols by crystallization, Schulze noted the presence of another substance which appeared to be gelatinous rather than crystalline. In order to accomplish an efficient separation, Schulze converted the alcohols into benzoates and crystallized the mixture from ether. After separating the platelets (cholesterol benzoate) from the needles, Schulze established that wool wax alcohols contain, besides the levorotatory cholesterol, a dextrorotatory alcohol which has a different melting point and crystalline form, but approximately the same elemental analysis as cholesterol. For this alcohol Schulze coined the name "isocholesterol." Since this material changed its melting point on purification, Schulze concluded years later, that "isocholesterol" is likely to be a mixture of alcohols.

Schulze made another important contribution to the investigation of wool wax alcohols: based on the hydroxyl number of wool wax alcohols and the acid number of the wool wax acids, Schulze concluded that: 1. wool wax alcohols must contain some alcohols with higher hydroxyl numbers than cholesterol and isocholesterol; 2. these additional alcohols must belong to the aliphatic series.

It does therefore appear from the above that before the end of the 19th century, the following basic characteristics of wool wax alcohols were established: wool wax alcohols do not contain glycerol; they do contain cholesterol, "isocholesterol," and aliphatic alcohols.

Consequently, a large volume of publications which appeared until 1945 dealt with detailed investigations of the components of wool wax alcohols. In reviewing this literature, one cannot fail to notice that a very large part of the publications was devoted to the identification of the alcohols in the aliphatic series. This should not be surprising since this group of alcohols is the most complex one.

In an excellent review of the work devoted to the identification of the aliphatic alcohols, Knol (7) analyzed the evidence which various authors presented as proof of identity. The aliphatic alcohols which Knol reviewed were reported during 1884-1944; they are listed in Table I.

Based on his critical evaluation of the evidence presented by each of the authors for the identity of these alcohols, Knol concludes that: ". . . exceedingly few reliable results have been obtained by the classical methods of analysis. The main reason is that the aliphatic wool wax alcohols are a mixture of many complex substances for which only modern methods of analysis can give reliable results . . . ."

The investigation of isocholesterol was hampered by the lack of an adequate method to separate isocholesterol from wool wax alcohols. Such a method became available in 1926 when Lifschutz and Vietmeyer (8) reported that isocholesterol does precipitate from a hot solution of methanol at ca. 55 C. Shortly afterwards Drummond and Baker (9) precipitated a mixture of cholesterol and isocholesterol from methanol at room temperature and separated the cholesterol from isocholesterol by the digitonin method. The recrystallized isocholesterol is described by Drummond et al. as follows: "Its color reactions have been examined. In some respects they resemble those of certain members of the sterol group. It is unsaturated, but the degree of unsaturation has not been established . . . . Its analysis indicated a smaller carbon content than would be required for an isomeride of cholesterol, $C_{27}H_{46}O$, and further work will be necessary before a satisfactory formula

TABLE I

Various Aliphatic Alcohols Reported as Constituents of Wool Wax Alcohols (1884-1944)

Alcohol	Formula	Author[a]
n-Octanol	$C_8H_{17}OH$	Guetta
Decenol	$C_{10}H_{19}OH$ (unsaturated)	Darmstadter & Lifschutz
Hendecenol	$C_{11}H_{21}OH$	Darmstadter & Lifschutz
Dodecenol	$C_{12}H_{23}OH$ (unsaturated)	Lower
Lanolin Alcohol	$C_{12}H_{23}OH$ (unsaturated)	Marchetti
n-Hexadecanol	$C_{16}H_{33}OH$ (cetyl alcohol)	Cochenhausen
Lanooctadecanol	$C_{18}H_{37}OH$	Kuwata & Katuno
Oleine Alcohol	$C_{18}H_{35}OH$	Linder
Lanyl Alcohol	$C_{21}H_{40}(OH)_2$	Kuwata & Katuno
Carnaubyl Alcohol	$C_{24}H_{49}OH$	Darmstadter & Lifschutz
Ceryl Alcohol	$C_{26}H_{53}OH$	Various Authors
Isoceryl Alcohol	$C_{27}H_{55}OH$	Bourdet
Myricyl Alcohol	$C_{30}H_{61}OH$	Bourdet
Melissyl Alcohol	$C_{31}H_{63}OH$	Bourdet
Unsaturated Alcohols		Darmstadter & Lifschutz

[a] References to authors can be found in Knol's review (7).

can be assigned to the substance. Meanwhile, we recommend that the misleading name isocholesterol be replaced by the less commital lanosterol . . . ."

Shortly afterwards Windaus and Tschesche (10) attempted to identify the components of isocholesterol. To this end, they separated crude isocholesterol from wool wax alcohols using methanol as the solvent, converted it to an acetate, and fractionally crystallized the acetate from ethyl acetate. This procedure led to the isolation of an 8% fraction which was called Agnosterol ($C_{30}H_{48}O$). The major fraction was named Lanosterol ($C_{30}H_{50}O$), the same term as used by Drummond et al. to describe the total isocholesterol. Since agnosterol and lanosterol contain 30 carbon atoms, Windaus et al. concluded that these two constituents of isocholesterol are not derived from cholesterol. Both are dextrorotatory and unsaturated: lanosterol has two double bonds, while agnosterol has three double bonds. Both give color reactions with the Lieberman-Burchard reagent.

A further important contribution to the identification of isocholesterol's constituents was made by Ruzicka, Rey and Muhr (11) in 1944. These investigators used an acetone extract of wool wax alcohols from which they separated the aliphatic alcohols by column chromatography. From the remaining alcohols Ruzicka et al. removed cholesterol using boiling methanol and converted isocholesterol to an acetate which was fractionally crystallized. This method led to the isolation and identification of two more constituents of isocholesterol:

dihydrolanosterol ($C_{30}H_{52}O$)
dihydroagnosterol ($C_{30}H_{50}$ O)

Agnosterol was found to be present in trace amounts.

Very little work which is devoted to separation from wool wax alcohols of any sterols besides cholesterol can be traced during 1900-1944. The only significant work in this field was published in 1930 by Behring, Hummel, and Schoenheimer (12): these authors claim that wool wax alcohols contain a few percent of saturated sterols such as cholestanol (dihydrocholesterol).

IDENTIFICATION OF THE ALIPHATIC WOOL WAX ALCOHOLS

The year 1945 is an important date in the study of the composition of wool wax alcohols. It was during 1945 that: 1. Daniel, Lederer, and Velluz (13) published the results of the complete chromatographic separation of wool wax alcohols; 2. Weitkamp (14), by his work on structure-elucidation of wool wax fatty acids, proved that more sophisticated methods will have to be used in the study of wool wax components because of the exceptional complexity of the material.

Daniel et al. (13) carried out a separation of wool wax alcohols on aluminum oxide by passing through the adsorbent a petroleum ether solution of the alcohols and eluting the column with petroleum ether, benzol, ether, mixture of the above solvents and acetone. A most interesting finding in this study is the presence of 0.2% hydrocarbons in wool wax alcohols which was found in the first chromatographic fractions. The claim is made that the hydrocarbons are not impurities acquired during processing; they are present in the wax when extracted from the wool.

The composition of wool wax alcohols as found by Daniel et al. is listed in Table II.

According to Daniel, the cholesta-3,5-diene-7-one is not a constituent of wool wax; it is being formed during the hot saponification of the wool wax.

What is listed in Table II as ceryl alcohol is probably a mixture of several aliphatic alcohols.

Weitkamp (14) confined himself to the study of the composition and structure of the wool wax acids. He was able to prove the complexity of the wool wax acids by establishing the presence of normal-, hydroxy- and branched chain (iso and anteiso) fatty acids. Weitkamp's work had a great impact on the subsequent studies of wool wax constituents by inducing various investigators to use modern isolation and identification techniques.

A few years after Weitkamp's work was published, a new fractionation method became known which had a great impact on the identification of the components of wool wax alcohols.

In a German patent application, 12438, 1940, Bengen reported the ability of urea to complex with normal aliphatic chemicals, but not with branched chain or cyclic chemicals.

Bengen's work became known after World War II when

TABLE II

Composition of Wool Wax Alcohols (Daniel, 1945)

Component	Weight %
Insoluble in acetone (predominantly ceryl alcohol)	15-20
Hydrocarbons	0.2
Unsaturated dextrorotatory ketone	0.05
Cholesta - 3,5 - diene - 7 - one	0.6
Cholesterol	20-30
β-Cholestanol	2-6
Isocholesterol	20-26
Dextrorotatory product (last filtrate)	5

TABLE III

Composition of Aliphatic Wool Wax Alcohols (Murray et al. 1952, 1955)

Aliphatic alcohols	Number of identified alcohols	Chain-length	Chain length of major fractions	% of wool wax alcohols
Monoalcohols - normal	7	C_{18} - C_{30}	C_{26} - C_{18} in decreasing amount	2-3%
Monoalcohols - iso	4	C_{20} - C_{26}		18-19% (1:1)
Monoalcohols - anteiso	6	C_{17} - C_{27}		
1,2 Diols - normal				
1,2 Diols - iso				1.5%
1,2 Diols - anteiso				
Total				22.5%

TABLE IV

Composition of Unsaponifiable Matter of Wool Wax Samples (Horn, 1958)

	Unsap. matter of inner fleece	Unsap. matter of outer fleece	Hartolan[a]
% Hydrocarbons	0.9	0.5	1.4
% Urea-complexing alcohols	14.7	23.7	17.0
% Isocholesterol	44.2	7.3	15.0
% Cholesterol	32.5	8.0	16.0
% Diols	3.2	2.4	4.0
% Unresolved resinous residue	3.0	53.5	41.0
Total recovered	98.5	95.4	94.4

[a] Commercial wool wax unsaponifiables.

the Technical Missions studied the German technical literature which was not available to the Allied countries during the war. No time was wasted to check this method and its utility. Truter (15) realized soon the importance of this method for the separation of wool wax components and published in 1951 a study of "Urea Complexes of Some Branched Chain and Cyclic Esters."

The complex which urea is forming with straight chain compounds is of the clathrate-type. "The most important requirement for the formation of a urea clathrate compound is that the endocytic component should have a straight chain. As in all clathrate compounds, the chemical class of the components to be enclosed does not matter. Thus, urea will form complexes with hydrocarbons, ethers, alcohols, aldehydes, ketones, acids, esters, nitriles, amines, halides, etc., and with molecules containing one or more functional groups . . . ." (Truter [16].)

During 1951, Tiedt and Truter (17) published the results of the fractionation of a commercial wool wax alcohol ("Hartolan") using urea. These investigators found that 20% of Hartolan formed an additional compound with urea. The alcohols were recovered from the complex, acetylated and complexed again with urea: one-fifth of the acetates did not form urea complexes, this fact leading to the belief that these alcohols must have secondary alcohol groups which yield branched chain esters on acetylation.

The remaining complexed alcohols were fractionated from benzene-ethanol and recovered. The five normal monoalcohols which were identified by Tiedt and Truter range in chain length from C_{18} to C_{26}.

The previous investigation was reported in more detail by Tiedt and Truter in 1952 (18). In addition to n-alcohols, they see some evidence for the presence of a group of optically active alcohols.

While Tiedt and Truter's work was carried out at the Textile Chemistry Laboratory of the University of Leeds, similar work was going on at the South African Council for Scientific Research and the Australian Commonwealth Scientific and Industrial Research Organization.

Horn and Hougen (19) reported in 1951 the presence of alkane-1,2-diols in wool wax alcohols. These were "isolated from that portion of the unsaponifiable material which is relatively strongly adsorbed in activated alumina from an ether solution (and) by fractional distillation of the acetates of this material through a small spinning-band fractionating column. The five main fractions were crystallized to purity from methanol . . . and the respective acetates saponified to yield the corresponding diols." The molecular weight of the diols was determined by oxidation with periodic acid: each diol yielded about one equivalent of formaldehyde. The five diols range from $C_{16}H_{34}O_2$ to $C_{24}H_{50}O_2$.

Horn and Hougen isolated ca. 2% diols from "Hartolan" and 4-5% diols from the unsaponifiable of the wax extracted from a local Merino fleece.

The same investigators found a considerable depression in the melting point of a synthetic n-octadecane-1,2-diol with the corresponding natural diols. It therefore seemed to them likely that "the alkyl chains of these natural diols may have a single methyl branch as occurs in the iso- and anteiso- fatty acids present in wool wax."

Thus we have here the interesting indication that there may exist a structural similarity between the wool wax fatty acids and the aliphatic portion of wool wax alcohols.

In order to establish the structure of the diols, Horn and Hougen (20) oxidized the individual diols with lead tetraacetate in a stream of air and obtained acids which were compared with synthetic acids. This method, in addition to infrared studies of the diols, established the structure of one normal diol and four iso diols.

Von Rudloff (21) attempted in 1951 to use the urea complexing method to separate the aliphatic alcohols from the total wool wax alcohols. Von Rudloff was able to separate 21% of the total alcohols and a small amount of dihydric alcohols. However, Von Rudloff was not able to separate the monohydric alcohols into individual components.

Murray and Schoenfeld (22) attempted during the early fifties to fractionate the aliphatic wool wax alcohols as acetates using Weitkamp's low pressure distillation technique (14). The crude aliphatic alcohols were derived from wool wax which was extracted from Merino wool and saponified by the Barnes et al. method (23). The total recovered alcohols (44% of the wool wax) were freed from the triterpene alcohols by crystallization from methanol

TABLE V

Analysis of Wool Wax Samples (Horn, 1958)

Wax samples	Sap value	Acid value	Ester value	% Unsap. matter	% α-keto-ene in Unsap. matter
Wool from Merino ewe Transvaal					
A. Inner fleece	92	4	88	51	5
B. Outer fleece	123	17	106	39	24
Wool from Merino ewe Cape Province					
C. Inner fleece	104	5	99	51	1.0
D. Inner fleece stored in the dark, 9 months	102	6	96	48	10
E. Outer fleece	112	11	101	---	15
F. Inner fleece exposed to the weather, 9 months	148	38	110	25	19
G. Commercial wax by acid cracking	120	34	86	38	---

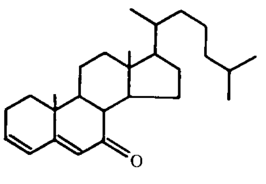
and subsequently from cholesterol by Hackman's zinc chloride method (24). At this point, the composition of the total alcohols was found to be as follows:

Triterpene alcohols	20%
Cholesterol	30%
Residual alcohols	50%

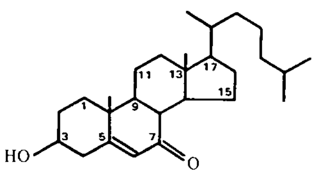
The residual alcohols were converted to acetates and these were fractionally distilled using a column of the spinning-band type. An involved distillation scheme, urea complexing, and column chromatography led to the isolation of 10 alcohols which were identified by oxidation to the corresponding acids. These in turn were identified using known iso- and anteiso- acids.

TABLE VI

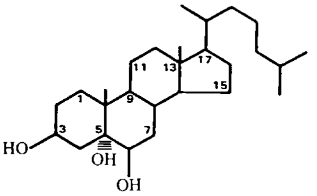
Structural Formulae of Autoxidation Products



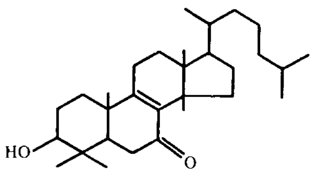
Cholesta-3,5-diene-7-one



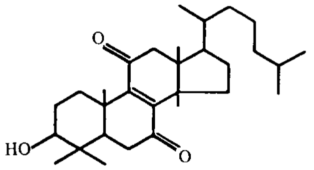
7-Oxocholesterol



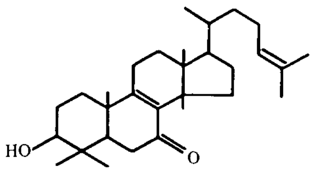
Cholestane 3β, 5α, 6βtriol



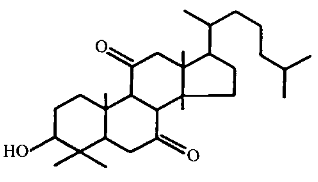
3β-Hydroxylanost-8-ene-7-one



3β-Hydoxylanost
-8-ene-7:11-dione



3β-Hydroxylanost
-8,24-diene-7-one



3β-Hydroxylanost-7:11-dione

Murray and Schoenfeld were able to identify six anteiso-alcohols (C_{17} to C_{27}) and four iso-alcohols (C_{20} to C_{26}), but could not isolate any normal alcohols. The amount of the identified alcohols represents 22.5% of the total alcohols. The diols were estimated to be 1.5% of the total alcohols.

Because of their failure to identify the normal aliphatic alcohols, Murray and Schoenfeld (25) fractionated the acetylated unsaponifiable with urea. The acetylated aliphatic alcohols were converted to isobutyrates and these were again fractionated with urea. The recovered normal alcohols were converted to acetates and fractionally distilled. This step was followed by the recovery and recrystallization of the alcohols. Seven alcohols (C_{18} to C_{30}) were identified as normal alcohols by their m.p., crystal spacing, the b.p. of the acetates, and microoxygen analysis.

Based on Murray and Schoenfeld's total work, the composition of the aliphatic wool wax alcohols appears as listed in Table III.

At this point in the study of aliphatic wool wax alcohol, it has been definitely established that there is a structural similarity between the aliphatic wool wax alcohols and the wool wax acids. This can be seen from the following comparison of the structural characteristics of the acids and aliphatic alcohols:

Constituents of	
Wool wax acids	Wool wax aliphatic alcohols
n - acids	n - alcohols
iso - acids	iso - alcohols
anteiso - acids	anteiso - alcohols
α - hydroxy - n - acids	n - alkane - 1,2 diols
α - hydroxy - iso acids	iso - alkane - 1,2 diols

Since the presence of cholesterol and triterpene alcohols in wool wax alcohols has been established before 1945, the attention of some investigators was turned to the identification of the autoxidation products in wool wax alcohols. At the same time, advantage was being taken of new analytical methods such as gas chromatography, mass spectroscopy, and TLC.

IDENTIFICATION OF AUTOXIDIZED WOOL WAX ALCOHOLS

Horn and Ilse (26) published an article in 1956 dealing with the autoxidation of wool wax. Since the analysis of both the acid fraction and the unsaponifiable was about complete at that time, Horn and Ilse felt that it "now remains only to identify the autoxidation products which are normal constituents of the commercial product."

Horn and Isle's findings were published in greater detail

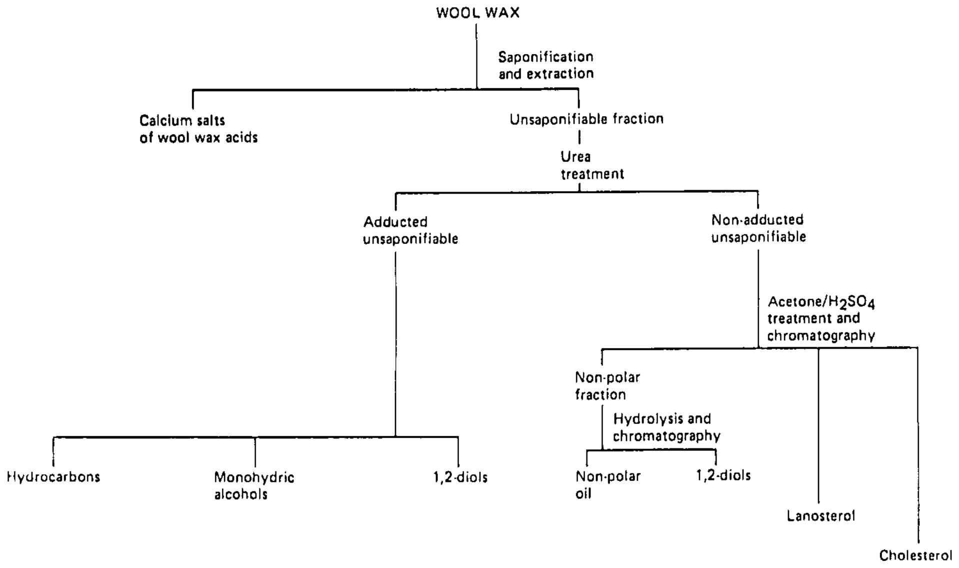


FIG. 1. Fractionation of wool wax into classes of constituents (Downing et al. 1960).

during 1958 by Horn (27). The unsaponifiable material which Horn used in his investigation derived from: 1. freshly secreted Merino wax obtained from the inner third of wool fiber and the outer third of the same fiber; 2. commercial wax.

The α-keto-ene system, which results from autoxidation, was determined by infrared absorption at 5.95μ, using 7-ketodihydrolanosterol as a standard.

The composition of the unsaponifiable materials can be found in Table IV.

The acid value, sap value and ester value of the original wool wax samples, as well as the % unsaponifiable and % α-keto-ene in the unsaponifiable are listed in Table V.

The data in Table IV and V suggest the following conclusions: 1. autoxidation reduces drastically the % cholesterol and isocholesterol in the unsaponifiable; 2. the drop in % cholesterol and isocholesterol is parallel to an increase in resinous residue; 3. autoxidation leads to an increase of the acid and ester values of the wool wax and a decrease in the % unsaponifiable.

The methylene groups adjacent to the double bonds in the wax are, according to Horn, the site of primary autoxidation.

It is Horn's conclusion that "besides (the) hydrocarbons, the unsaponifiable of Merino wool wax contains, as its major components, the . . . aliphatic alcohols and diols, lanosterol, dihydrolanosterol, and cholesterol. Other substances, such as agnosterol, dihydroagnosterol and oxygenated derivatives of cholesterol and lanosterol which have been isolated from the commercial wax and not detected in the fresh unsaponifiable material, are clearly artefacts produced by autoxidation."

The presence of autoxidation products in wool wax alcohols was reported by several investigators. Daniel et al. (13) reported cholesta-3,5-diene-7-one as being formed during hot saponification. Milburn, Truter and Woodford (28) investigated the presence of 7-oxocholesterol which according to Truter (29) ". . . is formed during storage of the wool wax alcohols or their esters."

Besides 7-oxocholesterol, Milburn et al. (28) reported the following autoxidation products in wool wax alcohols: Cholestane - 3β: 5α. 6β triol; 3β Hydroxylanost - 8 - ene - 7 - one; 3β Hydroxylanost - 8 - ene - 7:11 - dione.

Brieskorn and Dertinger (30) reported in 1968 two more autoxidation products in wool wax alcohols: 3β Hydroxylanost - 8,24 - diene - 7 - one; 3β Hydroxylanost - 7:11 - dione.

The presence of the members of the Vitamin D group or their precursors is quite controversial. It does appear to Truter (31) ". . . that wool wax itself contains no precursors of Vitamin D, but that the alcoholic fraction (possibly by auto-oxidation after saponification) does."

It should be noted that the publications dealing with autoxidation products in wool wax or wool wax alcohols contain numerous analytical methods for the identification of these artifacts.

In Robert P. Cook's monograph, "Cholesterol," (Academic Press, 1958) one can find ample information concerning the oxidation of cholesterol (pp. 76-77). After reviewing the various autoxidation products derived from cholesterol and the mechanism by which they are formed, the author states that ". . . the view held generally now is that when large amounts of these substances are isolated from natural sources, they are probably artifacts, but that small amounts are indeed present in tissues, where they are intermediates in cholesterol metabolism. (cf. Prelog et al. 1943; Haslewood, 1944.)."

The structural formulae of possible autoxidation products in wool wax alcohols can be found in Table VI.

COMPLETE ANALYSIS OF WOOL WAX ALCOHOLS

An investigation of wool wax constituents which appeared in 1960 and was authored by Downing, Kranz, and Murray (32) is an in-depth study of both the fatty acids and alcohols using gas chromatography. Starting with fresh wool wax, Downing et al. proceeded with saponification

TABLE VII

Composition of the Unsaponifiable Fraction of Wool Wax (Downing et al. 1960)

Unsaponifiable fraction (51.8% by wt. of wax)	Weight %	Horn and Ilse (1956) Weight %
Urea-adducted	(13.7)	14.7
Hydrocarbons	0.3	0.9
Monoalcohols	9.5	—
1,2-Diols	1.5	—
Not urea-adducted		
Cholesterol	31	32.5
Lanosterol	44	44.2
1,2-Diols	5	3.2
Undetermined	8.7	4.5

TABLE VIII

Composition of Wool Wax Alcohols (Downing et al. 1960)

Components	Number of identified alcohols	Chain length	Chain length of major fractions	% of wool wax alcohols
Monoalcohols, normal	8	C_{16} - C_{30}	C_{20}, C_{22}, C_{24}, C_{26}	1.8
Monoalcohols, iso	7	C_{16} - C_{28}	C_{20}, C_{26}	3.5
Monoalcohols, anteiso	9	C_{17} - C_{33}	C_{25}, C_{27}, C_{29}	4.2
1,2-diols, normal	10	C_{14} - C_{24}	C_{16}	1.5 (urea adducted)
1,2-diols, iso	6	C_{16} - C_{26}	C_{18}, C_{20}, C_{22}, C_{24}	5.0
1,2-diols, anteiso	6	C_{15} - C_{25}	C_{21}, C_{23}	
Cholesterol				31
Lanosterol				44
Hydrocarbons				0.3
Undetermined				8.7
Total				100.0

TABLE IX

Composition of Wool Wax Alcohols (Fawaz et al, 1974)

Components	Number of identified alcohols	Chain length	Chain length of major fractions	% of wool wax alcohols[a]
Monoalcohols, normal	16	C_{14} - C_{34}	C_{24}, C_{26}	1.6
Monoalcohols, iso	11	C_{14} - C_{36}	C_{20}, C_{22}, C_{26}	6.5
Monoalcohols, anteiso	11	C_{17} - C_{35}	C_{21}, C_{25}, C_{27}	9.0
1,2 diols, normal	14	C_{12} - C_{25}	C_{16}, C_{18}, C_{20}	0.4
1,2 diols, iso	9	C_{14} - C_{30}	C_{18}, C_{20}, C_{22}, C_{24}	5.9
1,2 diols, anteiso	8	C_{15} - C_{29}	C_{21}, C_{23}	2.4
Cholesterol				38
Dihydrocholesterol				trace
Cholesta-3,5-diene-7-one				3.6
Lanosterol				14.8
Dihydrolanosterol				10.3
3-hydroxy-lanosta-8-ene-7-one				1.6
Hydrocarbons				5.9
Undetermined				
Total				100.0

[a] Calculated from Fawaz's data.

and fractionation which involved urea complexing and column chromatography for the unsaponifiable. The fractionation method as used by Downing can be found in Figure 1.

The quantitative results derived from the fractionation method in Figure 1 can be found in Table VII.

In order to investigate the composition of each mixture of aliphatic alcohols, these were converted to iodides and reduced with lithium aluminum hydride to hydrocarbons. The hydrocarbon mixtures were gas chromatographed, and the identities of the individual corresponding alcohols were established.

As can be seen from the data in Table VII, Downing's figures for the composition of the unsaponifiable match closely the figures given by Horn. The composition of wool wax alcohols was calculated from Downing's data on hydrocarbons derived from the wool wax fractions (Table VIII).

What appears from Table VIII is as follows.

1. Monoalcohols, normal: Besides the seven C_{18} to C_{30} alcohols reported by Murray (25), Downing reports the presence of a small amount of C_{16} alcohols and small amounts of three alcohols with odd carbon numbers (C_{19}, C_{21}, C_{23}).
2. Monoalcohols, branched: Besides the branched alcohols reported by Murray (22), Downing found six more constituents of this series.
3. Diols: Besides the normal- and iso-diols reported by Horn and Hougen (19,20), Downing claims to have found some anteiso-diols.

As for the similarity between the acid and aliphatic alcohols fraction, Downing claims on the basis of the chromatograms that "... the monohydric alcohols and non-hydroxylated acid fractions, as well as the 1,2 diols and α-hydroxylated acid fractions have somewhat similar compositions above C_{20}, but are quite different below this carbon number."

The gas chromatography of the hydrocarbons which derived from the various fractions of the aliphatic alcohols offers great advantages over previously used methods because of the stability and rapid elution of the hydrocarbons and the availability of reference hydrocarbons.

Recently, Fawaz, Chaigneau and Puisieuz (33,34) published the results of an extensive analysis of the unsaponifiable derived from lanolin. The fractionation was carried out by separating the alcohols into two fractions with digitonin followed by chromatography of each fraction on silica gel. This method established the composition of the alcohols as follows:

Aliphatic monoalcohols	17.1%
Aliphatic alkane-diols	8.7%
Sterols and Triterpene alcohols	68.3%
Unidentified and polyols	5.9%

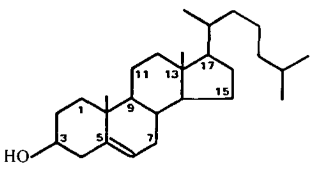
On further investigation using gas chromatography, mass spectroscopy and TLC, the authors identified 38 monoalcohols, 31 alkane-diols and 68.3% of sterols and triterpene alcohols.

The monoalcohols consist of normal - (9.3%), iso - (37.8%) and anteiso - (52.9%) alcohols.

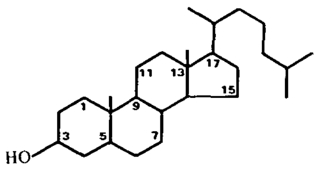
The 1,2 - alkane-diols consist of normal (4.5%), iso (67.5) and anteiso (2.8%) diols.

TABLE X

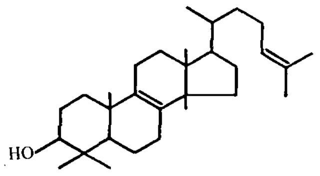
Structural Formulae of Sterols and Isocholesterol Components in Wool Wax Alcohols



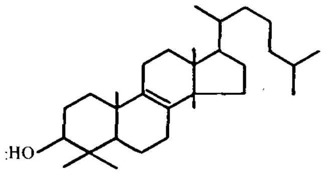
Cholesterol $C_{27}H_{46}O$



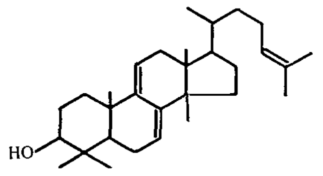
Dihydrocholesterol $C_{27}H_{48}O$



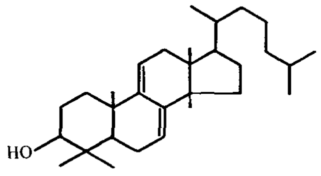
Lanosterol $C_{30}H_{50}O$



Dihydrolanosterol $C_{30}H_{52}O$



Agnosterol $C_{30}H_{48}O$



Dihydroagnosterol $C_{30}H_{50}O$

The composition of the lanolin alcohols can be found in Table IX.

The authors conclude that the only real constituents in the group of sterols and triterpene alcohols are cholesterol, lanosterol and dihydrolanosterol. No agnosterol or dihydroagnosterol were found in this group. Any other materials identified in this group are considered as autoxidation products. These conclusions are similar to the ones made by Horn (27).

The structural formulae of the sterol and isocholesterol components of wool wax alcohols can be found in Table X.

SUMMARY

The efforts made during the past 25 years by various investigators to determine the composition of wool wax alcohols produced detailed data for both the aliphatic and cyclic alcohols.

While the total amount of aliphatic alcohols is estimated to be 22% of the unsaponifiable, the number of the components of aliphatic alcohols reported between 1955 and 1974 rose from 17 to 69; the more detailed results are of course due to the use of more sophisticated analytical methods.

In our attempts to present the average composition of wool wax alcohols, we could not overlook the fact that each investigator uses a wool wax of his choice which he saponifies by his preferred method, separates and fractionates the alcohols according to his own scheme, and identifies the components using the most advanced analytical methods. In view of the above, it is understandable that the averaging of the reported results for the percent of various alcohols in the unsaponifiable can at best reflect an approximate result. Nevertheless, the results reported by Murray et al. (1955), Horn (1958), Downing et al. (1960), and Fawaz et al. (1974) do have this in common: they were obtained from wool wax alcohols which these authors prepared themselves. Also, with the exception of Fawaz, who used lanolin as a starting material, the other authors extracted their wool wax from the wool. Because of the care which every one of the authors gave to each step, the resulting wool wax alcohols had only a small amount of autoxidized material. It would therefore appear that the percentages given by these authors for the various alcohols are close to the percent composition of the wool alcohols originally present in a wool wax containing very little, if any, autoxidized products.

With this in mind, we proceeded to average the percent composition using the data presented by Murray, Horn, Downing, and Fawaz. These averages can be found in Table XI.

As it will appear from Table XI, cholesterol and the triterpene alcohols (also known as isocholesterol) are the major components of wool wax alcohols. They are present in about equal amounts and together they represent ca. 72% of the total alcohols. The aliphatic monoalcohols as well as the alkane 1,2-diols are predominantly branched chain materials; the total aliphatic portion represents ca. 22% of the total alcohols. The hydrocarbons form ca. 1% of the alcohols, while the percent of autoxidation products will depend on the quality of the original wool wax, saponification procedure, and method for the separation of the alcohols.

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TABLE XI

Summary of the Average Composition of Wool Wax Alcohols (1955-74)

Components	Chain length[a]	% of wool wax alcohols
Normal mono-alcohols	C_{14} - C_{34}	2
Iso mono-alcohols	C_{14} - C_{36}	13 (1:1)
Anteiso mono-alcohols	C_{17} - C_{35}	
Normal alkane 1,2-diols	C_{12} - C_{25}	1
Iso alkane 1,2 diols	C_{14} - C_{30}	6 (1:0.5)
Anteiso alkane 1,2 diols	C_{15} - C_{29}	
Cholesterol		34
Lanosterol		38
Dihydrolanosterol		
Hydrocarbons		1
Autoxidation products and undetermined		5
Total		100

[a] Fawaz et al.

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