Wool Wax Hydrocarbons: A Review

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ABSTRACT

A review of the literature on wool wax hydrocarbons reveals that the hydrocarbons represent about 0.5% of wool wax and that they consist of a large number of normal and branched homologs. This, in turn, shows a structural similarity between the hydrocarbons and the wool wax acids or wool wax aliphatic alcohols: all three materials contain normal, iso and anteiso series. The wool wax hydrocarbons also contain highly branched alkanes as well as cycloalkanes.

PRELIMINARY INVESTIGATIONS (1945-1958)

Daniel, Lederer and Velluz (1) were the first to report in 1945 the presence of hydrocarbons in the unsaponifiable portion of wool wax. The hydrocarbons were separated from 3 unsaponifiables derived from commercial wool wax and 1 unsaponifiable derived from a wool wax which the authors extracted from wool. The separation of the hydrocarbons from the unsaponifiable material was accomplished by column chromatography on aluminum oxide.

The hydrocarbons were found to represent 0.2% of the unsaponifiable and Daniel suggested these hydrocarbons are naturally occurring components of the original wool wax.

Martin and Garcia (2) carried out column chromatography studies of wool wax alcohols during 1954 and confirmed Daniel's conclusion that wool wax contains hydrocarbons.

Horn (3) separated the hydrocarbons from the unsaponifiable portion of the inner fleece wax, the outer fleece wax and a sample of commercial wool wax alcohols. The separation was done by column chromatography on aluminum oxide. The quantitative results of this separation are listed in Table I.

The hydrocarbons from the commercial wool wax unsaponifiables (Table I) were rechromatographed and next distilled in a microspinning band fractionating column at 1 mm. The distillation "showed this material to be a complex mixture of saturated and unsaturated hydrocarbons ranging from C_{16} to C_{32}. The possibility exists that this material was contaminated with small amounts of mineral hydrocarbons from the recovery and processing plant used for the manufacture of this commercial product" (3).

COMPLETE ANALYSIS OF WOOL WAX HYDROCARBONS

Downing, Kranz and Murray (4) were the first investigators to gas chromatograph the naturally occurring hydrocarbons which are present in the wool wax unsaponifiable. The wool wax was obtained "from the fleece of a merino ewe which had not been dipped for 3 years and which had worn a canvas covering during the 12 months since the previous shearing. The inner third of the staple was cut off and extracted with hot redistilled commercial hexane" (4).

The wax from the inner third of the staple was saponified by the Barnes et al. method (5) and the bulk of the unsaponifiable material removed with hot hexane. An additional small amount of unsaponifiable material was removed by extraction of the calcium soaps with acetone.

The combined unsaponifiable fraction (51.8% of the wool wax with hydroxyl value 152) was complexed with urea and the adducted portion chromatographed on aluminum oxide: the hydrocarbon fraction was found to represent 0.3% of the unsaponifiable. This fraction was gas chromatographed and the gaseous stream passed through a column containing Linde Molecular Sieve Type 5A, which absorbed the normal hydrocarbons. The number and chain length of the normal, iso- and anteiso-hydrocarbons as found by Downing et al. are listed in Table II.

The isohydrocarbons in Table II are homologs of even carbon numbers whereas the anteisohydrocarbons are homologs of odd carbon numbers.

Mold, Means, Stevens and Ruth (6,7) became interested in Downing's work because they found anteiso series of paraffin hydrocarbons in tobacco leaf wax. Mold et al. started with a hexane solution of centrifugal wool grease that was extracted with aqueous methanol. The hydrocarbons were separated from the dried hexane solution by column chromatography on aluminum oxide: the hydrocarbon fraction was found to represent 0.53% of the starting wool grease. At this point, Mold et al. were probably the first investigators to work with a hydrocarbon fraction that was separated directly from wool grease instead of from the unsaponifiable fraction.

The hydrocarbons were first fractionated by complexing with urea in n-propyl alcohol; this step separated the "highly branched" hydrocarbons from the normal- and "slightly branched" hydrocarbons. The hydrocarbons from the urea complex were dissolved in isooctane

TABLE I

Percent Hydrocarbons in Wool Wax Unsaponifiables (3)

Unsaponifiable matter	% Hydrocarbons
Unsap. matter of inner fleece wax	0.9
Unsap. matter of outer fleece wax	0.5
Commercial wool wax unsaponifiables	1.4

TABLE II

Naturally Occurring Hydrocarbons in Wool Wax Unsaponifiable

Hydrocarbons	Number	Chain length
Normal hydrocarbons	21	C_{14}-C_{32} C_{13}-C_{33}
Isohydrocarbons	10	C_{14}-C_{32}
Anteisohydrocarbons	8	C_{15}-C_{29}
Total	39	

and shaken with Linde Molecular Sieve Pellets 5A; this step separated the normal hydrocarbons from the "slightly branched" hydrocarbons. The percentages of each group of hydrocarbons can be found in Table III.

The 74% recovery from the fractionation procedure indicates that the separation of the hydrocarbons from some complexes was incomplete.

The identity of the hydrocarbons in each group was established by gas liquid chromatography (GLC) and mass spectrometry (MS): (a) the 24 normal hydrocarbons (including those in trace amounts) had chain lengths varying from C_{13} to C_{35}. The major components were C_{19}, C_{20} and C_{29}. This homologous fraction consisted of a low-molecular-weight group (C_{13} to C_{25}) "with even and odd numbers of carbon atoms in equivalent amounts" and a high-molecular-weight group (C_{25} to C_{35}) "consisting principally of compounds with odd numbers of carbon atoms" (b) the "slightly branched" hydrocarbons (the ones which complexed with urea) were found to consist of series I, II and III based on their elution time. The components of series I were in trace amounts. In series II (28 hydrocarbons with chain lengths from C_{17} to C_{44}) the methyl alkanes have the methyl group on carbon 8, 11, 12 or 13, whereas in series III the methyl alkanes have the methyl group on carbon 2 or 3. Besides these methyl alkanes, series II and III contain cycloalkanes; and (c) the "highly branched" hydrocarbons—the most abundant group of hydrocarbons—were found to form a very complex mixture. One component of this mixture was found to be pristane (2,6,10,14-tetramethylpentadecane, $C_{19}H_{40}$). This component was previously found to be present only in the wax of marine origin.

Simmonds, Nooner, Zlatkis and Oro (8) used wool wax extracted from the wool of Texas live adult sheep. The wool wax was fractionated on a silica gel column which was eluted with n-heptane. The hydrocarbon fraction was analyzed by gas chromatography (GC) and MS.

According to Simmonds et al., the major components of the n-alkanes are C_{29} and C_{31}. Besides the previously reported two groups of n-alkanes, there is a third group (C_{11} to C_{15}) with a slight even carbon predominance. Besides pristane, these authors claimed to have identified phytane (2,6,10,14-tetramethylhexadecane).

Fawaz, Chaigneau, Giry and Puisieux (9) published "Mass Spectrometry Study of Lanolin Hydrocarbons." These authors separated the hydrocarbon fraction from a French pharmaceutical-grade lanolin by column chromatography using silica gel: the hydrocarbon fraction was found to represent 0.57% of the original lanolin.

Using urea and molecular sieves, the hydrocarbons were separated into normal-, "slightly branched" and "highly branched" fractions. Each fraction was investigated using GC and MS. The results of this investigation suggested: (a) the normal hydrocarbons (16% of the total hydrocarbons) have a chain length of C_{13} to C_{42}. There are also trace amounts of C_9 to C_{12} and C_{43} to C_{50}. The major fractions are C_{19} and C_{31}. Fawaz et al. confirmed Mold's results that the normal hydrocarbons consist of 2 distinct families: C_{13} to C_{24} and C_{25} to C_{42}; (b) the "slightly branched" hydrocarbons

TABLE III

Naturally Occurring Hydrocarbons in Wool Wax (6,7)

Hydrocarbons	% of total hydrocarbon fraction
Normal hydrocarbons	16
"Slightly branched" hydrocarbons	8
"Highly branched" hydrocarbons	50
Total recovered	74

(7% of the total hydrocarbons) consist of 3 series, I (trace amounts), II and III based on the order of elution. This fraction contains methyl alkanes, cyclohexyl alkanes and phenyl alkanes. The individual members vary from C_{16} to C_{48}; and (c) the "highly branched" hydrocarbons (77% of the total hydrocarbons) vary from C_{16} to C_{45}. They consist of paraffinic hydrocarbons (similar to pristane), cyclohexyl alkanes and phenyl alkanes. The chromatogram of this fraction shows 90 pics.

Fawaz, Choix, Miet and Puisieux (10) claimed the complete recovery of the normal hydrocarbons from the molecular sieve complex requires the treatment of the complex with hydrochloric acid followed by an extraction with hexane.

Wool wax contains normal-, iso- and anteisohydrocarbons—an interesting fact—since wool wax acids and the aliphatic portion of wool wax alcohols also contain normal, iso and anteiso series (11, 12).

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