TABLE II
Increase In Ingredient Cost of Mixed Feeds When Fat Is Included

Price of Fat per pound	Increase in Ingredient Cost in Dollars per Ton for Various Levels of Fat					
	1%	2%	3%	4%	5%	10%
3¢	0	0	0	0	0	0
4¢	$0.20	$0.40	$0.60	$0.80	$1.00	$ 2.00
5¢	0.40	0.80	1.20	1.60	2.00	4.00
6¢	0.60	1.20	1.80	2.40	3.00	6.00
7¢	0.80	1.60	2.40	3.20	4.00	8.00
8¢	1.00	2.00	3.00	4.00	5.00	10.00
9¢	1.20	2.40	3.60	4.80	6.00	12.00
10¢	1.40	2.80	4.20	5.60	7.00	14.00

turing cost. Feeders however are reasonable people and are willing to pay higher prices for better quality feeds. Upon proof of quality by feeding in their own feedlots, resales may be expected. Data of the type presented above plus the improvements in physical characteristics should suffice to introduce fats into our mixed feeds on a wide scale. Whether it will become a permanently popular feedstuff remains to be seen. Much may depend upon cooperation between the fat and feed industries and upon prices which are in line with the nutritive value of the fats. Under favorable circumstances the potential use of fat is enormous. If we accept estimates of the total volume of commercial mixed feeds in this country of 35 million tons, a 1% enrichment of all feeds with fat would utilize 700,000,000 pounds of fat. At 3%, an amount which most feeds will carry without becoming at all greasy, over 2 billion pounds could be used. When this is compared with the estimated production of inedible tallows and grease for 1951, 2.25 billion pounds, the possible significance of current trends may be appreciated.

Summary

Fats are nutritious; they improve physical characteristics of feeds, and they have shown their value when used in practical tests. They present manufacturing problems, but they also sometimes contribute to the ease and efficiency of feed mixing. If their prices remain within the range which the feed industry can afford, fats should become common feedstuffs and should be used in large volume.

The Aliphatic Woolwax Alcohols. A Review

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WOOLWAX is a mixture of esters of higher fatty acids with higher alcohols. The alcohols may be divided into three classes: sterols, triterpene alcohols, and aliphatic alcohols. Although much is now known about the composition and structure of the fatty acids, sterols, and "triterpene alcohols,"[1] this is not the case with the aliphatic alcohols, which have not had the same extensive study which Weitkamp (24) has made of the fatty acids.

Recently investigations with urea adduct have been published by Truter (28) and von Rudloff (29); Horn and Hougen (30) have had results with chromatography whereas Murray and Schoenfeld (35) are engaged in analysis by low pressure fractional distillation. The results of these modern analyses are very remarkable and will be discussed later.

Moreover it is obvious that in several reviews in recent years the facts, available from literature, have not always been critically summarized. In some cases even corrections of wrong results or wrong conclusions published long ago have been overlooked! It is the purpose of this article to draw attention to this situation and to remove some of the misunderstandings. As each alcohol is considered, the validity of the available information will be critically examined. They will be dealt with in sequence of increasing molecular weight.

n-Octanol. $C_8H_{17}OH$. In 1887 Guetta (3) announced that he had isolated octyl alcohol from the products of distillation of woolwax. Hannau (4) could not confirm this alcohol in distilled woolwax. Lewkowitsch (5) imputed this to the fact that higher alcohols form hydrocarbons when distilled, but he failed to state that this also holds for octyl alcohol. As this alcohol is not mentioned by other investigators, it can be ignored.

Decenol. $C_{10}H_{19}OH$. In 1895 Darmstädter and Lifschütz (7) announced the isolation of an unsaturated alcohol $C_{10}H_{19}OH$. After a year they recalled this communication however (8) as on further investigation the compound proved to be not an alcohol, but lanocerinacidanhydrid. This alcohol has not been mentioned by other investigators so that it was incorrectly included in some recent reviews (22, 23, 26).

Hendecenol. $C_{11}H_{21}OH$, too, was discovered by Darmstädter and Lifschütz (7), who thought it to be the second alcohol in a series of which decenol should be the first and lanolinalcohol the third homologue. After a year however they announced that they doubted the existence of this alcohol, and further information was promised (8) but never published. So this alcohol also, not being mentioned in other publications, was incorrectly included by Warth (26) and Lower (22, 23).

Dodecenol. $C_{12}H_{23}OH$. Lower (22, 23) is also the only reviewer who refers to an unsaturated alcohol with 12 C-atoms besides lanolinalcohol. However no source of information is given so that this compound can be ignored.

Lanolinalcohol. $C_{12}H_{23}OH$. There is much confusion in literature about this alcohol. In 1895 Marchetti (6) announced the isolation from woolwax of an unsaturated alcohol with 12 C-atoms, which he called lanolinalcohol. It did not absorb bromine however and formed 1% of the woolwax (and not 0.1% as Röhmann (12) incorrectly recorded). In 1916 Röhmann (12) described lanocerinacidanhydrid, a substance isolated from carnauba wax by Stürcke (2) in 1884 and from woolwax by Darmstädter and Lifschütz (8) in 1895, and mentions that Lifschütz had told him that lanocerinacidanhydrid was identical

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[1] Ruzicka *et al.* (37, 39) and Curtis c.s. (38) recently demonstrated that the "triterpene woolwax alcohols" have not the structure of triterpene alcohols but the cyclopentanoperhydrophenanthrene skeleton of the sterols, the side chain attached at the same point! The three extra methyl groups however appear to be located like those in the triterpenes.

with the lanolinalcohol of Marchetti. [The comment of Kuwata and Katuno (19) that Darmstädter and Lifschütz had already denied the existence of lanolinalcohol in 1896 is not correct. In the reference given by Kuwata and Katuno, Darmstädter and Lifschütz only remark that decenol previously reported by them was identical with lanocerinacidanhydrid (7).]

Stürcke (2), Darmstädter and Lifschütz (8), Röhmann (12), and later Heiduschka and Nier (13) gave similar descriptions of the lanocerinacidanhydrid found by them, which closely resembled the description of lanolinalcohol by Marchetti. So lanocerinacidanhydrid was not only considered to be decenol (7) but also lanolinalcohol.

On reading moreover that in 1924 Grassow (13), who also isolated lanocerinacidanhydrid, had already stated correctly that Marchetti was the first to isolate this anhydrid and considered it to be an alcohol,[2] it is incomprehensible that Lower (22, 23), Warth (26), Bourdet (20), and Schwartz (17) should include this "alcohol" in their review, the more as it is not mentioned by other investigators.

n-Hexadecanol. $C_{16}H_{33}OH$, or cetylalcohol. By crystallization of the sulfonic acid salts of woolwax alcohols v. Cochenhausen (11) succeeded in separating a product, which was supposed to have been very largely cetylalcohol. The remark of Linder (16) that Cochenhausen definitely identified cetylalcohol in a pure state is strongly exaggerated. Other investigators (5, 12) took the possibility of the presence of cetylalcohol into account but obtained no confirmation of this. Drummond and Baker (14) however succeeded in isolating and identifying an alcohol in a fairly pure state, which they supposed to be pure cetylalcohol:

	Cetylalcohol	Found by D and B
M.p. of alcohol	51°	50-50.5°
M.p. of phenylurethan	73-74	72

It has to be said however that these apparently convincing data are preceded by the information that the substance was obtained from a fraction with a boiling range of 190-230°C. at 3 mm. pressure. Considering that cetylalcohol has a boiling point of ± 170°C. at 3 mm. pressure, it cannot be said with any certainty that Drummond and Baker isolated cetylalcohol. This doubt is strengthened by the fact that Truter (28), who claims to have isolated five aliphatic n-alcohols, mentions C_{18} as the lowest members of the series found by him, nor could Murray and Schoenfeld (34) isolate cetylalcohol by vacuum fractional distillation. Most reviewers (16, 21, 22, 23, 26, 27, 28, 32) who mention cetylalcohol as a woolwax alcohol probably did not appreciate the significance of the high boiling point given by Drummond and Baker.

Lanooctadecanol. $C_{18}H_{37}OH$ was isolated by Kuwata and Katuno (19). It has a melting point of 42-43°C. (n-octadecanol melts at 59°C.). Therefore it has to be considered as an isomeric alcohol of n-octadecanol, suggesting that the aliphatic alcohols may also contain branched-chain molecules, like the woolwax acid fraction. This work has not yet been confirmed by others.

Oleinealcohol. $C_{18}H_{35}OH$. Linder (21) states that 3% of an alcohol can be isolated from woolwax alcohols "when handled properly," which consists mainly of oleinalcohol. No data are given however, and this alcohol is not reported by others.

Lanylalcohol. $C_{21}H_{40}(OH)_2$ is an odd-numbered, unsaturated diol that does not absorb bromine. It was isolated by Kuwata and Katuno (19). This alcohol also has still to be confirmed by others.

Carnaubylalcohol. $C_{24}H_{49}OH$ was found only by Darmstädter and Lifschütz (9) in 1896. Röhmann (12) and later Heiduschka and Nier (13) tried to isolate this alcohol but in vain. Although no investigators other than Darmstädter and Lifschütz have reported this alcohol, it has still been included in practically all reviews (17, 20, 22, 23, 26, 27, 32). Warth (26) even calls it "the alcohol of woolwax!"

Cerylalcohol. $C_{26}H_{53}OH$. There is much uncertainty regarding this alcohol. Several authors have isolated an impure compound from woolwax alcohols, which they supposed to consist mainly of cerylalcohol:

Author	Reference	M.p. of "ceryalcohol" in °C.
Buisine	(1)	?
Lewkowitsch	(5)	57-58
Darmstädter and Lifschütz	(9)	77-78
von Cochenhausen	(11)	62, 65
Röhmann	(12)	70-71[a]
Heiduschka and Nier	(13)	75.5
Drummond and Baker	(14)	72
Lederer and Velluz	(25)	73-76
n-Hexacosanol		**80°**

[a] Truter (28) wrongly refers to the M.p. found by Röhmann as 77°C.

A typical example of the general confusion is given. While Lewkowitsch thought to have definitely identified cerylalcohol on account of the melting point 57-58°C., Drummond and Baker regard their product, melting at 72°C., as too impure to confirm its presence. von Cochenhausen concluded from his product, melting point 62°C., that it seemed to consist mainly of cerylalcohol, but Lindner (16) thought that von Cochenhausen had, without doubt, identified cerylalcohol. Because of the work of Röhmann (12), Lederer and Velluz (25) in a recent review call cerylalcohol the only definitely identified aliphatic alcohol. They overlooked however that first, Heiduschka and Nier and even Darmstädter and Lifschütz have isolated a product with a higher melting point than Röhmann, second, Röhmann himself considered his product to be impure, and third, Röhmann (like Darmstädter and Lifschütz) was speaking of $C_{27}H_{53}OH$ and not of $C_{26}H_{53}OH$.

The remark of Truter (28) that "the identity of cerylalcohol as a single compound cannot be considered seriously" is perfectly right. It will be remembered that Piper *et al.* (15), who investigated many aliphatic alcohols of various origins, showed "cerylalcohol" to be a mixture of several alcohols and suggested that the use of this name be discontinued except perhaps for a mixture.

Isocerylalcohol. $C_{27}H_{55}OH$, M.p. 60°C., has been reported only by Bourdet (20) as a woolwax alcohol, without mentioning however his source of information. It is better ignored, as well as *myricylalcohol*

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[2] Grassow incorrectly referred to $C_{10}H_{19}OH$ instead of $C_{12}H_{23}OH$.

$C_{30}H_{61}OH$ and *melissylalcohol* $C_{31}H_{63}OH$, mentioned as woolwax alcohols by the same reviewer.

Unsaturated alcohols. Darmstädter and Lifschütz (9) assumed the presence of an unsaturated alcohol other than hendecenol on account of the iodine number of a certain fraction. Further information, which they promised, has not appeared. Lindner (16) accepts the presence of unsaturated aliphatic alcohols on account of the iodine number of the optically inactive alcohol fraction isolated by Drummond and Baker, which he thinks are identical with the unsaturated aliphatic alcohols from spermaceti oil. He fails however to support his assertions with further details. Other mention of unsaturated woolwax alcohols could not be found.

IT will be apparent from the foregoing that exceedingly few reliable results have been obtained by the classical methods of analysis. The main reason is that the aliphatic woolwax alcohols are a mixture of many complex substances, for which only more modern methods of analysis can give reliable results. Accordingly, after several years of silence, recent communications have appeared, announcing a new period of systematic research. By means of modern methods of analysis, including urea complex formation, chromatography, and low pressure fractional distillation, Tiedt and Truter (31, 40) succeeded in isolating 5 normal alcohols, Horn and Hougen (30) could separate 5 dihydric alcohols, whereas Murray and Schoenfeld (35) identified 10 branched chain alcohols: six belonging to the group of iso alcohols and four to the ante iso alcohols. These discoveries taken together reveal the remarkable fact that the aliphatic woolwax alcohols are composed of the same four series as the woolwax acids: the normal, hydroxy, iso, and ante iso compounds!

The Normal Alcohols

Complex formation with urea has led to the separation of a group of saturated aliphatic alcohols from woolwax (29, 31, 40). Tiedt and Truter (40) claim to have isolated and identified C 18, C 20, C 22, C 24, and C 26 straight chain alcohols, whose meeting points and those of their acetates agreed with some already given in the literature.

As already mentioned, Tiedt and Truter did not isolate the precursor of this series, which Drummond and Baker (14) claimed to have identified: n-hexadecanol. No evidence of the presence of higher members of this series of alcohols could be obtained by Tiedt and Truter.

Did Tiedt and Truter mention that about 20% of the unsaponifiable material formed an addition complex and that half of it is formed by the n-alcohols (40), Murray and Schoenfeld (35), who also isolated about 20% of the unsaponifiable material, did not isolate, by low pressure distillation, any normal alcohol but only branched chain alcohols. Murray and Schoenfeld suppose that the normal alcohols are present as major constituents and that their presence would have been manifest by the low-pressure method. It is probable that they will be found in small amounts in intermediate fractions, and Murray tries to clear up this point definitely. By the urea separation method of Weitkamp and Bowman (41) Murray has indeed isolated seven normal alcohols (36): C_8, C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{30}. This method depends on the fact that when the woolwax alcohols are esterified with a branched acid (*e.g.,* iso butyric acid) the esters of the branched alcohols do not form complexes with urea whereas the normal isobutyrates do.

More will be published when the presence of the n-alcohols has been confirmed by their physical properties and long crystal spacings as well as those of their acids. The fact that the aliphatic woolwax alcohols of different groups are characterized by the same distinctive crystal habits as the different groups of woolwax acids (36) will be of great value for the demonstration of the presence of the normal alcohols.

Dihydric Alcohols

Rudolff (29), also Tiedt and Truter (31) report the separation of a group of dihydric alcohols by means of complex formation with urea, but they are not yet identified. They are supposed to be of the same type as those obtained by Horn and Hougen (30), using chromatography. Horn was able to isolate five 1-2 diols in a pure state by means of vacuum fractional distillation:

Proposed diol formulae	M.p. °C.	M.p. of acetate
$C_{16}H_{34}O_2$	83.7-84.4	
$C_{18}H_{38}O_2$	74.0-75	16-7
$C_{20}H_{42}O_2$	80.5-81.0	26-7
$C_{22}H_{46}O_2$	84.0-84.5	33.3-33.8
$C_{24}H_{50}O_2$	85.5-86.0	37.5-38.5
n-Octadecane-I : 2-diol (synthetic) $C_{18}H_{38}O_2$	81.0-81.8	38.5-38.7

Horn was able to isolate about 5% of the non-saponifiable fraction of woolwax as dihydric alcohols. This amount was in agreement with that found by Truter (31) (±4%). Oxidation of each diol with periodic acid yielded nearly one equivalent of formaldehyde, thus identifying them as 1:2 diols. For the identification of the exact structure, n-octadecane-1:2-diol was synthesized, which however showed a considerably depressed melting point with the corresponding natural diol, indicating that the natural compounds are not of the same series. It is supposed that the alkyl chain of the natural diols may have a single methyl branch.

Branched Chain Alcohols

Murray and Schoenfeld removed the "triterpene alcohols" from the non-saponifiable fraction of woolwax with methanol, and the cholesterol with $ZnCl_2$ (35). The remaining fraction was investigated by low-pressure fractional distillation of the acetates (35) with a spinning band column (32). It is considered very remarkable that no normal alcohols could be found. However they were able, after 150 distillations (!) to isolate and identify 10 branched chain alcohols. They comprise the dextrorotatory ante-iso alcohols (terminal group, sec-butyl) of odd carbon number C_{17}-C_{27} and the iso alcohols (terminal group, isopropyl) of even carbon number C_{20}-C_{26}. Murray and Schoenfeld account for 22.5% of long chain alcohols in the total non-saponifiable fraction, including the diols present which they have estimated to be about 1.5% of the total non-saponifiable fraction. The following data were given:

	M.p.	Opt. rot.	
		$(\alpha)^{CHCl_3}_D$	
14-me-hexadecanol C_{17}	18.4	+	4.4
16-me-octadecanol C_{19}	27.5-31		—
18-me-eicosanol C_{21}	40.1	+	4.4
20-me-docosanol C_{23}	48.5	+	4.0
22-me-tetracosanol C_{25}	54.6	+	3.8
24-me-hexacosanol C_{27}	61.0	+	3.5
18-me-nonadecanol C_{20}	50.3	—	
20-me-heneicosanol C_{22}	57.1	—	
22-me-tricosanol C_{24}	62.4	—	
24-me-pentacosanol C_{26}	67.2	—	

Murray identified the branched chain alcohols by oxidation to the corresponding acids, which appeared identical with the branched chain woolwax acids isolated by Weitkamp (24), showing also the same distinctive crystal habits. A rough indication of the distribution of the branched chain alcohols can be obtained from the weights of the acetates calculated by Murray from the temperature record of the distilled fraction, which quantities include the acetates of the diols present (estimated 1.5% of the original unsaponifiable material):

$<C_{17}$	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	$>C_{27}$
14	8	8	11	43	37	23	23	37	40	50	50	12

As can be seen from these figures, a few alcohols lower than C_{17} and higher than C_{27} are still waiting for purification and identification.

It is striking that the amounts of aliphatic alcohols which could be isolated from the non-saponifiable part of woolwax in different ways are in close agreement: Truter about 20%, v. Rudloff 21%, and Murray and Schoenfeld 22.5%. Taking into consideration that the sterols form about 30% of the non-saponifiable matter and the "triterpene alcohols" about 25%, there remains an unknown of about 25%, which needs further investigation.

Conclusion

The composition of the group of aliphatic woolwax alcohols has been the subject of investigation by many chemists for more than 60 years. The fact that woolwax unsaponifiable matter is a very complex mixture, containing many compounds differing in type and properties, has led to contradictory statements. The confusion has been increased by the sometimes misleading summaries of several reviewers.

Two periods of research can be distinguished. The first period has brought very few results: the possibility of the presence of unsaturated alcohols, the probability of the presence of branched chain alcohols, but no certainty of the presence of any one alcohol. The second period, started after 1950, is characterized by systematic research.

Twenty-two alcohols have been isolated, belonging to four series of alcohols: normal alcohols, diols, iso, and ante-iso branched chain alcohols. It is striking that none of the investigators mentions the presence of unsaturated alcohols. Seven normal alcohols are claimed to have been identified, but closer investigation on this subject seems desirable. Five 1-2 dihydric alcohols have been isolated, the identification of which is hampered by the fact that they probably have a branched chain. Ten branched chain alcohols have been completely identified, six belonging to the ante-iso series of odd carbon number, four being isoalcohols of even carbon number. Finally circa 25% of the woolwax alcohols is still unknown material and waiting for further elucidation.

These systematic investigations of recent years have revealed the remarkable fact that the aliphatic woolwax alcohols are composed of the same four series of components as woolwax acids, namely: the normal-, hydroxy-, iso, and ante-iso series. Much more has to be done however to gain a complete insight into the total composition of the aliphatic woolwax alcohols, and the words of Lewkowitsch (5), written in 1896, still hold good: "the composition of woolwax represents perhaps the most interesting amongst the many unsolved problems in the chemistry of fats and waxes."

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