The Constitution of Woolwax[1]

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ALTHOUGH a considerable literature exists concerning the components of woolwax (1) a thorough knowledge of its constitution in respect to its specific properties still appears to be lacking. About 32 component acids have been reported to be present, among which are mentioned nine normal saturated fatty acids, at least two hydroxy acids (about 4% of the distilled methyl-esters), and 21 iso-fatty acids. In the unsaponifiable part of woolwax there are about 16 alcohols including cholesterol (by far the largest constituent), five other sterols, two triterpene alcohols, and about eight normal fatty alcohols.

According to Lifschütz (2), lanocerinic acid ($C_{30}H_{60}O_4$) and lanopalmitic acid ($C_{16}H_{32}O_3$) are the most characteristic hydroxy acids of woolwax. Drummond and Baker (3), however dispute the identity of the first-named acid, which they regard as a monohydroxy acid rather than a dihydroxy acid as suggested by Lifschütz.

Consideration of the results obtained from an extensive analysis of two authentic woolwaxes of known origin, recently examined in the author's laboratory, has now shown convincingly that hydroxy acids are not only the most characteristic acids of the waxes but also constitute the major part of them. They appear to be present for the greater part as diestolidic acids, esterified with the alcohols of the unsaponifiable part of the waxes. The presence of these components of high molecular weight may be considered as the cause of the outstanding emulsifying properties of woolwax. This hypothesis at least offers some explanation for the fact that none of the constituents hitherto isolated from woolwax has shown any markedly better emulsifying properties in relation to its proportion in the wax than the whole wax itself. Moreover, the content of diestolidic esters has been shown to be proportional to the emulsifying values as measured by a steam-emulsion test.

Experimental

An American and an Australian crude woolwax were used for the analysis. These were given a mild acid treatment at a low temperature (50°C.), followed by filtration to remove impurities and mineral substances.

Table I shows the analytical data obtained.

TABLE I

	American wax	Australian wax
Acid value, mgr.KOH/gr.	11.9	5.9
Saponification value, mgr.KOH/gr.	114.6	102.4
Hydroxyl value, mgr.KOH/gr.	52.5	36.0
Iodine value (Hanus)	54.75	34.35
Viscosity in cps at 50°	345.0	216.4
Viscosity in degrees Engler at 50°C.	49.5	31.0
Unsaponifiable %	39.5	51.45
Total acids %	60.5	52.7
Hydroxyl value of the acids, mgr.KOH/gr.	167.6	102.6
Hydroxyl value of the unsaponifiable, mgr.KOH/gr.	145.3	154.0
Free sterols %	0.82	0.02
Mean molecular weight of the acids by titration	329.0	327.0

We may get a general check on some of the analytical figures by comparing the calculated amounts of combined carboxyl groups and combined hydroxyl groups, both being expressed as mgr.KOH/gr.

I. AMERICAN WAX

Carboxyl groups		Hydroxyl groups	
Saponification value	= 114.6	Unsaponifiable 39.5% at 145.3	= 57.4
Acid value	= 11.9	Acids 60.5% at 167.6	= 101.4
	−		+
Whence ester value	102.7	Total OH	158.8
		Deduct free OH in the wax	52.5
			−
		Hence esterified OH	106.3

II. AUSTRALIAN WAX

Saponification value	= 102.4	Unsaponifiable 51.45% at 154	= 79.2
Acid value	= 5.9	Acids 52.7% at 102.6	= 54.1
	−		+
Whence ester value	96.5	Total OH	133.3
		Deduct free OH in the wax	36.0
			−
		Hence esterified OH	97.3

Taking into account the scale of the values and the accuracy of the determinations, we may regard the agreement between these results as satisfactory.

Calculations and Discussion

A. The hydroxyl values (expressed in mgr.KOH/gr.) were as follows:

	American	Australian
a) Of the whole woolwax	52.5	36.0
b) Of the acids after saponification	167.6	102.6
c) Calculated on the amount of acids present in 1 gr. woolwax	101.4	54.1

As these waxes contain only a small amount of free alcohols (which we may expect to be about 1.2% for the American and 0.03% for the Australian wax, supposing the free alcohols to be present in the same proportion as the percentage of free sterols to total sterols in the unsaponifiable), the hydroxyl value of the whole wax must be due to the acids themselves. Allowance being made for the presence of 1.2% of free alcohols of hydroxyl value of 145.3 and 0.03% of alcohols of hydroxyl value 154 in the respective waxes, the hydroxyl values of the combined acids in 1 gr. of wax will be 50.8 and 36.0, respectively. Comparing these figures with those of c), we see that the saponification raises the hydroxyl value of the acid by 50.6 for the American and by 18.1 for the Australian wax. Thus saponification doubles the hydroxyl value of the acids of the American wax and raises that of the Australian wax by about 50%. A hydroxyl value of 167.6 for 1 gr. of acid with a mean molecular weight of 329 means that an average of 0.985 OH groups will be present per molecule of acid. Taking for granted that no di- or polyhydroxy acids are present, we may then assume that all component acids of the American wax are monohydroxy acids. As for the Australian wax, an OH value of 102.6 for 1 gr. of acid with a mean molecular weight of 327 means that on the average 0.60 OH groups are present per mol. of acid. So we may expect the acids

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of the Australian wax to contain about 60% of monohydroxy acids.

B. *The partition of the acids.*

The following calculations show that the usual hypothesis that woolwax is largely a mixture of free acids and normal esters of the acids with the alcohols of the unsaponifiable leads to quite impossible results.

	American wax	Australian wax
a) Total unsaponifiable %	39.5	51.45
b) Free alcohols %	1.2	0.03
c) Esterified alcohols % (a—b)	38.3	51.42
Mean mol. wt. of these alcohols calculated from the OH value	392.3	364.3
Mean mol. wt. of the fatty acids calculated from the titration equivalent	329.0	327.0
d) So the alcohols can bind at most fatty acids %	32.1	46.1
e) Total fatty acids present %	60.5	52.7
f) Therefore unesterified acids present (e—d) %	28.4	6.6
g) Free acids present (calc. from acid value and mean mol. wt.) %	7.0	3.45
Therefore acids unaccounted for (f—g) %	24.6	3.2

We consider the result for the American wax quite remarkable. In this way we are forced to the conclusion that an appreciable part of the combined acids must be present in some combination other than with the alcohols of the unsaponifiable. We may suppose that the above mentioned excess of acids is present either as lactones of hydroxy acids (which is the usual supposition) or as diestolidic esters.

The two suppositions lead to different compositions of the waxes and to different mean molecular weights as the following alternative computations will show:

I. *Supposing the waxes to be mixtures of:*

1. Free acids
2. Free alcohols
3. Normal esters of alcohols and acids
4. Lactones of hydroxy acids (or inner anhydrides)

we arrive at the following approximate compositions:

	American wax	Australian wax
1. Free acids %	7.0	3.45
2. Free alcohols %	1.2	0.03
3. Esters having a mean mol. wt. of	$392.3+329-18=703.3$	$364.3+329-18=673.3$
Present to the extent of % (calcd. from the amount of combined unsap. matter)	$38.3\times\frac{703.3}{392.3}=68.7$	$51.4\times\frac{673.3}{364.3}=95.0$
4. Lactones of hydroxy acids; by difference %	23.1	1.52
Or calculated from the acids unaccounted for, %	23.2	2.9
	100.0	100.0

From these compositions we can calculate the mean mol. weight of these waxes to be 582.9 and 655.7, respectively.

II. *Supposing the waxes to be mixtures of:*

1. Free acids
2. Free alcohols
3. Diestolidic esters
4. Monoesters

we come to the following approximate compositions:

	American wax	Australian wax
1. Free acids %	7.0	3.45
2. Free alcohols %	1.2	0.03
3. Diestolidic esters with mean mol. wt. %	$392.3+2\times329-2\times18=1014.3$	$364.3+2\times327-2\times18=982.3$
The quantity of which may be calcd. from the rise in OH value of the acids contained in 1 gr. wax produced by saponification as: %	$\frac{50.6}{56.1}\times1014.3=91.5$	$\frac{18.1}{56.1}\times982.3=31.7$
4. Mono esters, by difference %	0.3	64.8
	100.0%	100.0%

From these compositions we may again calculate the corresponding mean molecular weights of these waxes and now find 957.7 and 759.2, respectively; figures which differ substantially from those derived from supposition I.

It appeared then that a determination of the actual mean molecular weight of the wax might enable us to decide which of the two suppositions was the correct one. In this purpose we employed the cryoscopic method of Prahl (5) which has often given us very accurate results, at least when the experimental values have been extrapolated to zero concentration (which was not done by Prahl). Several determinations, however, in which either naphthalene or p. dichlorobenzene was used as solvent yielded quite erroneous results (much too low). Now cryoscopic measurements are known to yield low values in cases where the solvent is not "ideal" for the substance being studied (6). In the end we found a much better solvent in this respect in salol (salicylic ester of phenol) which itself is an ester of a hydroxy acid.

To confirm the accuracy of the Prahl method of cryoscopy with salol we first made the following determinations:

Substance	Mean mol. weight	
	Determined cryoscopically	Calculated from the OH values
Pure cholesterol	389	386.6
Unsaponifiable from the American wax	393	392.3
Unsaponifiable from the Australian wax	360	364.3

These figures show the reliability of the method for the substances used. The same method applied to the woolwaxes themselves, however, did not yield such exact figures but showed a larger "spread" in the empirical values; estimated values for the mean mol. weights were 875 (880 as the average of 17 determinations) for the American woolwax, and 792 for the Australian wax.

In comparing these figures with those derived by calculation according to suppositions I and II, we see that they agree much better with the composition based on the presence of diestolidic esters. Moreover the usual supposition I would lead to a higher molecular weight for the Australian wax than for the American product, which is not in accordance with our observations. The higher viscosity of the American wax and its superior emulsifying properties also point to a higher mol. weight for the American wax.

So we come to the conclusion that these woolwaxes must contain considerable amounts of diestolidic esters.

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Summary

Extensive analyses have been made of American and Australian woolwaxes. Combined hydroxy acids have been shown to be the most characteristic and important components of these waxes. Both contained considerable amounts (about 91.5% in the case of the American wax and 31.7% in the Australian sample) of diestolidic esters of the alcohols of the unsaponifiable fraction. This conclusion is supported by calculations of composition, by observations of viscosity and emulsifying properties, and by determinations of mean molecular weight by the Prahl method.

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Types and Mechanisms of Solubilization

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THE solubility of various compounds such as hydrocarbons, dyes, long chain alcohols, fatty acids, and insoluble soaps in water is increased by the addition of soluble soaps and other detergents. This phenomenon is usually designated as solubilization. A considerable number of investigators have studied the solubilization of compounds of varying polarity, size, charge, etc., with quite inconsistent results. An attempt is made here to show relationships between these various, seemingly conflicting, data and to add some new data from this laboratory which increases the validity of these correlations.

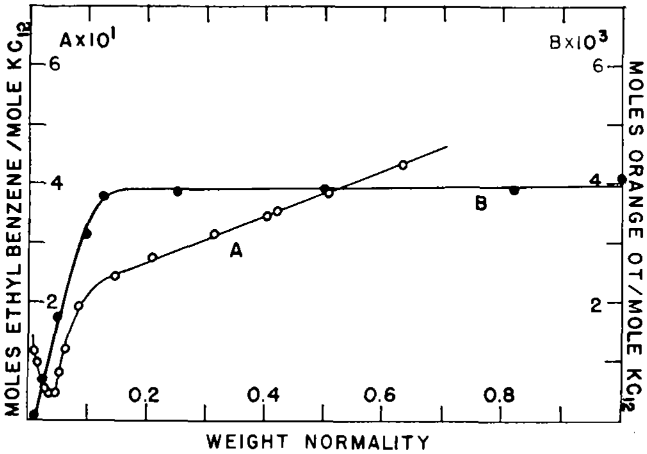

FIG. 1. Solubilization of ethyl benzene (A) and Orange OT (B) in potassium laurate solutions (25°C.).

Some typical solubilization data are shown in Fig. 1, where MR (moles of material solubilized per mole soap) is plotted as a function of soap concentration. Two main types of solubilization occur depending on the compound solubilized.

The first group is exemplified by hydrocarbons. For example, Curve A shows the solubilization of ethyl benzene in potassium laurate solutions (1) which is typical of systems in which MR increases at all soap concentrations, up to almost 1.0 M, above the critical micelle concentration (CMC). The initial decrease in solubility below the CMC is probably a salting out effect, and a minimum is reached at the CMC. Further examples of this type are the solubilization of benzene by cetyl pyridinium chloride as determined by Hartley (2), of propylene and other vapors by potassium oleate reported by McBain and O'Connor (3), and of liquid hydrocarbons such as n-decane and benzene solubilized by potassium laurate and by potassium myristate (4).

Curve B in Fig. 1 is taken from McBain and Green (5) and shows the solubilization of Orange OT (1-o-tolylazo-2-naphthol) in potassium laurate solutions. A constant MR at a concentration above 0.15 M potassium laurate is typical of compounds such as dyes, fatty acids, and long chain alcohols. Another example of this second type is shown by McBain, Merrill, and Vinograd for the solubilization of Yellow AB (phenyl-azo-p-naphthylamine) in aqueous sodium desoxycholate solutions and also in lauryl sulfonic acid solutions (6). A relatively unrecognized case of this type of solubilization is the increase in solubility of insoluble calcium dodecyl sulfonate and calcium dodecyl sulfate in solutions of their corresponding sodium salts (7). Soap mixtures such as potassium laurate and potassium palmitate, and sodium laurate and sodium palmitate (8) should be also included in this group for the palmitate should be considered to be solubilized by the laurate.

These two sets of data *indicate* that solubilization begins in the region of the CMC. Below this concentration, the soap acts like an electrolyte causing a decrease in solubility of the hydrocarbon or the polar compound, such as another soap, below that in water due to a salting out effect. This has been shown to occur in the case of ethylbenzene in the presence of potassium laurate (1) and in the decrease in solubility of calcium dodecyl sulfonate in solutions of sodium dodecyl sulfonate below the CMC of the latter soap (7). It might be supposed that solubilization begins below the CMC as observed in the appearance of color in insoluble dye-soap (below the CMC) mixtures (9). However, these amounts dissolved are so small, often only a few per cent more than is soluble