Composition and Polymerization of Chinese Wood (Tung) Oil*

Elaeostearic Acid Content Cited as Measure of Commercial Utility and Purity

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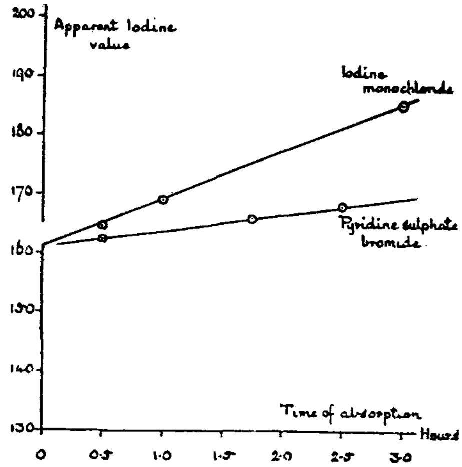
IN A previous communication (*Analyst,* 1926 *51,* 335) we have described a method for the determination of the polymerisable matter in Chinese wood oil, and have shown that the proportion varies within such narrow limits (70 to 74 per cent.) that its determination affords a satisfactory criterion of the purity of an oil. We have further suggested the proportion of polymerisable matter to be a measure of the commercial value of the oil.

During the past 4 years we have had further opportunities of examining a large number of samples, with results in confirmation of those given in our original communication.

Chinese wood oil is characterized by containing a large proportion of glycerides of elaeostearic acid, to which its power of polymerizing to a solid mass is due. It seemed to us, therefore, that if a correlation of the commercial value of the oil and the proportion of elaeostearic acid could be established it would provide a more satisfactory basis for the assessment of the commercial value than the general consideration of conventional constants that is at present customary. It was on this account that we sought to establish a relation between the proportions of polymerizable matter and elaeostearic acid in the oil; and we have succeeded in showing that these two quantities are, within experimental error, the same for every oil in which we have so far determined both.

Determination of Elaeostearic Acid.—Of the methods available for the determination of elaeostearic acid that described by Toms (*Analyst,* 1928, *53,* 69) has yielded results which we believe to be more consistent and accurate than any other yet published. This method is based on the assumption that a molecule of elaeostearic acid absorbs 6 atoms of bromine from bromine vapour, but only 4 atoms of halogen from Wijs iodine monochloride solution, and that all other fatty acids present absorb equivalent proportions of halogens from both reagents. While there seems to be no doubt that exactly 6 atoms are absorbed from bromine vapour, it is generally recognized that the absorption from Wijs solution, as usually applied, is by no means so simple as Toms has assumed, the iodine value usually obtained representing the absorption of rather more than the 4 atoms required by theory. Thus, Boughton (Seventh Int. Congr. Appl. Chem., London, 1909) has shown that the apparent iodine value of Chinese wood oil depends upon such experimental conditions as temperature, time of contact of oil and reagent, and concentration of the halogenating solution. It follows that Toms' method leads, in general, to low values for the proportion of elaeostearic acid in Chinese wood oil.



Absorption of halogen by Chinese wood oil.

Determination of True Iodine Value of Oil.—Böeseken (*Rec. Trav. Chim.,* 1927, *46,* 619) has observed that the four outer unsaturated carbon atoms, in the conjugated system in elaeostearic acid, are saturated with halogen by means of Wijs solution within 15 minutes, whereas the remaining two unsaturated atoms in this conjugated system become saturated only after many hours' contact with the reagent.

This observation would appear to indicate that the iodine value corresponding to the absorption of 4 atoms of halogen per molecule of elaeostearic acid could be obtained by limiting the action of the Wijs reagent to a very short period, say, less than 5 minutes. We

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have found such a method to give satisfactory Chinese wood oil, but, with others, consistent results are obtainable only when absorption is allowed to proceed for 20 minutes: figures so obtained are near enough to the true figure for practical purposes, though, admittedly, they are distinctly high.

By allowing Chinese wood oil to absorb halogen from both Wijs solution and pyridine sulphate bromide solution for varying periods of time, we have found that the first rapid stage is almost complete within five minutes, that most of the absorption is instantaneous, and that, during the second slow stage, absorption proceeds at a regular speed. This is shown in Fig. I, in which are plotted typical figures obtained by the action of the two reagents upon one specimen of the oil; the actual experimental results from which the curves are drawn are shown in Table I. In Fig. I it will be seen that the second slow stage is represented by a straight line, indicating that the increase in the apparent iodine value, during any given period of time, is constant for a given halogenating solution under the usual conditions of the determination. Since this increase is due to the slow saturation of the last two carbon atoms of each elaeostearic acid molecule, and such saturation begins as soon as the reagent comes into contact with the oil, it follows that the actual turning point of the curve may be measured by extrapolation to zero time of the straight line representing the second stage of absorption.

Table I.

Absorption of Halogen by a Chinese Wood Oil

Reagent.	Time of contact of oil and reagent. Hours	Apparent iodine value.
Wijs iodine monochloride	0.5	164.5
	1.0	169.0
	3.0	185.0
Pyridine sulphate bromide	0.5	163.5
	1.75	166.0
	2.5	168.0

In the case illustrated the turning point occurs at an iodine value of 160.8 with Wijs solution and 161.2 with pyridine sulphate bromide, and is thus the same, within the error of experiment, for both reagents. We find that this case is typical of all absorptions of halogen from these two reagents, the slope of the line representing the slow absorption varying from oil to oil and being dependent on the reagent used, while the turning point is constant and independent of the reagent. This we consider affords very strong evidence that at this turning point the oil has absorbed a proportion of halogen corresponding to 4 atoms per molecule of elaeostearic acid.

The instantaneous iodine value may best be determined graphically from the iodine values obtained after absorption has proceeded for 30 minutes and for 3 hours, or by calculation from these two quantities by means of the expression:

$$\text{“Instantaneous” iodine value} = \text{I.V.}_{30\text{ min.}} - 1/5\,[\text{I.V.}_{3\text{ hrs.}} - \text{I.V.}_{30\text{ min.}}]$$ in which:

$\text{I.V.}_{30\text{ min.}}$ is the Wijs iodine value obtained after 30 minutes' absorption.

$\text{I.V.}_{3\text{ hrs.}}$ is the Wijs iodine value obtained with the same solution after 3 hours' absorption.*

Proportion of Elaeostearic Acid in Chinese Wood Oil.—The bromine value of elaeostearin corresponding to saturation of all three double bonds of the acid, is 164.8, or, calculated in terms of iodine, 261.7; and the true iodine value corresponding to the absorption of 4 atoms of halogen per molecule of the acid is 174.5; the difference between the two values, expressed in terms of iodine, is, therefore, 87.2. Since the amount of iodine monochloride absorbed by all other constituents of Chinese wood oil is exactly equivalent to that of bromine, it follows that the proportion of glyceride of elaeostearic acid present in the oil may be obtained by dividing the difference between the bromine value and the true, or instantaneous, iodine value by 87.2 and multiplying by 100.

We have used the above method to determine the proportion of elaeostearic acid glyceride in a number of specimens of Chinese wood oil in which we have also determined the proportion of polymerizable matter by the previously described (*Analyst,* 1926, *51,* 335).

In Table II we have set out the results of these determinations, and it will be seen that the amounts of polymerizable matter and of the glyceride of elaeostearic acid are the same, within a small experimental error. This being so, we feel that we are justified in the assumption that the polymerizable matter consists entirely of the glyceride of elaeostearic acid, and, consequently, we suggest that our original method of determining the polymerizable matter in Chinese wood oil determines the glyceride of elaeostearic acid.

(*Turn to Page* 454)

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* Since this paper was read, Dr. Mitchell has drawn our attention to a thesis presented by van Loon, in 1929, to the University of Delft, in which the abnormal iodine values of fatty oils containing a conjugated system of double bonds is discussed. In our paper we have termed the iodine value given by Wijs solution an "apparent" iodine value, and we notice that the same phrase is used by van Loon, who approaches the problem of iodine values in a very ingenious manner and on distinctly different lines from those of our present communication."

Chinese Wood Oil

(*From Page* 448)

TABLE II.

PROPORTIONS OF ELAEOSTEARIC ACID AND POLYMERIZABLE MATTER IN CHINESE WOOD (TUNG) OIL.

		Iodine value			Bromine value. Toms' method	Glyceride of elaeostearic acid, calc. from bromine and iodine values Per Cent	Polymerizable matter (Bolton and Williams' method) Per Cent
		Half-hour.	Three hours.	Instantaneous value			
Pure Oils:	1.	168.5	175.5	167.1	229.0	71.0	70.0
	2.	165.4	175.7	163.3	226.2	72.2	71.5
	3.	162.0	169.2	160.6	223.8	72.5	71.8
	4.	166.5	176.2	164.6	228.2	73.0	73.0
	5.	169.7	174.8	168.7	223.2	74.0	73.0
	6.	166.6	178.1	164.3	228.5	73.6	74.7
Adulterated oil containing approx. 15 per cent. soya bean oil		161.6	169.0	160.1	221.2	58.7	58.1

The method which we have described in this communication requires very careful manipulation, particularly with regard to the weighing of the brominated compound, and for this reason we feel that it is less simple to operate than the determination of the polymerizable matter.

Conclusion.—From the results put forward above, the following conclusions may be drawn:

(1) Elaeostearic acid glyceride may be determined in Chinese wood oil by the separation of the polymerizable matter previously described by us (*Analyst,* 1926, *51,* 335).

(2) If the iodine value of elaeostearic acid is to be defined as the percentage of halogen in terms of iodine absorbed by exactly four of the unsaturated carbon atoms—the absorption by the remaining two being entirely excluded—then this figure may be obtained with sufficient accuracy for practical purposes by an absorption limited to 20 minutes, or, where great accuracy is required, it may be obtained by the more elaborate method described in this communication.

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