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Notes on Japanese Vegetable Oils.

By

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1. Japanese Wood Oil (*Kiri-abura*).

(*a*) The iodine value.

Whereas Japanese wood oil dries more rapidly than linseed oil, the iodine value of the former is lower than that of the latter. The iodine value of this oil is, however, variously stated by different observers. Thus, it is 169.02 according to K. HIGUCHI, 159–161 according to DE NEGRI and SUBURLATI, 167 (HÜBL's method) and 169.5 (WIJIS' method) according to INGLE, 149.7–165.7 according to JENKINS, and 155.4–165.6 according to WILLIAMS. Even the highest value 169.5, given by INGLE, is lower than that (170–188 according to different observers) for linseed oil. H. INGLE (J. S. C. I., 1902, 187) is of the opinion that the lowness of the iodine value of Japanese wood oil may be due to its previous oxidation, stating at the same time that "there are reasons for supposing that wood oil has a different constitution from the other drying oils."

In order to examine the fresh oil I procured the seeds of *Elæococca vernicia* from Echizen and pressed them myself in the cold, taking care to expose the oil as little as possible to the air. The oil pressed out was slightly turbid, so it was passed through a filter paper by the aid of a water-pump. The clear oil thus obtained was directly used for the following determination of the iodine value.

0.1489 gr. of the oil was dissolved in 10 c.c. of chloroform, and 25 c.c. of Hübl's solution was added. After standing for about 24 hours in the dark, the excess of iodine was titrated back with standard thiosulphate solution (1 c.c.=0.01231 gr. iodine), of which 29.3 c.c. was required, whilst in a blank experiment 48.7 c.c. of the thiosulphate solution was required. The iodine value is, therefore,

$$\frac{(48.7-29.3)\times 0.01231\times 100}{0.1489}=160.3$$

Two other such experimints gave 160.8 and 162.8, so that the mean of the three experiments was 161.3.

After storing the cold-drawn oil in an ordinary stoppered bottle in the dark for eleven months, its iodine value was redetermined according to Hübl's method. The results were 149.3 and 150.6, mean 150.0, so that during the eleven months the iodine value of the oil had decreased by 161.3−150.0=11.3. Meanwhile, the iodine value of the oil was also determined according to Wijis' method. Wijis' solution was prepared as follows:—

12.7 gr. of iodine was dissolved in one litre of glacial acetic acid; to this solution dried chlorine gas was passed until a sudden change in colour occurred. The solution was warmed on a water-bath, and the excess of chlorine changed into chloracetic acid. Using this solution the iodine value was determined in the same manner as in Hübl's method, but the time of standing was only 3–4 hours. The results of two experiments made with the cold-drawn oil, which has been stored in an ordinary stoppered bottle in the dark for three months, were 155.7 and 156.8, mean 156.3.

By Wijis' method we usually obtain an iodine value which is a little higher than that obtained by Hübl's method. But owing to the oxidation, which has taken place during the three months, the iodine value obtained by Wijis' method was found to be lower than the value obtained by Hübl's method with the original oil. Determination with Wijis' method was also repeated with the eleven months oil, which gave the values 153.6, 151.6 and 154.3, mean 153.2, so that during the eight months the decrease of iodine value amounted to $156.3-153.2=3.1$.

These experiments show that the fact that the iodine value of Japanese wood oil, which, as above found, is 161.3, or lower than that of linseed oil, can not be ascribed to previous oxidation, as has been believed by many, and that on oxidation the value is much diminished.

The lowness of the iodine value is also apparent from a consideration of the composition of the oil. This oil, unlike linseed oil, contains none of the highly unsaturated acids, such as linolenic acid $C_{18}H_{30}O_2$, but consists of the glyceride of elæomargaric acid and olein, in the proportion, according to Cloëz, of 75% of the former to 25% of the latter. The theoretical iodine value of the former glyceride being 173.6 and that of the latter 86.2, the calculated iodine value of the oil, assuming the above proportion to be correct, is 151.8. Or, taking the above found iodine value, 161.3, the proportion of the two constituents may be calculated thus,

$$173.6\,x+86.2\,(1-x)=161.3, \qquad \therefore \quad x=0.8592\,;$$

that is, the oil consists of about 86% elæomargarin and 14% olein. This proportion, rather than the one given by Cloëz, seems to be justified by the yield of elæomargaric acid from the oil.

The iodine value of pure elæomargaric acid itself was determined and found to be 180.2 (HÜBL's method), and 183.1 (WIJIS' method); the iodine value calculated from the formula $C_{18}H_{32}O_2$ is 181.4, with which both of the above values are in fair agreement.

(*b*) Some other constants of Japanese wood oil were determined with the following results:—

Acid value 3.81.
Specific gravity $\left(\frac{24^\circ}{24^\circ}\right)$ 0.9307.
Saponification value 196.0.

(*c*) Existence of an enzyme in the seeds of *Elæococca vernicia.*

The seeds of *Elæococca vernicia,* after removing the outer husk were crushed in a mortar and extracted with water, and at other times with glycerin, and the precipitate obtained on the addition of alcohol was filtered, washed with alcohol, dried at low heat and powdered. The greyish brown substance thus obtained was added to a mixture of ethyl acetic ester or the Japanese wood oil itself and water, and the mixture titrated from time to time with baryta-water along with a blank mixture, phenolphthalein being used in both cases as the indicator. Though the saponifying action of the enzyme was not remarkable, its effect was apparent from the greater quantity of baryta-water required in each case to neutralize the liquid than in the blank experiment.

It is possible that this enzyme, being present in a small quantity in the oil itself, plays some part in the rapid drying of this oil.

2. Camellia Oil or Oil of *Thea japonica (L.) Nois*
(*Tsubaki-abura*).

The sample used was commercially pure.

Specific gravity $\left(\frac{15^\circ}{4^\circ}\right)$ 0.9138.

Iodine value (Hübl's method) 79.47; the oil, therefore, belongs to the class of non-drying oils.

The mixed acids obtained by saponifying this oil were oxidised by potassium permanganate according to Hazura's method, but at an ordinary temperature. A large quantity of white lustrous crystals of m. p. 128–130° was obtained. The acid equivalent was found to agree with that of dihydroxystearic acid. No sativic acid or linusic acid was obtained. From these facts it is evident that the principal acid in this oil is oleic acid.

No solid bromine addition product was obtained.

3. Oil of *Terreya nucifera S. et Z.*
(*Kayano-abura*).

This sample I made myself by pressing the seeds in the cold.

The iodine value (Hübl's method) was found to be 137.3.

The mixed acids obtained by saponifying the oil with alcoholic potash were recrystallized from acetic acid or from alcohol. White scaly crystals of m. p. 57.5° were obtained. This substance does not change in the air, nor absorbs bromine in acetic acid solution. The figures obtained for its acid equivalent were 270.3, 280 and 281; it therefore appears likely that the acid is stearic acid $C_{18}H_{36}O_2=284$, or possibly a mixture of stearic and palmitic acids.

A bromine addition product of the mixed acids was obtained in the usual manner, its melting point, 114°, agreeing with that of tetrabromostearic acid $C_{18}H_{32}Br_4O_2$. This oil therefore contains linolic acid $C_{18}H_{32}O_2$ or its isomers besides stearic acid.

4. Soja bean Oil or Oil of *Glycine hispida Maxim.*

(*Daidzu-abura*).

The sample used was pure oil obtained from Tokushima.

A bromine addition product of the mixed acids was obtained melting at 110°. This appears to be tetrabromostearic acid $C_{18}H_{32}Br_4O_2$.

Oxidation of the mixed acids by Hazura's method gave dihydroxystearic acid and sativic acid, the yield being about 27.5 parts of the former and 10 parts of the latter from 100 parts of the oil.

From these experiments it can be seen that the unsaturated acids in this oil are principally oleic acid and linolic acid, or its isomer.

5. Oil of *Perilla ymoides L.*

(*Eno-abura*).

A commercially pure sample was employed.

The bromine addition product of the mixed acids prepared in the usual manner separated out from hot glacial acetic acid as a white voluminous precipitate, which under the microscope showed no crystalline structure but consisted of fine oily drops, m. p. 181°. A bromine determination gave the following result:—

From 0.2235 gr. substance 0.3160 gr. AgBr was obtained, $\therefore$ Br=62.61%. Calculated for the formula $C_{18}H_{30}Br_6O_2$, Br=63.32%.

It appears therefore that linolenic acid or its isomer is contained in this oil.

The mixed acids were heated with aniline as in the preparation of the anilide of elæomargaric acid; a white non-crystalline substance of m. p. 60–62° was thus obtained. The acetic acid solution of this anilide absorbs bromine, so that it is still an unsaturated compound.