JAPANESE TUNG OIL*

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JAPANESE tung oil is obtained from the seeds or nuts of the tree, *Aleurites cordata.* Fukui Province, in the central part of Japan, is the chief producing district. For a great many years the oil has been expressed in Japan and used for technical purposes, including the waterproofing of paper and the manufacture of paints and varnishes. Owing to the limited production and the high esteem with which the oil is held in Japan, very little is exported.

During 1921, H. A. Gardner (Circular No. 138, Educational Bureau, Paint Manufacturers' Association of the United States) examined a sample of the nuts and the expressed oil which he received from Japan. From drying tests made in his laboratory it was found and reported that the oil, with added drier, gave films which were tougher, more brilliant, and more highly water resistant than those given by bodied linseed oil treated under the same conditions. Up to the present time apparently no other investigator in this country has made any further study of the oil.

The results of the investigation to be described were obtained with oil expressed from seed received through the assistance of the Division of Plant Exploration and Introduction of the Bureau of Plant Industry from the Yokohama Nursery Company, Yokohama, Japan. The average weight of the seed was 0.97 grams. The seed consisted of 63.9 per cent of kernel and 36.1 per cent of shell. The shells, which are thin and friable, easily permit the removal of the kernels. These kernels contained 67.5 per cent of oil and 2.9 per cent of moisture. The oil which was expressed from the kernels was light yellow. When several drops of the oil were placed on a 10 per cent chloroform solution of antimony trichloride the oil solidified at once, as is the case with Chinese tung oil. The reaction is characteristic of oils the chief constituent of which is elaeostearic acid. K. H. Bauer (Chem. Umschau 32, 3, 1925) had previously shown by other methods that Japanese tung oil contained this acid. This oil, like Chinese tung oil, after exposure to direct sunlight, gradually solidifies, owing to the conversion of the alpha-elaeostearic acid into higher melting beta form. H. A. Gardner (loc. cit.) found that the drying time of the raw oil on glass is 43 hours and that the opaque soft film is like that of untreated Chinese tung oil. We found that a drop or two of the oil placed on water solidifies in about 30 hours, during which time the oil expands to a sizeable, somewhat elliptical sheet having the appearance of crepe paper. One striking difference between these two oils is that the Japanese tung oil remains liquid after heating when the Browne heat test is used. This difference in behavior was observed by the Japanese many years ago.

The chemical and physical characteristics of the oil are given in Table 1.

TABLE 1

Chemical and Physical Characteristics.

Specific gravity at 25/25° C.	0.9313
Refractive index at 25°	1.5059
Acid value	0.60
Iodine number, calculated	209.6
Iodine number (Rosenmund-Kuhnhenn)	145.2
Thiocyanogen value (Kaufmann)	80.9
Saponification value	190.2
Unsaponifiable matter, per cent	0.57
Iodine number, unsaponifiable matter (R. & K.)	105.5
Saturated acids (Bertram) per cent	6.18

It will be observed that the oil has a high density and refractive index. As in the case of oiticica and bagilumbang oils, which have been investigated in this laboratory (Ibid 12, 146, 1935; 13, 10, 1936), it was found that the iodine number (Hanus) given by this oil varied greatly when different quantities were taken for the determination. For example, 150 and 51.5 milligram portions of the oil gave iodine numbers of 168.4 and 276, respectively. On the other hand, the experiments with the Rosenmund-Kuhnhenn procedure showed that the values obtained were independent of the size of the portion of oil taken when the time allowed for the reagent to act on the oil was one-half hour.

Pure beta-elaeostearic acid separated from the oil gave a thiocyanogen value of 91.2 and an iodine number of 182.4 by the Rosenmund-Kuhnhenn method. These values agree with those calculated for this acid, upon the assumption that only one double bond of the acid reacts with thiocyanogen and two double bonds react with the Rosenmund-Kuhnhenn reagent. The use of the iodine number by this method and the thiocyanogen value in calculating the percentages of the unsaturated acids of this oil will be shown further on.

Failure to obtain ether insoluble bromides indicates the absence of measurable quantities of linolenic acid. Bauer (loc. cit.) stated that with the Hazura permanganate oxidation procedure a hydroxy acid was isolated which he believed to be sativic acid. This would indicate that the oil contained linoleic acid No sativic acid could be obtained by applying the modified Hazura method (Green and Hilditch, Biochem. J. 29, p. 1554, 1935) to a portion of the fatty acids separated from the oil. An acid melting at 168° was isolated which, after several recrystallizations, melted sharply at 175°. An anlaysis showed its neutralization equivalent to be 372, which indicated without doubt that the substance was a linusic acid, an oxidation product of elaeostearic acid. Sativic acid, which melts at 173°, has a neutralization equivalent of 348. No evidence was obtained of any unsaturated acid in the oil other than elaeostearic and oleic acids.

With the Lapworth and Mottram permanganate method (J. Chem. Soc. 127, 1628, 1925) for an appropriate determination of oleic acid, a small quantity of an ethyl acetate insoluble hydroxy acid was separated which, after recrystallization from dilute alcohol, melted at 173°. This was identical with the linusic acid from the Hazura oxidation experiment. The quantity of di-hydroxy stearic acid obtained indicated the presence of 17.8 per cent of oleic acid in the oil.

The absence of linoleic and linolenic acid from the glycerides of the oil permits the calculation of the proportions of the oleic, elaeostearic

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and saturated acids by using the following equations:

(1) $182.4\ X + 89.9\ y = 100$ (Iodine number by R. K. method)
(2) $91.2\ X + 89.9\ y = 100$ (Thiocyanogen value)
(3) $95.6 - (X + y +$ unsaponifiable matter$) =$ per cent of saturated acids $X =$ per cent of elaeostearic acid. $y =$ per cent of oleic acid.

Inserting in equation (1) the iodine number of the Rosenmund-Kuhnhenn method and in equation (2) the thiocyanogen value, the solution of the equations indicated that the oil contains 70.5 per cent of elaeostearic acid and 18.5 per cent of oleic acid. The third equation gave 6.03 per cent of saturated acids. It will be observed that these calculated percentages for oleic and saturated acids are in good agreement with those by the Lapworth-Mottram (oleic acid 17.8 per cent) and Bertram (saturated acids 6.18 per cent) methods.

In view of this agreement, it seems that the above equations can also be applied to the determination of unsaturated acids in those oils of the genus Aleurites which contain elaeostearic acid, as we have been unable to detect the presence of either linoleic or linolenic acids in any of these olis.

From the percentages of elaeostearic acids, it was calculated that the true iodine number of the oil is 209.6.

SUMMARY

The chemical and physical characteristics of Japanese tung oil have been determined. This investigation indicates that the oil contains 70.5 per cent of eleaostearic, 18.5 per cent of oleic, and about 6.2 per cent of saturated acids.

It has been shown that the Rosenmund-Kuhnhenn method, together with the Kaufmann thiocyanogen method can be used in the determination of the unsaturated fatty acids in this and in other oils of the genus Aleurites which contain elaeostearic acid. It has also been shown that the Rosenmund and Kuhnhenn procedure gives an iodine number with elaeostearic acid which indicates that two of the three double bonds present are reacting. This iodine number is independent of the weight of the sample taken for ananlysis.

THE EFFECT OF VARIOUS ADSORPTIVE MEDIUMS UPON RANCIDITY AND THE KREIS TEST*

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IN DISCUSSION involving the Kreis test, it may be well to start with a brief summary of the various theories which have been advanced, dealing with the causes of rancidity in oils and fats. Every one of the theories offered in regard to rancidity may be justified insofar as the field which it covers is concerned.

The most generally accepted theory occurring in the literature is that rancidity is brought about by the presence of oxygen. The changes for which oxygen is responsible appear to be very complex. In the spontaneous auto-oxidation of fats it has been suggested that peroxides are formed at the double bond linkages on the unsaturated portion of the glyceride. These organic peroxides are believed to form ethylene oxide derivatives plus hydrogen peroxide, which in turn may break down with the liberation of active oxygen to form odoriferous aldehydes and ketones.

As the concentration of these odoriferous compounds increases the fat reaches the point of organoleptic rancidity, or is rancid to the sense of smell. This is really the ultimate test as to whether or not a fat is rancid, but it gives no indication as to when a fat is beginning to turn rancid nor is it dependable in determining the exact point of rancidity because there is a personal factor in a test of this sort under the most ideal conditions for running the test. In many cases the conditions of test are far from ideal because other odors natural to the fat or oil or which may develop during production may mask the rancid odor long after the point of organoleptic rancidity would have been passed had it not been masked by the other odor.

The work of King, Roschen and Irwin[1] in establishing the peroxide content of lard and other oils and fats at the point where organoleptic rancidity occurs is well known. They found this point to be approximately 20 milli-equivalents of peroxide per 1000 grams of lard. This value holds true only for the average pure lard. The peroxide content at the rancid point will vary for every type of fat or oil.

Experiments carried out by Coe and LeClerc[2] of the Bureau of Chemistry and Soils indicate that neither a color test such as the Kreis test, nor the peroxide test may show conclusively that a fat is rancid. Their evidence supports the theory that organoleptic rancidity may not be due to the formation of peroxides, but possibly to an independent compound, the formation of which accompanies and is simultaneous with the formation of peroxides under certain conditions. This was supported by the fact that corn oil and cottonseed oil, oxidized in the absence of light, showed no organoleptic rancidity even though their peroxide values were much higher than those of the same oil which had been exposed to light until it was very definitely rancid.

This may indicate that rancidity, although closely allied with peroxide formation, is not entirely dependent upon it.

There has been little if any criticism of the method for peroxide determination developed in the Swift laboratories in connection with the accelerated rancidity tests, although there may have been some question as to whether the conditions of the test reproduce accurately, conditions which may be encountered in the actual handling and storage of

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