The Characteristics of Domestic Tung Oils

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THE relative value of a drying oil is indicated by certain of its physical and chemical characteristics such as the refractive index, iodine number, and, in the case of tung oil, by the content of eleostearic acid and the time required to gel at 282°C. In trying to improve the qualities of domestic tung oil and perhaps widen its utilization, knowledge of the variation in characteristics is needed. Since no comprehensive information on the variation in characteristics of domestic tung oil has been published, the Bureau of Agricultural and Industrial Chemistry began in 1950 to collect samples of oil from the various domestic tung mills and to determine their more important physical and chemical characteristics. The samples were collected over three successive seasons, and a total of 74 samples of oil from continuous screw pressing operations was analyzed. The characteristics of these oils are reported in this paper.

Contents of total eleostearic acid, alpha-eleostearic acid, and beta- eleostearic acid, and the refractive index, optical dispersion, acid value, heat test value, and hydrogen and Wijs iodine values were determined on all samples. In addition, the specific gravity, viscosity, unsaponifiable matter, volatile matter, saponification value, and color were determined on all samples for the first two seasons.

Analytical Methods

Contents of alpha-, beta-, and total eleostearic acids in the oil samples were determined by measurement of ultra-violet absorption (6). The total eleostearic acid reported is the sum of the contents of the alpha- and beta- acids. Since the absorption for the separate acids at the flat peak of their respective curves can be measured more accurately than can the absorption for the total acid measured at the point where more steeply inclined parts of the curves for the separate acids intersect, the sum of the two values is a more accurate figure.

The refractive index was measured (1f) with a precision refractometer of the Abbe type. Measurements were made with both the sodium D line (5893 Å) and the mercury g line (4358 Å) at 25.0°C. The optical dispersion reported is the difference between these two refractive indices multiplied by 10^4. The differences in specific gravity of the tung oils are so small that the specific dispersions, calculated by dividing the optical dispersion by the specific gravity, are for all practical purposes proportional to the optical dispersions. Hence the same conclusions can be drawn from optical dispersions as can be drawn from specific dispersions, without the necessity of determining specific gravity.

The acid value was determined by titration with aqueous alkali in benzene-alcohol solution (1d). On 25 samples the acid values were compared by titrating in hot alcohol (1b) and in benzene-alcohol solution. No difference was found in the results hence the latter method was used as being the easier of the two to carry out.

The heat test used (7) differed slightly from the method specified by the American Society for Testing Materials (2a). In the method used, the samples in test tubes were inserted into an electrically heated oil bath, thermostatically controlled at 282°C. and of such large volume (1 gal.) that introduction of the sample tubes lowers the temperature imperceptibly. The A.S.T.M. method specifies heating a much smaller volume of oil to 293°C. with a gas burner, then inserting the test tubes containing the oil samples and allowing the temperature to drop to 282°, at which point it is held constant until gelation occurs. Comparison of results obtained by the two methods showed that the procedure used gave about 0.5 min. longer heat test than did the official method.

Hydrogen iodine values were determined by the method of Pack, Planck, and Dollear (8).

Iodine values were determined, using the Wijs method (1j). Inasmuch as the Wijs iodine value obtained for tung oil depends upon the weight of sample used (5), the weight of sample was held as close to 175 mgs. as feasible.

Official methods of the American Oil Chemists' Society were used for the determination of specific gravity (1g), unsaponifiable matter (1c), volatile matter (1a), saponification value (1i), and color (1e).

Results

The averages for these characteristics with the standard deviations and ranges are given in Table I. The values for the first 10 characteristics are the averages of 72-74 samples covering three milling seasons, the last five for 50 of these samples covering two milling seasons. The average eleostearic acid content was 78.7% with a range of 72.8 to 85.0, but two-thirds of all values fell between 76.2% and 81.2%, as can be calculated from the average and the standard deviation.

TABLE I

Physical and Chemical Characteristics of Domestic Tung Oils

Characteristic	Average	Standard Deviation	Range
Eleostearic acid, total, %.....	78.7	±2.45	72.8-85.0
Eleostearic acid, alpha-, %..	77.6	±3.92	55.6-85.0
Eleostearic acid, beta-, %.....	1.0	.....	0.0-23.1
Ref. index, 25°C., 5890 Å....	1.5173	±0.0008	1.5147-1.5187
Ref. index, 25°C., 4358 Å....	1.5452	±0.0012	1.5418-1.5470
Optical dispersion × 10^4.....	277.5	±1.0	269-282
Acid value.....	1.03	±0.76	0.28-3.92
Heat test, min.....	11.8	±0.79	10.6-13.5
Hydrogen iodine value.....	230.2	±3.9	220.6-241.2
Wijs iodine value.....	162.2	±2.03	157.8-165.9
Specific gravity 25°/25°.....	0.9364	±0.0004	0.9351-0.9378
Viscosity, 25°C., Stokes.....	2.20	±0.08	2.0-2.4
Unsaponifiable matter, %.....	0.38	±0.04	0.32-0.48
Volatile matter, %.....	0.06	±0.03	0.02-0.14
Saponification value.....	192.0	±0.68	190.7-193.6
Color, Gardner standards.....	.....	.....	3-8

The optical dispersion of tung oil is so high in comparison with that of other common vegetable oils that it is of value in indicating the purity of tung oil. For instance, the dispersions (4) of linseed, cottonseed, and olive oils are 131, 118, and 116, respectively,

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as compared to an average of 278 for tung oil. It is of interest to note that the optical dispersion of tung oil varies less than does the refractive index. The spread between the maximum and minimum values for dispersion was 0.0013 while the spreads for the refractive indices were 0.0040 (n_D) and 0.0052 (n_g).

The acid value is the only characteristic that is likely to change during processing of the fruit for oil. The average acid value was 1.0 with a range of 0.3 to 3.9. Since A.S.T.M. specifications permit an acid value of 8.0, the domestic mills do a very good job of holding the acid value low.

An inspection of the table shows that domestic oils are of very uniform quality as measured by these characteristics. Practically all of the oils met the A.S.T.M. specifications, except that the Wijs iodine values of many of the oils were slightly below the minimum specified (163.0), although all samples were authentic samples of tung oil.

Correlations Between Characteristics of Tung Oil

The correlations between certain of the characteristics of tung oil were calculated.

Since eleostearic acid differentiates tung oil from all other commercial oils, the eleostearic acid content was correlated with properties that differentiate tung oil from other oils, such as high refractive index, high refractive dispersion, and the heat test value. The correlation coefficients (10) of the eleostearic acid content with these three characteristics are 0.69, 0.73, and —0.62, respectively (the latter is the partial correlation for constant acid value). The correlations of these characteristics with the eleostearic acid content are high enough so that any one of them can be taken as a rough measure of the eleostearic acid content, and equations could be set up for calculating the approximate eleostearic content from each of the other three characteristics, or *vice versa.*

Because the unsaturation expressed by the iodine value is mostly that of the eleostearic acid present, a high correlation between the eleostearic acid content and the Wijs and hydrogen iodine values was anticipated. The correlation coefficients were found to be 0.48 and 0.53, respectively, for the Wijs and hydrogen iodine values.

The heat test is probably the most valuable test made on tung oil as far as the manufacturer of protective coatings is concerned, as this determines how the oil behaves in the cooking kettle. The highest of all correlation coefficients found (—0.81) was that of the heat test with the refractive index. The correlation of the heat test with the Wijs iodine number was —0.71, showing that the refractive index is a better measure of the quality of a tung oil than is the Wijs iodine number. Correlation of heat test with hydrogen iodine value is only —0.25.

The correlation between heat test and eleostearic acid content is —0.62; between heat test and acid value it is 0.28. Both are significant. There is also a significant negative correlation (—0.31) between acid value and eleostearic acid content. It is well known (9) that the free alpha- and beta- eleostearic acids are much less stable than the corresponding triglycerides. The probable explanation of a negative correlation between eleostearic acid content and acid value is due to destruction of the free acids in oils of high free fatty acid content.

It is also known that high acid values increase the time of the heat test (3). The partial correlation coefficient between acid value and heat test for a constant eleostearic acid content is 0.16, which is not significant. This shows that the increase in the time of the heat test for oils of high acid value is at least in part due to the lower content of eleostearic acid rather than to the free acid itself.

Conclusion

Domestic tung oil is a very uniform product as shown by the determination of the chemical and physical properties of 74 samples taken over three successive milling seasons.

The refractive index, refractive dispersion, and heat test are correlated with the total eleostearic acid content, the correlation coefficients being 0.69, 0.73, and —0.62 respectively, which indicates that any one of these values can be taken as a rough measure of the eleostearic acid content. The correlation of the eleostearic acid content with the Wijs and hydrogen iodine values was lower, 0.48 and 0.53, respectively. A correlation of —0.81 was found between refractive index and heat test.

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Correction

Gerald R. Lappin of Kingsport, Tennessee, has notified the Journal that the reference for the Lappin-Clark test for carbonyl compounds should read thus: Lappin, G. R., and Clark, L. C., Anal. Chem., *23*, 541 (1951). (His initials have been given by some authors as A. E., he reports.)