

The Seed Oil of *Garcia Nutans**

GEORGE S. JAMIESON, Senior Chemist

and

W. GORDON ROSE, Associate Chemist

Bureau of Agricultural and Industrial Chemistry, Agricultural Research
Administration, U. S. Department of Agriculture

The tree *Garcia nutans* (called Pinonchillo in Mexico), which is a member of the Euphorbiaceae family, is found growing in the southwestern part of Mexico in the States of Sinaloa and Tepic, Central America, Colombia, and probably elsewhere. Contributions from the United States National Herbarium, 23, 620 (1923), give the following description: Small or large tree; leaves alternate, oblong-obovate, 10 to 20 cm. long, long-petiolate, short-acuminate, entire; flowers monoecious, about 1 cm. long; capsule 2 or 3 seeded, about 2.5 cm. wide, fulvous-tomentulose.

The average weight of the brown mottled so-called nuts (seeds) received for this investigation from Mexico, which were the size and shape of small marbles, was 1.2 grams. The nuts consisted of 80.5% of kernel and 19.5% of shell. The kernels contained 53.8% of oil and 2.9% of moisture. The pale yellow oil, which was expressed from 75 kernels using the Carver laboratory hydraulic press, gave the following characteristics:

CHARACTERISTICS OF *GARCIA NUTANS* SEED OIL

Acid value.....	0.65
Iodine value (Wijs, 1 hr.).....	176.7
Diene value (Ellis-Jones).....	81.5
Carbonyl value (Leithe).....	0.0
n_D^{25}	1.5260
Saponification value.....	192.3
Heat test (Browne, 282°).....	7.25 minutes
Unsaponifiable.....	0.5%
Saturated acids (Bertram).....	2.2%

The acids resulting from the determination of the saponification value of *Garcia nutans* oil were precipitated by the addition of hydrochloric acid and taken up in ether; the ether solution was washed and dried in usual manner, after which the ether was evaporated. The residual acids were recrystallized twice from 5-ml. portions of absolute alcohol, yielding 2.1 g. acid (from 4.21 g. oil) that melted at 50-51°. For comparison, *a*-eleostearic acid was prepared from authentic tung oil¹; the twice recrystallized acid so obtained melted at 49-50°. A mixture of this eleostearic acid with acid obtained from *Garcia nutans* oil melted at 50-51°, showing that the two were similar.

The principal constituent acid of *Garcia nutans* oil is, therefore, *a*-eleostearic acid. Calculations based on the empirical Ellis-Jones diene value² of 89.5 indicate the presence of 91.1% eleostearic acid in the oil. Calculated on the basis of an empirical diene value of 85.5 for eleostearic tri-glyceride, the oil would contain 95.3% eleostearic glyceride. Calculated from the determined eleostearic acid content and the saponification value, eleostearic glyceride represents 95.2% of the oil.

It seemed possible, but not probable, that some acid other than eleostearic, such as licanic or parinaric

acid, having conjugated bonds, might be present in relatively small quantity. These acids, if present, would contribute to the diene value as determined, and would be included in the calculated eleostearic acid content. The carbonyl determination demonstrated the absence of licanic acid or any unknown keto acid having a similar system of conjugated double bonds. The absence of parinaric acid, or any unknown acid having a different system of conjugated bonds than that in eleostearic and licanic acids, was demonstrated by the determination of the ultra-violet absorption spectrum of the oil by scientists in another bureau of the Department of Agriculture. The ultra-violet absorption spectrum of *Garcia nutans* oil resembled that of tung oil, thus showing conclusively the absence of any known acid having conjugated double bonds, other than eleostearic and licanic acids which were found to have similar ultra-violet absorption spectra. From the absorption maximum of *Garcia nutans* oil and that of pure eleostearic acid it has been calculated that *Garcia nutans* oil contains 89.0% eleostearic acid, equivalent to 93.1% eleostearic glyceride in the oil. The agreement of this value with that determined by the Ellis-Jones diene procedure, 91.1% eleostearic acid or 95.3% eleostearic glyceride, is considered to be entirely satisfactory, in view of the degree of accuracy of the methods.

The content of saturated acids, amounting to only 2.2% of the oil is lower than has been found in any oil examined in this laboratory. Eleostearic and saturated glycerides and the unsaponifiable matter amount to 98.1% of the oil. The undetermined 1.9% probably consists of oleic and linoleic glycerides, but we were unable to obtain evidence for the presence of these acids from the small quantity of oil available at the time this investigation was made. The oil available was also insufficient for an examination of the saturated acids.

Because of the high diene value of *Garcia nutans* oil, it was interesting to calculate the characteristics of this oil, using the Frahm and Koolhaas equations³ for tung oil. These equations are as follows:

Diene value equals $1400 (n_D^{25} - 1.4681)$.

Wijs iodine value equals $1300 (n_D^{25} - 1.3883)$.

Time of gelation (282°) equals $71.4 - (6/7 \text{ diene value})$ plus 0.3 acid value.

The calculated and found values, respectively, for these characteristics are: Diene value 81.06, 81.5; Wijs iodine value 179.0, 176.7; time of gelation 1.7, 7.25 minutes. With the exception of the time of gelation, these calculated and observed values are in reasonably good agreement. In connection with the lack of agreement between the calculated and found time of gelation, it is of interest to note that a film of the oil on a glass slide dries much more slowly than

*Agricultural Chemical Research Division Contribution No. 118.

a similar film of tung oil. A thin film of *Garcia nutans* oil, exposed to the air, but not to the sun, required more than a week to dry. The dry film has the wrinkled surface characteristic of oils than contain acids having a conjugated system of double bonds. It appears probable that the oil contains substances that effectively retard polymerization or oxidation of the oil. Such substances would also retard gel formation in the Browne heat test.

The authors acknowledge with sincere thanks the assistance of Dr. Russel E. Davis and Mr. Harry Bastron of the Bureau of Animal Industry of this Department who kindly determined the ultra-violet absorption spectrum of the *Garcia nutans* oil.

BIBLIOGRAPHY

1. Nicolet, B. H., J. Am. Chem. Soc., 43, 938 (1921).
2. McKinney, R. S., Halbrook, N. J., and Rose, W. G., Oil & Soap, 19, pp. 141-3 (1942).
3. Frahm and Koolhaas, Rec. Trav. Chim., 57, 79 (1938).

Moisture Determinations on Tung Fruit and Its Components for Control Purposes

A. F. FREEMAN, F. C. PACK, and R. S. MCKINNEY

U. S. Tung Oil Laboratories*
Bogalusa, Louisiana, and Gainesville, Florida

Because the many control analyses required in connection with milling of tung oil in the South are costly and time consuming it is important to simplify procedures and equipment as much as possible and yet have methods that will yield reliable results.

The moisture content of material delivered and processed at the oil mill is of interest to the tung fruit grower and miller from a number of standpoints and any method which provides such information promptly is of considerable value to them. For example, tung fruits frequently are purchased at the mill by weight. Since there is a direct relation between the moisture content and oil content of tung fruit, a rapid method of determining the moisture content at the mill, and thereby affording information for promptly computing the value of each load, benefits both the seller and the buyer.

A method for moisture content described by McKinney and Freeman** required the heating of the components of tung fruits in a drying oven at 101-102°C. for a 24 hour period, but a simpler, quicker method for use at tung mills not provided with complete laboratory equipment seems desirable. It was found that several commercial devices were adequate for such determinations. The common feature of these devices is the blowing of a large volume of air over a heating element and thence through a vessel containing the sample. The vessels are of metal, and the bottoms are closed with metal filter cloths, which pass air very freely. Temperature control is effected generally by thermostats or rheostats. An outstanding feature of the devices is the short heating period required, which occasions a minimum of decomposition during drying.

With one such device it was found that the moisture content could usually be obtained after heating the sample at 260°F. for 10 to 15 minutes. This particular device is composed of a blower and a thermostati-

cally controlled element, so arranged that hot air can be blown through the sample, which is held in a pan 5¼ inches in diameter, 2 inches deep, and having a 500-mesh filter-cloth bottom. An electric interval-timing switch controls the heating period. It is essential, however, that the air blast be brought to the desired temperature before the determination is started. This is done, of course, by operating the heater and blower for several minutes before introduction of the sample. A long-stem thermometer, calibrated in degrees F. is mounted in the cone immediately over the sample pan to give the temperature of the air blast.

After grinding, the sample is weighed directly in the special pan, which has been previously tared, and the pan is placed in the drier for the required time. At the conclusion of the drying period the pan is transferred to a dessicator, in which it is allowed to remain over calcium chloride until the pan and contents have cooled sufficiently for weighing. The weight and percentage loss can then be determined. The percentage loss in weight is recorded as the moisture content.

In order to determine the temperature and time required for drying, materials were heated in this device at several temperatures, weights being taken at various intervals of time to observe progressive weight losses. Check determinations were made by heating a sample from the same lot under a vacuum of 28-29 inches of mercury at 110°C. for 4½ hours. The materials were prepared by grinding each component of the tung fruits twice in a Russwin food chopper, No. 1 type, using a sixteen-tooth cutter. The data obtained for ground tung kernels are given in Table I.

Due to the tendency of the tung oil to undergo oxidation and polymerization, these data indicate that, while the moisture content of tung kernels may be ascertained by drying for five minutes, the drying period at such a temperature and for kernels of such a moisture condition cannot be extended appreciably without increase of sample weight due to oxidation.

* Units of the Agricultural Chemical Research Division, Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Contribution No. 76.

** McKinney, R. S., and Freeman, A. F., Oil and Soap 16, 151-2 (1939).