

water, and 30 ml. phosphoric acid. After 2 minutes the excess permanganate is reduced by adding 5% sodium bisulfite solution. One ml. of a 10% solution of chromotropic acid (1,8-dihydroxynaphthalene, 3,6-disulfonic acid) is then added, followed by 10 ml. of concentrated sulfuric acid. The flask is cooled in an ice-water bath while the sulfuric acid is being added. The solutions are then heated for ½ hour in a boiling water bath, cooled, and diluted to the mark. To obtain a blank solution for the colorimetric measurement, a sample aliquot is carried through this same procedure with the exception of the oxidation step. In this way any material which reacts with the chromotropic acid is compensated by the blank.

The optical density of the solution is determined at 570 millimicrons by any suitable instrument. Equally good results were obtained by the Beckman D. U. Spectrophotometer and a Coleman Junior. By reference to a standard curve (Figure 1) the amount of methanol in the sample aliquot is determined. The grams of methanol divided by the sample weight represented by the aliquot and multiplied by 100 gives the percentage of methanol in the fat.

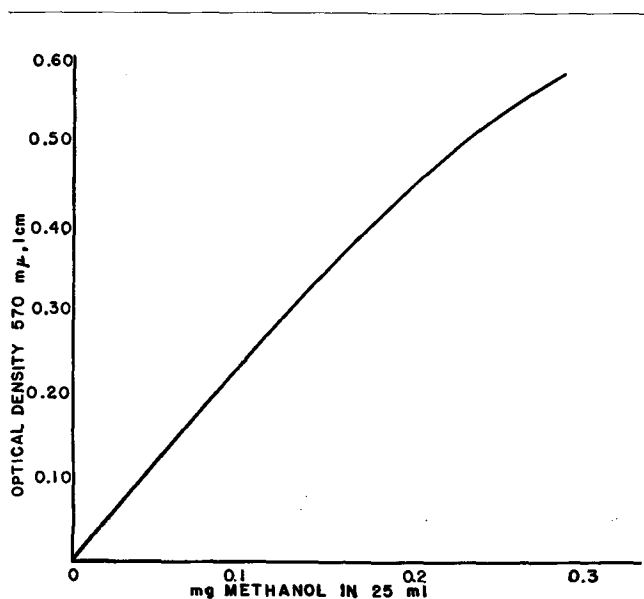


FIG. 1. Standard Curve

## Aceituno Seed Fat<sup>1</sup>

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THE aceituno tree, *Simarouba glauca* DC., which belongs to the family Simaroubaceae, grows to a height of 15 meters, is dioecious, and produces fruit 37 mm. long and 20 mm. wide, greenish yellow in one variety and violet to almost black in another. Because the fruit resembles olives in shape, size, and color, the tree is called aceituno, aceituno silvestre, or aceitillo in Central America (5, 7, 8). The fruit,

<sup>1</sup>A contribution from the Centro Nacional de Agronomía, a technical agricultural service organization for El Salvador, operated jointly by the Government of El Salvador and by the Office of Foreign Agricultural Relations, U. S. Department of Agriculture. United States participation in this work was carried out as part of the Point IV program in El Salvador, administered by the Technical Corporation Administration, U. S. Department of State.

The standard curve is determined in solutions containing aliquots of the sample distillate. Measured amounts of methanol are added to a series of flasks which contain an aliquot of the sample solution. The oxidation and reactions with chromotropic acid are carried out and the optical density of the solutions is determined by the use of the sample aliquot which contains no added methanol as a blank. In this way the effect of any unknown material in the sample distillate is internally compensated.

Table I shows some results obtained by this procedure.

TABLE I  
Results of the Determination of the Methoxyl Content of Fats

| Sample                                    | Methoxyl added | Methoxyl found |
|---|----------------|----------------|
|   | %              | %              |
| Lard.....                                 | 0              | 0              |
| Lard + 0.01% methyl oleate.....           | 0.0011         | 0.0010         |
| Lard + 0.01% methyl oleate.....           | 0.0011         | 0.0012         |
| Lard + 0.01% methyl oleate.....           | 0.0011         | 0.0011         |
| Rearranged lard before deodorization..... | 0              | 0.21           |
| Rearranged lard after deodorization.....  | 0              | 0.0006         |

The solvent used in the saponification step must be checked for methanol and formaldehyde content. Materials such as ethylene glycol, propylene glycol, cellosolves, and polyethylene glycol were found to give very high reagent blanks. However diethylene glycol gives a very low blank and therefore may be used in the procedure.

Also it was found that the commonly used antioxidants did not interfere with the determination.

### Summary

A method for the determination of the methoxyl content of fats has been developed using chromotropic acid. The fat is saponified and the methanol recovered by distillation, oxidized, and reacted with chromotropic acid. The optical density of the colored solution at 5,700 Å is proportional to the methoxyl present.

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which contains a sweetish pulp with an astringent aftertaste, is a favorite, especially with children, and is sold in the markets.

The seed is ovoid in shape, about 20 mm. long and 12 mm. wide, deeply veined, and easily broken. The kernel is greenish in color and has an intensely bitter and persistent taste.

The seeds contain about 30% kernels and 70% shells. The kernels contain between 55% and 65% fat and 14% moisture. No difference in yield of fat has been observed between the white and "black" varieties.

The tree grows wild from Mexico to Panama, and a related species is found in the Caribbean area (2, 6).

In El Salvador it is found in dry areas at altitudes ranging from between sea level to about 600 meters (2,000 feet), but it can be grown at higher elevations. Because the tree grows on semiarid soils, it is being planted in some areas in El Salvador where no other plants of economic value can be grown. It begins to produce fruit at about four years of age, but not until it is about six years old does it come into full production (Table I). Harvesting of the fruit is done by hand and consists simply of picking the fruit from the ground.

TABLE I  
Yield of Aceituno Fruit at Various Ages,  
per Tree, per Hectare, and per Acre

| Age of tree   | Per tree <sup>a</sup> | Per hectare <sup>b</sup> | Per acre <sup>c</sup> |
|---------------|-----------------------|--------------------------|-----------------------|
|               | lbs.                  | lbs.                     | lbs.                  |
| 4 years.....  | 7                     | 1,575                    | 637                   |
| 6 years.....  | 20                    | 4,500                    | 1,820                 |
| 10 years..... | 30                    | 6,750                    | 2,730                 |

<sup>a</sup> Calculated from yield of individual wild trees.

<sup>b</sup> Calculated on basis of 225 trees per hectare.

<sup>c</sup> Calculated on basis of 91 trees per acre.

To establish commercial stands, growers plant seed in seedbeds and transfer seedlings to the field at about 2½ months of age.

At the present time the tree has no known diseases, but it is attacked by the larvae of *Atteva floridana* (Neum), which eat the leaves of young trees and are found also in the flowers. This pest is not yet very serious; but as the concentration of trees increases through cultivation, it may possibly become important. However the larvae can be destroyed by dusting with BHC or DDT.

The wood of the aceituno tree is white and soft and is used for making cheap furniture, boxes, and match sticks. It is also used as a source of an antimalarial (3) and an antidiarrhetic.

The fat contained in the kernels of the seed has been used by the natives for making soap in the home. For such use the fat is extracted by crushing the seed and boiling it in water. After most of the nonfatty residue has been separated, wood ashes are added to the fat to saponify it. Although the method is primitive, the soap obtained is of relatively good quality.

The first attempt to utilize aceituno fat commercially was in the production of soap. In view of the similarity of the fat in consistency, color, and other characteristics to related edible fats, aceituno was fed to rats in order to determine if the bitter principle contained in the seed had been completely removed during refining. The tests proved that aceituno fat compared favorably with the other edible fats, and later Squibb *et al.* (4) confirmed these results. As a result of these tests, aceituno fat is now used primarily for edible purposes, and only the refinery soap stock is used for making soap.

### Processing

The only difficulty encountered in decorticating aceituno seed is the separation of the kernels from the hulls; both have similar densities and therefore they are difficult to separate by applying aspiration. On the other hand, the hulls are brittle and do not adhere to the kernels. The one factory that processes aceituno in El Salvador purchases kernels rather than seed. These kernels have been hand-shelled by the

grower or collector, and the factory cracks and rolls them in a manner similar to that used for preparing cottonseed kernels.

For the preparation of laboratory samples of aceituno fat a Carver hydraulic press has been used to press ground kernels at a temperature of 100° C. and a pressure of 5,000 p.s.i. The moisture content of the seeds has usually been 14%, and yield of fat has not been observed to differ appreciably with variations in the moisture content. The residual cake obtained contains about 18% oil.

The first commercial production of aceituno fat was made in a box hydraulic press operated at a pressure of 5,000 p.s.i., with meal cooked at 220° F. for 20 minutes. Residual cake contained about 17% oil. Subsequently the fat was expressed in a Super Duo Expeller, which reduced the residual fat in the cake to about 7%.

### Characteristics of the Fat

The crude fat, obtained either by pressure or by extraction with a solvent, is pale green, has a mild odor, and a slightly bitter taste. It is a solid or plastic fat at ordinary temperatures and, once solidified on a chill roll, remains solid even at room temperature. The characteristics and glyceride composition of aceituno fat are given in Tables II and III.

TABLE II  
Characteristics of Aceituno Fat<sup>a</sup>

| Characteristic                      | Value  | Characteristic           | Value |
|-------------------------------------|--------|--------------------------|-------|
| Refractive index N <sub>D</sub> 40° | 1.4596 | Unsaponifiable matter, % | 0.4   |
| Specific gravity 25/25°             | 0.908  | Reichert-Meißl value     | 1.4   |
| Melting point, °C.                  | 28.00  | Polenske value           | < 5.0 |
| Acid value, % oleic                 | 0.68   | Hehner value             | 1.76  |
| Iodine value                        | 57.6   | Kirschner value          | 0.12  |
| Saponification value                | 192.15 | Soluble acids, %         | 0.03  |

<sup>a</sup>All characteristics were determined as prescribed by the Official and Tentative Methods of the American Oil Chemists' Society (1).

TABLE III  
Composition of Aceituno Fat<sup>a</sup>  
(Expressed as percentage of glycerides)

| Constituent    | Per cent | Constituent    | Per cent |
|----------------|----------|----------------|----------|
| Oleic.....     | 59.1     | Diene.....     | 0.13     |
| Linoleic.....  | 3.3      | Triene.....    | 0.002    |
| Linolenic..... | 0.35     | Saturated..... | 31.7     |

<sup>a</sup>Determined at the Southern Regional Research Laboratory, Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, New Orleans, La. A.O.C.S. Method Cd 7-48.

Aceituno fat is refined in a manner similar to the one used for coconut oil, using 22° Bé. caustic soda in a proportion that is about 60% of that used for cottonseed oil, at a temperature of 45° C. (113° F.). The soapstock is solid and separates easily. During the alkali refining there is no reduction in color, but the fat is readily bleached with acid earth. The fat is generally deodorized for 4 hours at 232° C. (450° F.).

The finished product is snow-white and needs only to be passed over a chill roll and packaged. It is a natural vegetable shortening requiring no hydrogenation or blending with other fats. The refined fat is used for cooking and baking and is suited especially for making biscuits and crackers. In general, it can be used in the same manner and for the same purposes as the commercial shortenings.

The crude fat can be used directly for making soap. It is readily saponified and produces a soap with excellent lathering properties.

### Discussion

The storage of aceituno seed presents no special problems except that one must take care against insect infestation. The seed may be attacked by the larvae of the Indian meal moth, *Plodia interpunctella* (Hbn.), and the almond moth, *Ephesia cautella* (Wlkr.).

The residual cake is rich in proteins (50%), but it contains a bitter principle that is related to quassine and is probably similar to or identical with simarubin, isolated from *Simarouba amara* Aubl. The meal is toxic to livestock and is therefore now being used only as a fertilizer. The cake contains 8.12% nitrogen, 1.90% phosphoric acid as P<sub>2</sub>O<sub>5</sub>, and 1.17% potash (K<sub>2</sub>O).

Work is under way to develop an economical method of detoxication of the cake in order to permit its use as feed for livestock.

### Summary

The seed of the tree *Simarouba glauca*, which is known as aceituno, aceituno silvestre, and aceitillo in Central America, contains about 65% of a solid or plastic fat. The crude fat is greenish in color and has a slightly bitter taste, but after refining it yields a snow-white, odorless, and practically tasteless product having the same uses as commercial shortenings.

Refining is carried out in a manner similar to that used for coconut oil.

The fat is produced commercially in El Salvador, where it is used for practically all purposes in which vegetable shortening would be used. The residual press cake is toxic to livestock and can be used at present only for fertilizer.

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## The Hydrocarbons of Ouricuri Wax

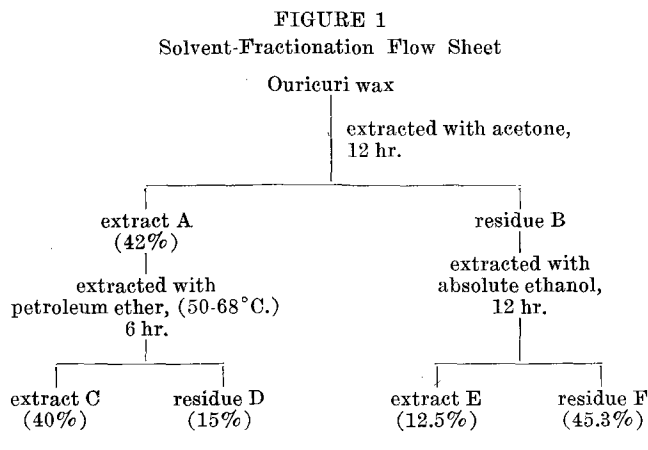
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THE ouricuri tree is one of Brazil's most important palm trees. Its seeds yield a fatty oil, and from its leaves while they are still green, there is recovered a hard wax by scraping them with glass or metal. It was not until some 15 years ago, following the adoption of improved purification techniques, that ouricuri entered the list of the several waxes exported from this country. To the United States at that time were sent a mere 3,075 kg. Three years later exports of this product to the States alone had increased over 100-fold (2).

Ouricuri wax finds use as a substitute for carnauba wax in floor waxes, shoe creams, other polishes, and inks used in producing typewriter carbon paper. Like carnauba it can also be used as a "melting point booster" for paraffin waxes. It is reported that ouricuri wax has been used in the finishing of bombing and fighter planes because of the high polished surfaces that can be produced with it so that they are resistant to air friction and to wetting or condensation (5).

The wide technological utilization of this wax stands in marked contrast to the paucity of available literature on chemical investigations pertinent to its constitution. The only intensive study of any significant merit appears to be that reported by Luedecke (1), who has claimed the presence herein, among other substances, of hydrocarbons and esters of myristic and cerotic acids.

In this communication we report the results of a study undertaken not so much to substantiate or to contradict existing views on the chemical composition



of ouricuri wax as to explore the possibilities of using an approach other than the conventional saponification-fractional crystallization techniques to the analysis of plant, and perhaps insect, waxes. The immediate objective however was the characterization of the hydrocarbon components of this wax. The following account will show that solvent-fractionation, molecular distillation, and column chromatography were successfully used to bring about not only the resolution of ouricuri wax into groups of its components but also the isolation of the individuals comprising the mixtures in question.

### Experimental

*Solvent-Fractionation.* The regular article of commerce, previously ground to a coarse powder in the laboratory, was extracted with acetone, petroleum

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