Licania Arborea (Cacahuananche) Seed Oil[*]

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Our attention was first called to the *Licania arborea* tree and its seed oil in December, 1940, by Frederico Mohor of Mexico City when he inquired about the possibility of using the oil as a lubricant. Shortly afterward he sent us a small sample of fruits and later, other botanical material. He wrote that the oil had been expressed in Mexico on a small scale for some years and was used along with other oils for making soap which, however, soon acquired a strong rancid odor; this probably accounts for his trying to find a more suitable use for the oil. At that time nothing was known in Mexico or elsewhere about the chemical nature of the oil. In addition to several small samples of fruits and oil received by us during 1942, a 25-pound and, later, a 58-pound sample of the fruits were obtained for experimental purposes through the assistance of the State Department from Mexico.

The tree *Licania arborea*, which is a member of the Rosaceae family, is found growing in certain regions of Mexico and Central America. In Mexico it is commonly known as cacahuananche; in Costa Rica, as alcornogue; and in Guatemala and Honduras, as encina. The names cana dulce and quirindal are also applied to this tree.

In Mexico the trees are particularly numerous in the States of Guererro, Marelos, Michvacan, and Oaxaca. As in the case of the Brazilian oiticica tree *(Licania rigida)*, it is found to thrive in open situations and not at all in regions covered by tropical jungle growths.

The mature fruits are dark-green in color and ovoid in shape. They vary much in size, ranging from 0.5 to 2.5 cm. in length and from 0.5 to 1.5 cm. in diameter. The average weight of the air-dried fruits received by us was 0.93 gram, but when harvested they weigh from one to four grams each. The fruits consist of an outer covering 1 to 3 mm. thick, under which is a shell, less than 1 mm. thick, enclosing a single reddish kernel having a striated surface similar to that of the much larger oiticica kernel. The kernels, which amounted to 45% of the air-dried fruits, contained 68.9% of oil (31% of whole fruit) and 3.2% of moisture.

The oil used in the present investigation was expressed from the fruits in a satisfactory manner using our half-sized Anderson oil expeller. A previous attempt with the separated kernels resulted in the ground material being extruded through the oil drainage slots of the expeller. A similar result was obtained earlier when an attempt was made to press them in a Carver laboratory hydraulic press. Some hours after expression, the oil began to solidify, which also is characteristic of the Brazilian oiticica oil, but like the latter, heating of this oil for about 20 minutes between 205° and 220°C. renders it permanently liquid under proper storage conditions.

The characteristics of the oil are given in the following tabulation:

CHARACTERISTICS OF OIL FROM *L. ARBOREA*

Refractive index at 25°	1.5163
Saponification value	187.3
Iodine number (Wijs—1 hr.)	153.0
Diene value (Ellis-Jones)	60.9
Carbonyl value (Leithe)	121.4
Acid value	0.8
Unsaponifiable substances, per cent	0.5
Saturated acids (Bertram), per cent	11.1
Browne heat test (minutes)	15.5

About 25 g. of the oil was saponified by heating for 15 minutes in the usual manner with a mixture of 13 ml. of a 50% potassium hydroxide solution and 25 ml. of 95% alcohol, diluting with 200 ml. of water, adding a distinct excess of hydrochloric acid, and extracting the mixed fatty acids with 200 ml. of ether. This solution was washed free from hydrochloric acid and the ether was distilled. The residual fatty acids were subjected to fractional crystallization from 75 ml. of a mixture of equal parts of alcohol and petroleum ether (88°-95°). The resulting crop of acids was then recrystallized from 50 ml. of petroleum ether, and finally from 20 ml. of alcohol. About 2.6 g. of acids was obtained which gave a melting point from 74.5° to 75.5° and this is identical with the melting point of the alpha-licanic acid from oiticica oil. Additional proof of the identity of the acid was obtained by the following experiment in which isomerization of the conjugated unsaturated acid was accomplished by the procedure described by Strain.[2]

Freshly prepared mixed fatty acids from 50 g. of the oil were dissolved in 200 ml. of 85% methyl alcohol, then 0.50 g. of iodine in 10 ml. of methyl alcohol was added. The mixture was exposed to direct sunlight for 30 minutes and allowed to stand overnight at room temperature. The next day, after cooling to 0°, the crystalline acid was filtered and the filtrate reserved for further investigation. The acid fraction, which melted between 92° and 96°, was recrystallized from carbon tetrachloride, and finally from alcohol. The purified product melted at 99.5°, which is the same temperature reported for pure beta-licanic acid by Brown and Farmer.[1]

The filtrate from the first crystallization of the beta-licanic acid, described in the previous paragraph, was mixed with an equal volume of water and the acids were extracted with petroleum ether. An insoluble fraction of the acids, which amounted to 2.7 g., was removed by filtration and found to be beta-licanic acid. After cooling the filtrate to —18°, a crop of solid acids (6.2 g.) was obtained which was found to be a mixture of saturated acids and some beta-licanic acid. The petroleum ether was distilled from the filtrate. The 11.8 g. of residual liquid acids obtained were dissolved in 80 ml. of acetone, cooled again to —18°, and then filtered. A crop of crystals of saturated acids (2.03 g.) was obtained which melted between 52° and 57°. The acetone was distilled from the filtrate, and a portion of the residual acids was

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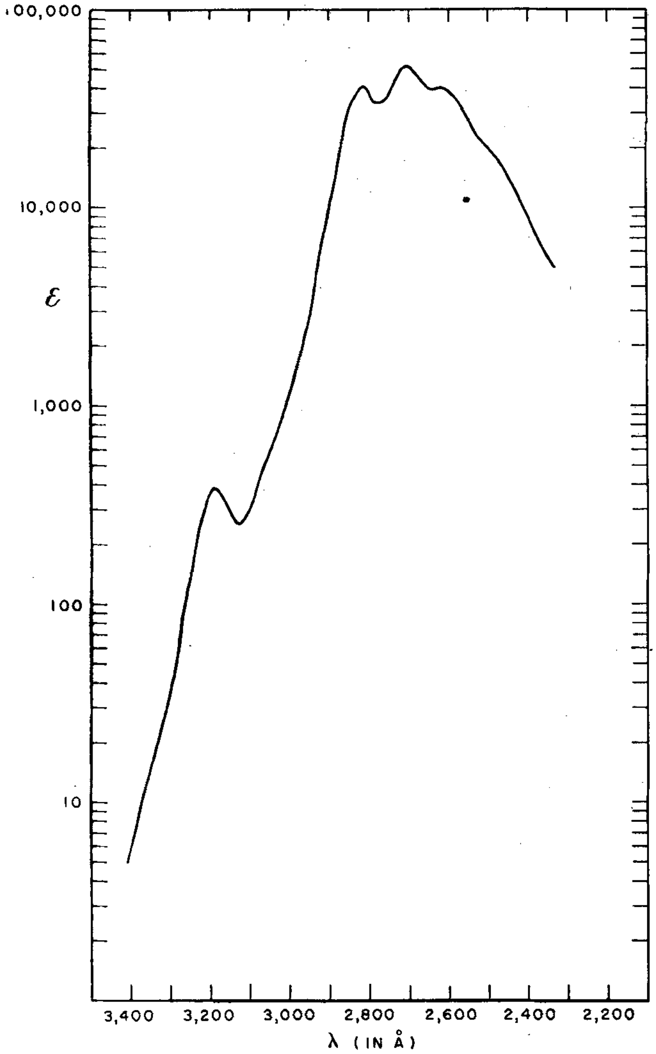

FIG. 1. Elaeostearic Acid. Concentrations, 0.00002-0.002 M, in ethyl alcohol.

oxidized to hydroxy acids using the Frankel-Brown [3] permanganate procedure. From this experiment, specimens of dihydroxy stearic acid melting at 129°-131° and tetrahydroxy stearic acid melting at 171°-172° were obtained and identified, which indicated that the oil contained both oleic and linoleic acids.

Direct evidence of the presence of elaeostearic acid was not obtained and it is possible that the oil does not contain any, although the calculations based on the use of the carbonyl and diene values indicate the presence of a small quantity. As will be discussed in more detail later, the determined diene values for both licanic and elaeostearic acids are somewhat below the calculated values, and the same is true of the carbonyl determination. Furthermore, it is possible that the errors in the empirical values used in these calculations, or an inherent error in the determination of the carbonyl value of the oil, account for the small quantity (1.6%) of elaeostearic acid calculated to be present.

The ultra-violet absorption spectra of the oil, licanic and elaeostearic acids, and methyl licanate were determined by R. E. Davis and H. Bastron of the Bureau of Animal Industry of this Department with the hope of being able to demonstrate the absence or pres-

TABLE I

Compound	Solvent	Conc.	Max. (Å)	ε*	Min. (Å)	ε*
Elaeostearic acid	Ethyl alcohol	0.002 to 0.00002 M	2705	52,000		
			2620	40,000	2640	39,000
			2810	41,000	2780	34,000
			3190	380	3130	250
Licanic acid	Ethyl alcohol	0.002 to 0.00002 M	2705	52,000		
			2610	38,000	2640	37,000
			2820	39,000	2780	35,000
			3180	100	3140	98
Ethyl licanate	Ethyl alcohol	0.2 to 0.00002 M	2690	52,000		
			2610	40,000	2630	39,000
			2790	42,000	2760	34,000
			3240	450	3190	420

TABLE II

Oil	Solvent	Conc. (gms. per liter)	Max. (Å)	k*	Min. (Å)	k*
Garcia mutans	Ethyl alcohol	0.0936 to 0.00936	2705	170	2640	140
			2610	145		
			2810	140	2770	130
		8.204 to 0.08204	3170	0.87	3130	0.80
Licania arborea	Ethyl alcohol	0.1248 to 0.01248	2705	130		
			2610	115	2640	110
			2810	105	2780	100
		8.568 to 0.08568	3170	0.38	3140	0.36
Tung	Ethyl alcohol	0.1082 to 0.01082	2705	155		
			2610	135	2640	130
			2810	125	2780	120
		9.230 to 0.0923	3180	0.51	3130	0.45

k = specific extinction = E/cd
ε = molecular extinction = k x mol. wt.
E = extinction = log. I_0/I
I_0 = incident intensity
I = transmitted intensity
c = concentration in gms. per liter
d = cell depth in centimeters

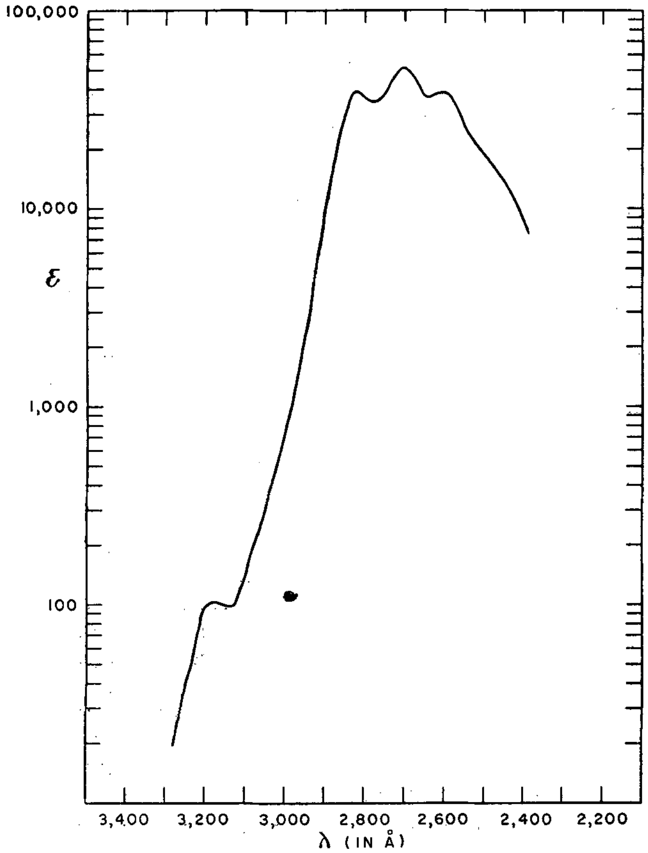

FIG. 2. Licanic Acid. Concentrations, 0.00002-0.002, in ethyl alcohol.

ence of elaeostearic acid in the oil. However, the curves obtained by plotting the natural logarithm of the molecular extinction against the wave length showed that the carbonyl group of the licanic acid does not affect the ultra-violet absorption; consequently the curves obtained for elaeostearic and licanic acids are practically identical. Although the prime object of these experiments was not accomplished, nevertheless the data obtained indicated that the oil contained 73% of conjugated licanic and elaeostearic acids, and this is in substantial agreement with the value of 71.9% calculated by using, as already mentioned, the carbonyl and diene values.

Data for these measurements are given in Tables 1 and 2 and from the curves shown in Figures 1 to 6.

The procedure of Morrel and Davis [4] was also used in an attempt to determine the presence of elaeostearic acid, but without success. No azelaic acid could be found in the oxidation products. This is not considered to exclude the possible presence of a small quantity of elaeostearic acid, because it has not been demonstrated that as little as 1.2% could be detected by this procedure.

The addition of bromine to a portion of the oleic-linoleic acids fraction described above, dissolved in ether, gave no precipitate of hexabromide, which showed the absence of linolenic acid.

In connection with the determinations and calculation of the percentages of the constituents of this oil, it should be mentioned that it has been shown [5] that both elaeostearic acid and its methyl ester react with maleic anhydride to the extent of 98.1% of the theoretical amount. A similar investigation made with pure alpha-licanic acid from the *L. arborea* oil, using the Ellis-Jones procedure, gave values of 84.7 and 84.5% of the theoretical. The average of these figures, 84.6, equals 97.5% of 86.8%; the theoretical or calculated value. This shows that both licanic and elaeostearic acids behave similarly in the determination of the diene value by the Ellis-Jones procedure.

Experiments with the Leithe [6] and the Kaufmann [7] procedures for the determination of the carbonyl value indicated that the former method possessed distinct advantages, including greater precision. Even with the Leithe procedure the use of free fatty acids for this determination was not satisfactory because of the difficulty with the end point of the titration, although an extraction of the ether solution of the fatty acids, as suggested by Leithe, was made. Consequently the methyl ester of licanic acid was used to ascertain the completeness of the reaction with hydroxylamine. This reagent was prepared by dissolving 10.0 g. of hydroxylamine hydrochloride in 5 ml. of water and adding 12 ml. of 6.7 N sodium hydroxide. To this solution, 400 ml. of absolute alcohol was added. The separated sodium chloride was filtered and washed with 50 ml. of absolute alcohol to remove the adhering hydroxylamine. For the determination, from 0.5 to 2.0 g. of the sample was accurately weighed into a 250 ml. flask having a ground-glass neck; 25 ml. of the hydroxylamine reagent was added and the mixture was boiled for 15 minutes under a reflux condenser having a glass joint for attachment to the flask. After pouring 50 ml. of water through the condenser tube into the attached reaction flask, the solution was titrated with 0.25 N hydrochloric acid using bromophenol blue as indicator. The titration was made using the light from a fluorescent titration lamp, and a spot plate to aid in the determination of the end point. The method was applied to ethyl α-licanate and

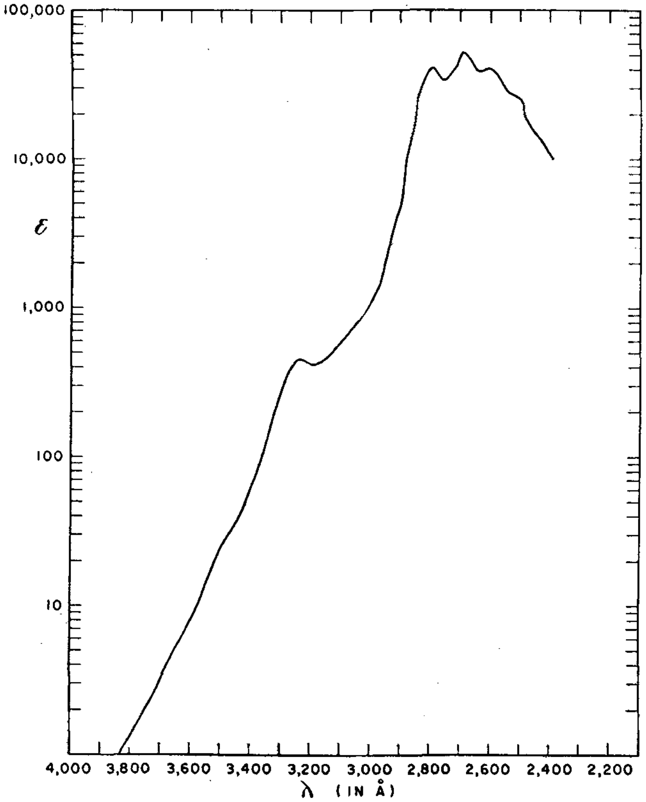

FIG. 3. Ethyl Licanate. Concentrations, 0.00002-0.2 M, in ethyl alcohol.

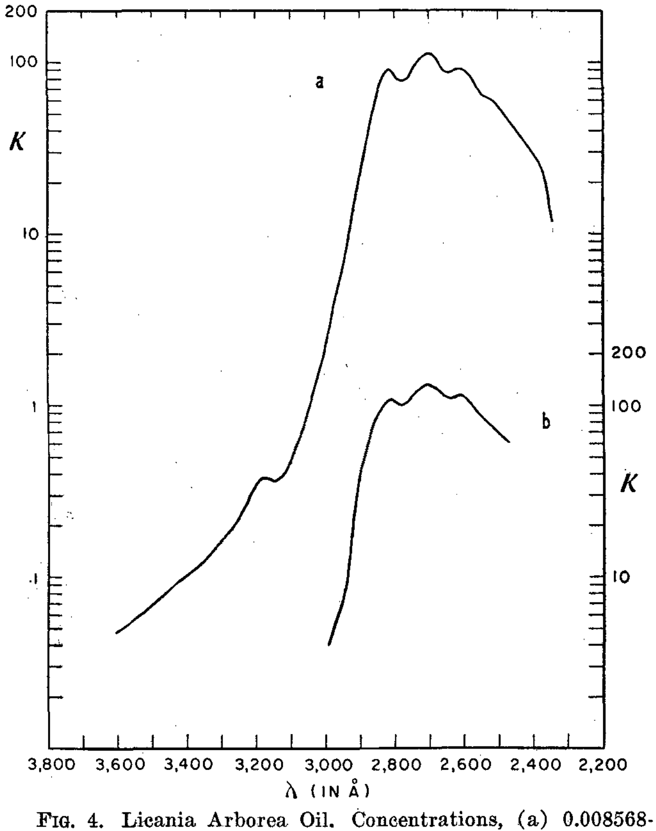

FIG. 4. Licania Arborea Oil. Concentrations, (a) 0.008568-8.568 gm./l, (b) 0.01248-0.1248 gm./l. Solvent, ethyl alcohol.

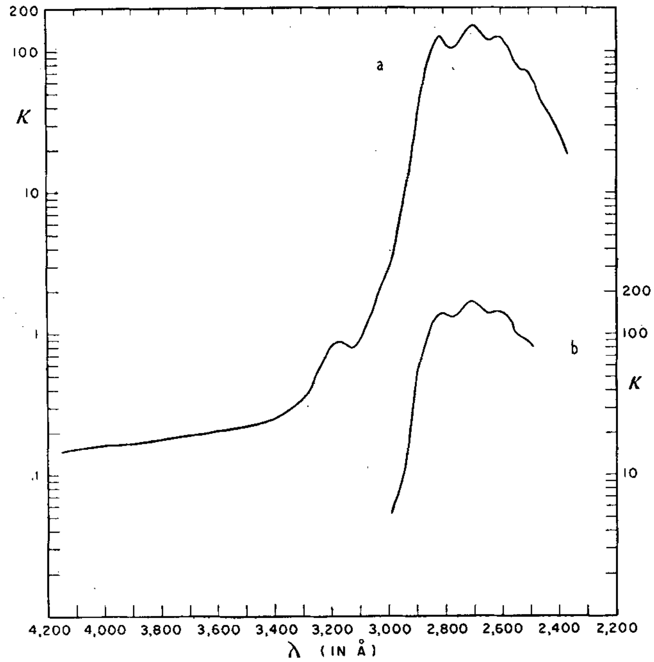

FIG. 5. Garcia Nutans Oil. Concentrations, (a) 0.008204-8.204 gm./l, (b) 0.00936-0.0936 gm./l. Solvent, ethyl alcohol.

carbonyl values of 157.2 and 156.8 were obtained. The average (157) of these results is 89.9% of the calculated value 175.1. The carbonyl values found for the methyl ester were 164.4 and 165.2. The average of these results (164.8) amounts to 90.1% of the calculated value 183.2.

The Wijs iodine number (1-hour reaction period, temperature, 20-23°) of pure alpha-licanic acid was 189.7, which is 109.3% of 173.6, the number for two double bonds. This is somewhat higher than that found for elaeostearic acid for which one of us[5] found the iodine number of 190.8 or 104.6% of the calculated value 182.3 for 2 double bonds. This finding is in agreement with the observation of Kaufmann and Baltes,[8] namely, that the enolization of the keto group of licanic acid results in the increased absorption of halogen. However, we do not agree in that the use of the iodine number must be excluded in calculations, because we have found that reproducible empirical results can be obtained provided standardized conditions are used for this determination. It may be possible that the Kaufmann bromine reagent gives less reproducible results in the case of licanic acid.

The licanic glyceride content of the oil was calculated using the carbonyl value of 121.4 and the empirical value of 165.5 for the triglyceride, which is 90.0% of the theoretical value (183.9). These calculations indicated that the oil contained 70.2% of licanic acid, corresponding to 73.3% of the triglyceride. The calculated diene value, on the basis that the oil contained 73.3% of the triglyceride of licanic acid, is 59.55, whereas the determined value was 60.9. This difference indicates the presence of 1.6% of elaeostearic acid but, as previously mentioned, no confirmatory evidence could be obtained.

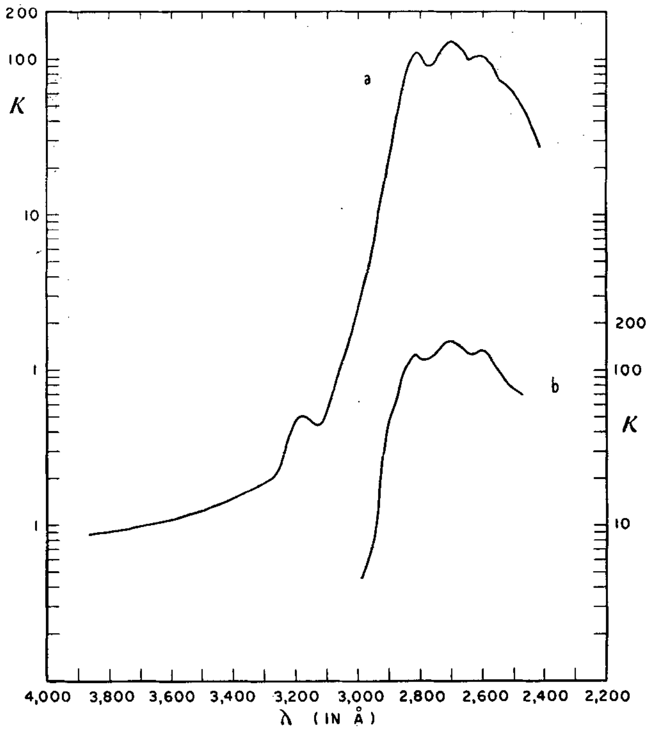

FIG. 6. Tung Oil. Concentrations, (a) 0.00923-9.23 gm./l, (b) 0.01082-0.1082 gm./l. Solvent, ethyl alcohol.

The saturated-acid glycerides, which were calculated from the quantity of acids found by the Bertram method, was 11.6%. The sum of the glycerides of licanic and elaeostearic acids and the unsaponifiable matter is 87.0%, which leaves 13% to be accounted for by the oleic and linoleic glycerides. The following experiments were made to determine the proportions of these substances in oil: A fraction containing these acids and similar to that previously described in connection with their identification was prepared, and esterified with ethyl alcohol. The mixture of esters gave a carbonyl value of 19.7, a diene value of 11.4, a thiocyanogen value of 76.5, and a Wijs (1 hour) iodine number of 116.4. Calculations indicated that the ester mixture contained 12.5% of ethyl licanate and 2.1% of ethyl elaeostearate. From these figures it was calculated that the ethyl licanate accounted for 21.6 of the iodine number and 11.6 of the thiocyanogen value of the ester mixture, and the ethyl elaeostearate accounted for 3.6 of the iodine number and for 1.7 of thiocyanogen value of the mixture of esters. After deduction of these values, there remains an iodine number of 91.2 and a thiocyanogen value of 64.9, both of which were due to the oleic and linoleic esters. By substituting these values in the equations

$$\text{Linoleic acid} = 1.2485\ (\text{I-SCN})$$
$$\text{Oleic acid} = 1.224\ \text{I} - 2.5146\ (\text{I-SCN})$$

it was calculated that the ester mixture contained 32.8% oleic acid and 45.5% linoleic acid. On the assumption that these acids are present in the oil in the same proportions as in this ester mixture, *L. arborea* oil contains 7.6% linoleic glyceride and 5.4% oleic glyceride. The above assumption is justified, since any losses incurred in the experiments performed in obtaining this mixture would be entrainment losses, and should result in a loss of the acids in direct proportion to the extent that they are present.

The calculated composition of the oil, as detailed above, is given in the following table:

Acids	Oil	
	Mixed Glycerides	Fatty Acids
	Pct.	Pct.
Licanic	73.3	70.3
Linoleic	7.6	7.3
Oleic	5.4	5.2
Elaeostearic	1.6	1.5
Saturated	11.6	11.1
Unsaponifiable	0.5	.....
Total	100.0	95.4

The following calculation was made of the iodine number of the oil, using the above percentages of the glycerides present, and the empirical iodine values of licanic and elaeostearic glycerides.

Licanic....................73.3% × 181.9 = 133.3
Linoleic.................... 7.6% × 173.2 = 13.2
Oleic.................... 5.4% × 86.0 = 4.6
Elaeostearic.................... 1.6% × 182.4 = 2.9
154.0

The calculated iodine value of 154.0 is in satisfactory agreement with the experimental value of 153.0.

In conclusion, it should be mentioned that a sample of *Licania arborea* seed oil was supplied to Dr. Henry A. Gardner of the National Paint, Varnish and Lacquer Association, who prepared varnishes from it. Gardner[9] reported that the drying times of these varnishes were similar to those made with oiticica oil. The results of cold and hot water tests made on the varnish films were found to be satisfactory. He concluded that if made available the oil could be used to advantage by the paint and varnish industry.

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The Chemical Composition of Depot Fats In Chickens and Turkeys*,**

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The scientific literature contains but little data on the chemical composition of the depot fats of chickens and turkeys. In the present investigation the depot fats of several breeds of these two species were analyzed to extend these data and determine whether chicken fat is different from turkey fat in any important respect.

Review of Literature

The chemical and physical characteristics of chicken and turkey fat reported in the literature are summarized in Tables I and II.

In 1897 Amthor and Zink (1) determined a few of the chemical and physical characteristics of fats from many species of animals and birds. The outstanding feature of their work with chicken fat was the finding of an unusually high acetyl value. In 1911 Ross and Race (2) reported high acetyl values for both turkey and chicken fats. Grossfeld (3) determined a few of the constants of chicken fat and made a rough estimation of component fatty acids, while Pritzker and Jungkunz (4) limited their investigation to a determination of the iodine number. Hilditch, Jones and Rhead (5) estimated quantitatively the component fatty acids of Light Sussex hens. They found no significant differences between fats from the gizzard, abdomen and neck of hens seven

TABLE I

Chemical and Physical Data on Chicken Fat (from Literature)

Investigator	Amthor and Zink (1)		Ross and Race (2)		Grossfeld (3)	Pritzker and Jungkunz (4)	Hilditch, Jones and Rhead (5)	Brown and Sheldon (6)	
Determination	Fat	Fatty acids	Fat	Fatty Acids	Fat	Fat	Fat	Fat	Methyl esters
Sp. Gr. 30/30°C.	0.9241	0.9283	0.9065	0.8866					
M.P. °C.	33-40	38-40	23-27	27-30					
Sol. Point °C.	21-27	32-34							
Ref. Index 40°C.					1.4610-1.4620				
Sap. No.	193.5	200.8	204.6	208.6	195.2-195.3			{ 194.5 { 195.8	{ 194.2 { 195.2
Iodine No.	Hübl 66.7	Hübl 64.6	Wijs 71.5	Wijs 73.6	Hanus 69.9-78.2	Hanus 69.0-73.1		76.7-77.2*	73.8-74.8*
SCN No.					62.5-62.8				
Acetyl No.	45.2			25.4					
Reichert-Meissl			1.8						
Polenske			2.1						
Hehner			94.6						
Satd. Acids %							30.35		
Palmitic %					18.4-19.3		24.0-26.7		
Stearic %					8.9- 7.5		4.1- 7.1		
Unsatd. Acids %									
Oleic %					54.7-55.4		36.9-43.0		
Linoleic %					17.9-17.8		18.4-22.8		

* = method not given.

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