geometric and positional isomers react with equal ease. If the probabilities of reaction of all the isomers were not equal, the theoretical equilibrium ratio proposed by Blekkingh (3) would seldom, if ever, be attained under varied conditions of temperature, catalyst concentration, and dispersion of hydrogen.

The data also indicate that the concentration of hydrogen in the oil and therefore on the catalyst surface influences the comparative rates of saturation and isomerization of the double bond. For example, the hydrogenation shown in Figure 2, carried out under pressure with efficient agitation, thus producing a high concentration of hydrogen on the catalyst, reached isomerization equilibrium just before complete saturation occurred. However Figure 4 shows that in the hydrogenation in which the hydrogen concentration on the catalyst was low, isomerization occurred at a much greater rate than hydrogenation. This can be explained by the hydrogenation-dehydrogenation concept. If there is a very high concentration of hydrogen on the catalyst surface, the chance of a hydrogen being taken off a half-hydrogenated molecule before another is added is less than in a system in which the concentration of hydrogen on the catalyst is low. Therefore, under conditions in which all of the active catalyst is kept saturated with hydrogen, no isomerization would occur. But, also, without some hydrogenation no isomerization will occur. Therefore it is believed that an exchange reaction between the catalyst and the unsaturated material takes place as the half-hydrogenation-dehydrogenation concept would indicate.

Summary

It was found that during the hydrogenation of octadecenoic acids, migration of the double bonds takes place equally in each direction. The positional isomers that are formed are composed of the 1:2 equilibrium mixture of *cis* and *trans*. A partial hydrogenation-dehydrogenation theory may be applied to explain the simultaneous formation of both positional and geometrical isomers.

Acknowledgment

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REFERENCES

1. Allen, R. R., and Eggenberger, D. N., Anal. Chem., *27*, 476 (1955).
2. Blekkingh, J. J. A., Discussions Faraday Soc., *1950*, No. 8, 200-201.
3. Blekkingh, J. J. A., Bull. Soc. Chim. France, *1950*, 278-282.
4. Boelhouwer, C., Gerckens, J., Ong Tian Lie, and Waterman, H. I., J. Am. Oil Chemists' Soc., *30*, 59-61 (1953).
5. Feuge, R. O., Pepper, M. B. Jr., O'Connor, R. T., and Field, E. T., J. Am. Oil Chemists' Soc., *28*, 420 (1951).
6. Higuchi, T., Hill, N. C., and Corcoran, G. B., Anal. Chem., *24*, 491 (1952).
7. Hilditch, T. P., and Vidyarthi, N. L., Proc. Roy. Soc., London, *A122*, 552 (1929).
8. Jackson, F. L., and Callen, J. E., J. Am. Oil Chemists' Soc., *28*, 61 (1951).
9. Moore, C. W., J. Soc. Chem. Ind., *38*, 320T (1919).
10. Swern, Daniel, Knight, H. B., Shreve, O. D., and Heether, M. R., J. Am. Oil Chemists' Soc., *27*, 17-21 (1950).

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The Mbocayá Palm: An Economic Oil Plant of Paraguay

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THE MBOCAYA PALM (*Acrocomia totai* Mart.) is one of about 25 species of spiny palms belonging to the genus *Acrocomia,* which abounds from the West Indies and Mexico to Paraguay and Argentina and encompasses a climatic range from tropical to temperate. From the economic and utilitarian point of view the mbocayá is of greater importance to Paraguay than any other of the 10 or more species of indigenous palms. It is closely related to, and difficultly distinguishable from *A. sclerocarpa* Mart., which is said to occur over a wide area of Brazil. It has been referred to in the literature by a variety of common names (Paraguay: mbocayá, mbocayá Cayiete; Bolivia: cayara, totai; Brazil: grou-grou, mbocayá-ubá, mocaje, mucujá, noz do Paraguay; elsewhere: Paraguay palm; totai palm). Unfortunately mbocayá, or variants thereof, has been applied to at least five and perhaps more species of palms (19). In Paraguay the palm is frequently referred to as coco, cocotero-paraguayo, and occasionally as coquito del Paraguay. These names are unfortunate because the palm and its fruit are totally dissimilar to the true coconut palm *(Cocus nucifera).*

Because of the confusion of names and identities of the *Acrocomias* some of the previously reported chemical analyses of the fruit and oil of *A. totai* cannot be relied on as they refer to *A. sclerocarpa* or some other species.[2] In 1920 Junelle (12) commented on this confusion as follows: "et la confusion est facilité par le fait que les fruits de tous ces *Acrocomia* sont sphériques et que, d'autre part, tous ces *Acrocomia* portent, en Amérique du Sud, le nom indigéne de *mocaja* ou *mbocaya.*" This confusion still persists as reference to the latest monograph (8) on fats and oils reveals. *A. sclerocarpa* of Brazil was described by Martins in 1824 and *A. totai* of Paraguay and Bolivia in 1847, and the genus *Acrocomia* was the subject of a monograph by Bailey (3) in 1941.

The mbocayá palm has many uses (1, 19, 22), most of which are not germane to the present report, and their mention is therefore omitted here. They are however discussed in another article by this author (16) together with much additional information concerning this palm.

Although almost all parts of the mbocayá palm are important in the rural economy of Paraguay, it is the

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[2] The analysis reported for Paraguay kernels (*Acrocomia* sp.) by Bray and Elliott (6) almost certainly pertains to *A. totai.*

fruit that has the greatest value industrially and as a cash crop to the farmer. Like the fruit of most oil-palms of the Western Hemisphere, that of the mbocayá was probably utilized by the natives long before the arrival of Europeans. The early settlers no doubt learned of its uses and values from the Guaraní. It has been particularly prized for its sweet pulpy fruit, which has served as food and feed for man and animals. The aromatic oily pulp is eaten by farm animals and is relished by children and even by their elders. When eaten by humans, the tough outer hull of the fruit is removed, and the mucilaginous pulp is sucked in the same manner as the mango. The hard inner nut or seed to which the pulp fibers adhere tenaciously is often thrown away, but sometimes it is saved and allowed to dry prior to cracking it to remove the inner kernel. Non-ruminant animals suck or chew the fruit to extract the mucilaginous pulp and reject the seed or nut. Ruminants, particularly the ox, beef and dairy cattle, eat the whole fruit and subsequently disgorge the depulped nut during the night or other periods of rest. Occasionally the nut may be passed through the digestive tract and be excreted in the feces. The act of regurgitation or excretion often occurs at some distance from the place where the fruit was digested, thus providing an effective means of disseminating the plant.

When left undisturbed on the ground, the outer hull and pulp of the fruit disintegrate through the action of the elements and attacks by insects and microorganisms, leaving the relatively clean hard nut. The nuts are frequently collected, dried, and cracked to release the oily and protein-rich kernels, which are consumed in the home and sold in the markets. The dried nuts can be stored for long periods without deterioration. They are frequently carried by travellers and by laborers when employed at considerable distances from their homes.

The recovery of oil from the kernels has been practiced since remote times by the time-honored method of roasting the kernels, grinding them, and boiling the ground meal with water to release the oil which floats to the surface. This practice was followed by aborigines throughout South and Central America wherever oil palms were prevalent.

When the fruit was first subjected to commercial exploitation for oil is not known with certainty,[3] but the kernel oil has been used in Paraguay for the manufacture of soap for about 50 years. The oil was also known in Europe prior to 1900. In 1896 Negri and Fabris (18) and somewhat later Grimme (11) reported the results of chemical examinations of the kernel oil. However it was not until about 1940 that serious efforts were made to mechanize the processing of the fruit for pulp and kernels. By 1951 the production of kernel oil reached 2,849 metric tons annually but declined somewhat during the following two years owing to unfavorable weather conditions. The production of pulp oil began somewhat later, and to date maximum production has not exceeded 1,125 tons annually.

Prior to 1952 the kernel oil was used commercially only for the manufacture of soap, but in that year the oil was refined and marketed for edible use. The excess over domestic consumption was exported, principally to Argentina. In November 1953 refining of mbocayá oil for edible use was prohibited (10), and the excess over that required by the domestic soap industry was diverted to export. However in October 1954, owing to a critical shortage of edible oil pending arrival of cottonseed oil from Argentina and the United States, refiners were authorized (17) to refine mbocayá kernel oil and mix it in the proportion of 1:1 with refined cottonseed oil.

The pulp oil, which is inferior to the kernel oil, has been used locally for soap and the remainder exported. This inferiority is not an inherent defect in the composition or quality of the oil as it occurs in the fruit at maturity but is a result of the treatment which the fruit receives prior to processing.

The growth of the processing industry can be traced in the figures in Table I. In addition to the export of oil there is also considerable export of kernel meal and cake, and of extracted pulp. The combined volume of exports of these by-products amounted to 6,188 metric tons in 1949. Although there is a great need in Paraguay for protein feeds for livestock, it is only in the past few years that these by-products have been fed *per se* or in the form of mixed feeds, principally to dairy cattle.

TABLE I

Production and Exports of Mbocayá *(A. totai)* Kernel and Pulp Oils [a]

Year	Kernel oil		Pulp oil	
	Production m. tons	Export m. tons	Production m. tons	Export m. tons
1940	883	13	......	......
1941	1190	254	......	......
1942	1833	1300	......	......
1943	2404	1417	......	126
1944	1602	871	......	222
1945	1949	967	170	109
1946	1277	727	171	471
1947	2694	1587	501	386
1948	2664	1547	501	381
1949	2499	2588	620	2074
1950	1189	1001	985	719
1951	2849	1056	1125	416
1952	2456	1062	881	350
1953	1924	14	852	158

[a] Source: Department of Economic Studies of the Bank of Paraguay and the Central Bank of Paraguay.

Description of the Mbocayá Palm

Various descriptions (3, 5, 7) of the mbocayá palm (*Acrocomia totai* Mart.) have been published, and although they agree with respect to the principal characteristics, none is complete and in some aspects they are contradictory. So far as the writer has been able to ascertain, the mbocayá palm has never been thoroughly studied and described from the area of its principal occurrence and greatest abundance, namely, Paraguay. In 1951 the writer collected a large amount of authentic material supplemented with photographs and sent it to Miriam L. Bomhard, U. S. Forest Service, for study and comparison with the extant herbarium specimens and descriptions of the mbocayá palm. Unfortunately she did not complete this study prior to her fatal illness.

The following incomplete description is given from the field notes of the writer (14). The mature mbocayá palm is generally 8 to 12 meters in height to the crown, but occasionally very old trees may reach 20 meters or more. The trunk is generally cylindrical, but it may be curved or bent, especially in very tall trees, and quite frequently it is slightly bulged or depressed for several feet somewhere near the middle. The circumference of the trees vary from 30 to 45 cm.

[3] According to one report kernel oil was produced as early as 1894 (21).

at the base, and from 25 to 30 cm. at 1.5 meters above the base.

The trunks vary greatly with respect to persistence of the spines, which are arranged in incomplete circles in proximity to the leaf scars. Some trees are almost devoid of spines except for a short distance below the crown; others are covered with spines from the base to the crown, and all gradations between these two extremes are observed in close proximity to one another. The spines of the trunk vary in length up to 17 cm. but are generally 7.5 to 12.5 cm. (Figure 1).

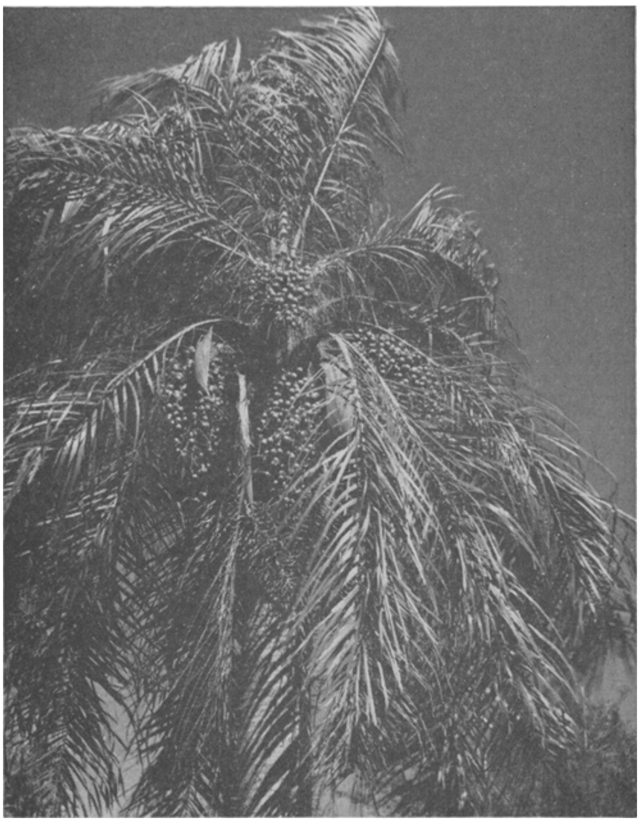

FIG. 1. Fruiting Mbocayá palm (*Acrocomia totai* Mart.) of Paraguay.

Generally the petiole bases or boots are not persistent, but occasionally young trees are observed with persistent petioles from the base to the crown, a distance of about 3 to 4 meters.

Undisturbed crowns are not often observed in settled areas owing to the practice of cutting the leaves for fodder. Normal crowns contain 20 to 25 leaves, 2.5 to 3.0 meters in length. During the dry season in settled areas, where the leaves are used for fodder, the number of leaves per crown may be reduced by cutting to 7 or 8 and sometimes to no more than 2 or 3. Mature leaves contain 100 to 114 leaflets on each side of the rachis, which is covered with spines up to 8.0 cm. in length.

All of the *Acrocomias* are monoecious with the sexes separate in each spadix or flower-cluster. The ratio of staminate to pistillate flowers appears to be very variable, resulting in marked variations in the numbers of fruits per bunch.

The fruit of the mbocayá palm, like that of other *Acrocomias,* is a drupe consisting of an outer hull or

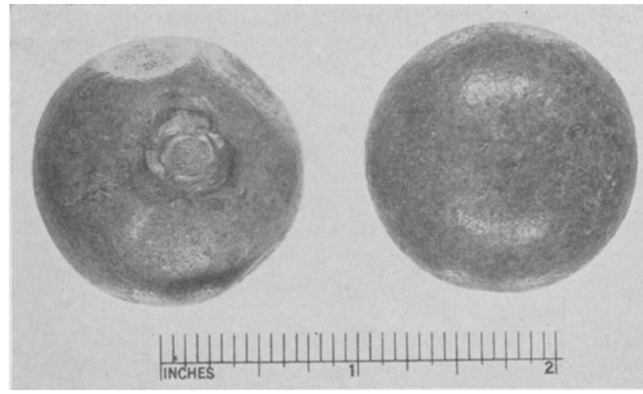

FIG. 2. Mature mbocayá *(A. totai)* fruit.

rind (epicarp) and an inner fibrous pulp (mesocarp) which surround a nut or seed. The latter is composed of a hard shell (endocarp), enclosing an oily white kernel or meat to which adheres a paper-thin reddish brown skin or testa (Figures 2 and 3). At maturity the oily, mucilaginous pulp is dark orange in color owing to the presence of carotene, and it possesses a sweet aromatic flavor.

The mature golden yellow fruit is nearly spherical in shape, varying slightly in size depending on the age of the tree, soil, rainfall, and the amount of defoliation to which the tree has been subjected. Measurements made on 75 mature fresh fruit from a tree from which no leaves had been cut for several years

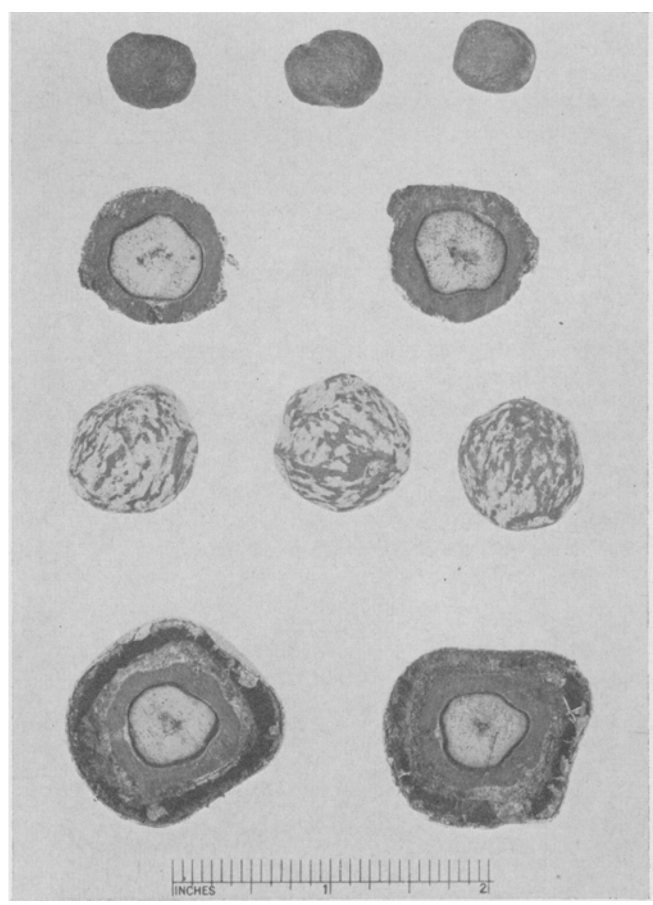

FIG. 3. Cross section of mbocayá fruit, whole nut, cross section of nut, and whole kernel.

varied from 2.9 to 4.1 cm. (av. 3.76 cm.) in diameter and 3.0 to 4.1 cm. (av. 3.69 cm.) in height. Measurements made on 200 mature fruit sent to the U. S. Forest Service were 3.27 to 3.85 cm. (av. 3.56 cm.) in diameter and 3.04 to 4.17 cm. (av. 3.57 cm.) in height. The great majority of mature fresh fruit fall within the dimensions 3.0 to 4.0 cm. diameter and height.

The thickness of the various parts of the fruit varies with the over-all size of the fruit and irregularities in the shape of the kernel and the surrounding envelopes. In the case of a mature fruit (30 x 30 mm.) the outer hull is about 0.6-0.7 mm., the pulp about 3.4 mm., the hard inner shell about 2.5-3.0 mm. in thickness, and the kernel about 10-15 mm. in diameter.

At maturity and while the fruit is still attached to the tree, the pulp practically fills the space between the outer hull (rind) and inner shell. Since the pulp contains about 50% water, it begins to shrink as the fruit dries after it separates from the tree and possibly even before. Consequently a free space develops between the pulp and the outer hull, which may be 2.3 mm. or more by the time the whole fruit attains an equilibrium moisture content, *i.e.*, about 8 to 10%. When the fruit reaches this moisture content, the hull becomes very brittle and is easily crushed and removed by hand. The pulp however dries to a tough fibrous mass that adheres tenaciously to the nut and is removed only with considerable difficulty. When however the fruit is permitted to lie on the ground, both the hull and fiber disintegrate and germination of the nut or seed soon follows.

Distribution and Number of Mbocayá Palms

The number and distribution of mbocayá palms in Paraguay have been a subject of much conjecture and no little dispute. Most published reports generally refer to millions of these palms (21), one report mentions 8 million (9), and another 28 millions. One widely disseminated map showing the distribution of this palm includes areas where none is found or only a few widely scattered ones.

Owing to the growing importance of the mbocayá palm to the vegetable oil industry [4] of Paraguay and the need for expanding the number of fruit-collecting centers and hulling and cracking plants, it became necessary to have as reliable data as possible regarding the distribution and density of this palm. To supply this information John L. Young of Algodones S. A.[5] and the writer made a ground and arial survey of all areas in Paraguay which were reported to contain exploitable quantities of this palm (15).

Areas accessible by road were surveyed from the ground, and inaccessible areas were surveyed by plane with landings at such places as were feasible. Estimates were first made of the densities of the stands by making tree counts over a series of areas of approximately one hectare (2.47 acres) in extent, and a code was developmed to indicate different densities. These were found to vary from 0 to 150 or more palms per hectare. With increasing experience it was relatively easy to estimate the density of trees without making actual counts. In the case of the ground survey, estimates were made along both sides of the highways kilometer by kilometer over the visible distance between the highway and horizon. The latter distance varied from a kilometer or less up to five or more kilometers. These estimates were recorded, and later, after checking them one or more times from the air, they were transferred to a large-scale map.

In the case of the aerial survey the densities were indicated on a map along both sides of the line of flight. A number of the areas were observed several times when they were crossed going to or from previously unsurveyed areas. When a second or third estimate of an area was made, usually from a different direction from the previous observation, an estimate of the density was made without reference to any prior estimate.

After the survey was completed, all of the results were transferred to one of two maps having scales of

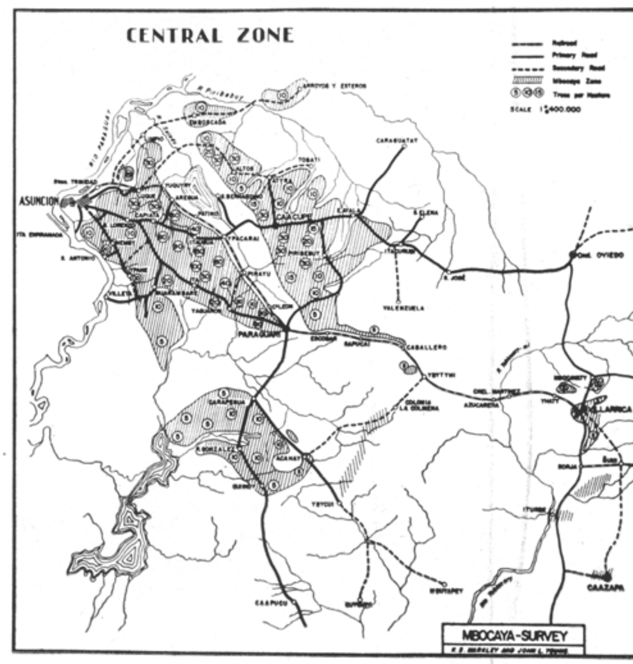

FIG. 4. May of distribution and density of mbocayá in Central Zone of Paraguay.

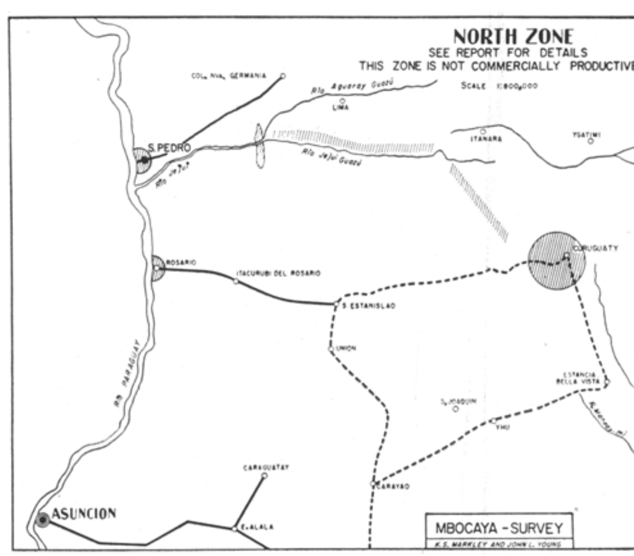

FIG. 5. Mbocayá areas in North Zone.

[4] In 1953 Paraguay had a total of 26 vegetable oil mills, many of which processed mbocayá kernels.

[5] Paraguayan subsidary of Anderson, Clayton, and Company, Houston, Tex.

1:400,000 for the Central Zone (Figure 4) and 1: 800,000 for the area designated as the North Zone (Figure 5). The extent of the various mbocayá palm areas were then determined from the maps by means of a planimeter, and the area was multiplied by the weighted density factor to give the total number of palms for the zone.

The estimated numbers of palms for individual areas and the grand totals for the Central and North Zones are given in Tables II and III. The data presented in these tables indicate that the Central Zone contains about 6 million mbocayá palms with somewhat more than a half million in the North Zone. Scattered palms throughout these two zones probably do not exceed 10% of the total. The number of palms calculated on the basis of the present survey is in reasonably good agreement with the estimated 8 million mentioned in a footnote of a report by Espinosa and Mendaro (9).

TABLE II

Distribution of *A. totai*
Central Zone

Region [a]	Area hectares [b]	Density		Total estimated palms
		Range	Weighted mean	
Asunción-Paraguarí	89,440	5–150	40	3,577,600
Altos-Escobar	70,240	5–30	20	1,404,800
Carapeguá-Quiindy	40,640	5–10	8	325,120
Villarrica-Mbocayaty-Ayaty	6,480	3–5	4	25,920
Arroyos y Esteros	5,440	....	10	54,400
Emboscada	4,480	....	10	44,800
Escobar-Caballero	1,600	....	5	8,000
Ybytimí	400	....	5	2,000
La Colmena-Ybycuí	Scattered [c]	....	....	....
Borja-Iturbe	Scattered [c]	....	....	....
Caazapá	Scattered [c]	....	....	....
Grand Total	218,720	....	....	5,442,640

[a] See map.
[b] One hectare equals 2.47 acres.
[c] Few palms scattered over wide area. Total scattered palms throughout Central Zone probably less than 10% of total.

TABLE III

Distribution of *A. totai*
North Zone

Region [a]	Area hectares [b]	Average density	Total estimated palms
Curuguaty	46,080	10 [c]	460,800
San Pedro	5,760	5	28,800
Rosario	5,120	5	25,600
Jejuí-Aguaray Jct.	3,840	5	19,200
Jejuí-guazú valley	Scattered [d]	....	....
Grand total	60,800	....	534,400

[a] See map of North Zone.
[b] One hectare equals 2.47 acres.
[c] Range 5 to 40.
[d] Few scattered over wide area. Total scattered palms throughout North Zone probably less than 10% of total.

Comparison of the accompanying maps and tabular data for the number of mbocayá palms with previously published maps and data indicate that the area of occurrence and numbers of these palms have in the past been grossly exaggerated. Large areas included in the "mbocayá zone" of these earlier maps are devoid of mbocayá palms or contain so few as to have no significance while other areas contain only caranday or yatay palms.

For a more detailed discussion of these maps and the cause and significance of the distribution of the mbocayá palm in Paraguay, the reader is referred to the previously mentioned more comprehensive article on this palm (16).

Yield of Fruit

Correlated with the problem of determining the number and distribution of the mbocayá palms in Paraguay is that of estimating the annual production of fruit. The oil milling industry is less interested in the number of palms than in the annual yield and availability of the fruit. The latter is difficult to determine with exactness because of the many factors involved, principal of which is the variation in the yield of fruit per individual tree. This yield is influenced by the age of the tree, its location, its treatment (cutting of its leaves, number and degree of burns it has suffered, severing of roots during plowing and cultivation), climatic conditions, particularly rainfall and temperature throughout the year, the number and severity of attacks by insects and microorganisms, etc. Besides the variation in individual trees there is an annual variation, which is a response to climatic conditions, and the cycle of high and low productivity. Consequently the total productivity for two successive years may vary greatly.

Many thousands of trees, especially in the Central Zone, produce exceedingly little fruit, sometimes no more than 2 or 3 poorly developed bunches per year. On the other hand, isolated trees may produce 8 to 10 large well-filled bunches. In the older and more intensely cultivated fields of the Central Zone the yield of fruit is generally low and probably does not average more than 10 kilos of air-dry fruit per tree. The yield of mature fresh fruit (averaging about 35% moisture content) is, of course, higher. However it is only the yield of thoroughly mature, air-dry fruit which is of interest to the oil miller.

A report attributed to a Unilever Ltd. Mission to Paraguay in 1937 estimated a possible annual harvest of 100,000 metric tons of fruit within access of oil mills with possibly an additional 100,000 tons that could be made available by improved transportation. The same year the Banco Agrícola estimated that 500,000 tons of fruit were produced annually by the mbocayá palms of Paraguay. The report "Aceite de Coco en el Paraguay" (21) contains a map on which a figure of 1,200,000 tons of "whole nuts" is indicated, of which 1,000,000 tons is attributed to the Curuguaty area. A more recent report (9) refers to the production "each year of millions of tons of fruit" in Paraguay.

Such figures have usually been calculated on the basis of an assumed number of palms and an assumed annual yield of fruit per tree. The most widely quoted figure is 3 to 5 bunches of fruit per tree. This figure was used by Bertoni (4) and appears to be reasonably accurate, at least in the cultivated areas of the Central Zone.

In one field along the Asunción-Caacupé highway, the number of bunches of fruit was observed by the writer to vary from 3 to 8 and averaged 5 for all of the trees observed. Isolated and especially young trees were noted in other places (chicken lots, yards, etc.) which had as many as 17 bunches of fruit. On the other hand many trees, especially very immature and very old ones, had none to at most two bunches of fruit.

Equally variable have been the reports of the number of fruit per bunch. The Unilever Mission estimated that the mbocayá palm produced an average of 10 bunches of fruit per year with 500 fruits per bunch. In a recent report (9) two bunches of fruit

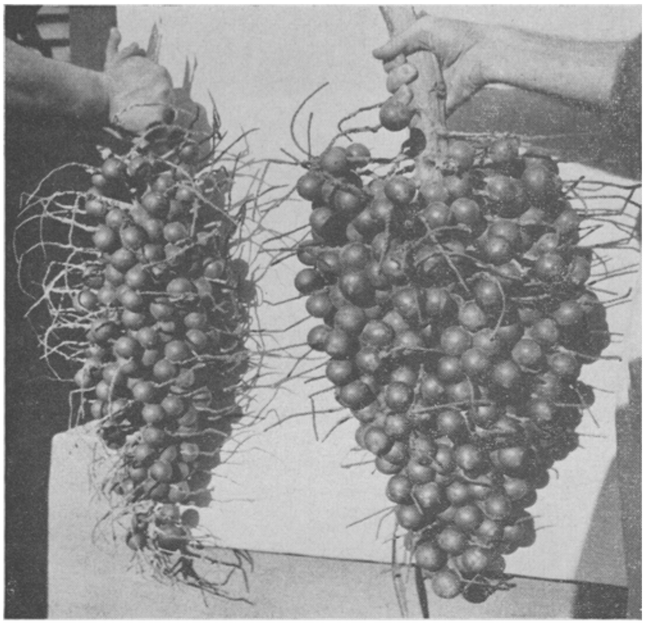

FIG. 6. Bunches of mbocayá fruit (left 273 and right 520 fruit).

are shown, one with 520 fruits and the other with 273 (Figure 6). Fruit-counts made by the writer on randomly selected, well-filled bunches collected in the Central Zone ranged from 75 to 340. Many bunches were noted with no more than a few dozen fruits. No doubt bunches are produced occasionally with 500 or more fruits, but they are relatively rare. As exhibit material they are interesting, but they are of little or no value in arriving at figures for average yields. Perhaps five bunches and 200 fruits per bunch is a good average for mature trees in the Central Zone.

Reported data for the average weight per bunch (including the stem) are likewise very variable. Past reports give figures of 22, 20 to 30, 25 to 35, and 15 to 50 kilos per tree. Whether fresh (mature) or air-dry weight is seldom stated. The fresh mature fruit contains about 35% moisture, but, after separation from the tree and air-drying until an equilibrium moisture content is reached under normal climatic conditions in Paraguay, whole fruit will contain about 8 to 10% moisture. In other words, fresh fruit will lose 25 to 30% of its weight in drying to equilibrium moisture content.

One oil mill made a careful analysis of the fruit and obtained an average value of approximately 10 g. per fruit having an average moisture content of approximately 8%. A sample composed of 40 fruits randomly selected by the writer from a group of 300 had an average weight of 9.1 g. and a moisture content of 8.9%.

Using a figure of 5 bunches of fruit per tree, 200 fruit per bunch, and 10 g. per air-dry fruit, the average yield of fruit per tree can be calculated to be 10 kilos or considerably less than the previously reported 15 to 50 kilos.

If it is assumed that the 5.5 to 6 million mbocayá palms of the Central Zone each produce an average of 10 kilos of mature air-dry fruit per year, the total production would be 55,000 to 60,000 metric tons. If the estimated yield per tree were doubled as it might be in an unusually good crop year, the total production might be 110,000 to 120,000 tons. The latter figures agree fairly well with the estimate of 100,000 metric tons within access to oil mills made by the Unilever Mission in 1937.

If it can be assumed that the annual yield of mbocayá fruit in the Central Zone fluctuates between 55,000 and 120,000 metric tons, it cannot be assumed that this tonnage would be available for processing. In well cultivated fields (Figure 7a) much fruit is covered up during preparation of the land and cultivation of the crops. In the fallowed, brushy, and wooded areas (Figure 7b) much of the fruit becomes lost in the undergrowth so that it is difficult or impossible to collect it. This latter condition occurs in

FIG. 7. Mbocayá palms in a) cultivated land, b) abandoned land.

an area like Curuguaty where collection of fruit in the dense forest is practically impossible. Thus a certain percentage of the crop is unavailable for processing. How much of the remainder may be collected and eventually arrive at the oil mill depends on the price, availability of labor, availability and cost of transport, and other factors.

Production, Composition, and Utilization of Mbocayá Oils

Processing mbocayá fruit for oil presents difficulties not generally encountered with most oil-bearing materials. To understand these difficulties it is necessary to understand the structure and composition of the fruit. The fruit of the *Acrocomia* palms differs from that of the larger and thicker shelled *Orbignya* (babassu) and *Scheelea* (coroba) and from the smaller and thinner shelled African oil palm (*Elaeis guineensis*). The fruit of *A. totai*, like that of the African oil palm, is composed of an outer thin epicarp, a pulpy mesocarp, a hard endocarp or shell, and an inner kernel. However the epicarp (hull) of the mbocayá fruit is much tougher and more difficult to remove in the fresh state than is that of the fruit of the African oil palm. The shell of the mbocayá nut or seed is also somewhat thicker and more difficult to crack than is that of the African oil palm.

The outer hull of the fruit and the hard shell of the mbocayá nut, being essentially cellulosic, are valuable only as fuel. The pulp and kernel however are rich in glyceride oils and other nutrient materials and possess considerable economic value.

The weight, the percentage of the total weight, and the moisture content of each component of mature fresh fruit are given in Table IV. Fresh mature fruit (35% moisture) weighs approximately 14 g. whereas air-dry fruit (8 to 10% moisture) weighs 9 to 10 g. The moisture is unequally distributed throughout the various parts of the fruit, being lowest in the kernel and highest in the pulp and outer hull.

TABLE IV

Distribution of Components and Moisture in Fresh Mature Fruit of *A. totai* [a]

Component	Weight g.	Weight, % of total	Moisture content, %
Hull (epicarp)	2.5	18.1	44.3
Pulp (mesocarp)	6.2	44.9	51.1
Shell (endocarp)	3.9	28.3	15.2
Kernel	1.2	8.7	14.9
Whole Fruit	13.8	100.0	36.5

[a] Data furnished through the courtesy of John L. Young, Algodones S.A., Asunción, Paraguay.

Other workers have determined the percentage distribution of the components of this fruit, apparently air-dried to different moisture contents. Based on these data which are collected in Table V it can be said that the fruit of the mbocayá palm is composed of 15-20% hull, 30-45% pulp, 28-41% shell, 7-11% kernel, depending on the moisture content. The nut therefore represents 40-50% of the weight of the whole fruit.

TABLE V

Percentage of Components of *A. totai* Fruit [a]

Component	Range-Mehl (22) (Av. 8 samples)	Commercial firm [b] (Av. 10 samples)	Commercial firm [c]	Landmann (13)
Hull, %	16.7	19.6	14	15–18
Pulp, %	42.5	36.6	30	33–34
Shell, %	29.0	34.3	40	39–41
Kernel, %	7.6	9.5	9.5	9–11

[a] Air-dried to different moisture contents.
[b] Unpublished analytical data (1948).
[c] Yields of products in processing plant located at Tobatí, unaccounted for loss 5.5%.

Bertoni (4) states that the content of moisture and oil of the pulp at the time of processing varies between 12 and 20% each. He also quotes Andrada (2) to the effect that 10 to 14% of oil is extracted commercially compared to analytical values up to 24% oil content found in the laboratory. Landmann (13), on the other hand, states that the pulp contains 30 to 32% oil and that 17 to 20% is recovered in the mill. All of these yields are very poor and apparently refer to hydraulic pressing.

Data with respect to the oil content of the pulp and kernels from fruit dried to various moisture contents are collected in Table VI. These figures indicate that air-dry pulp contains 25 to 30% oil, or 8 to 10% of the weight of the whole air-dry fruit, and that the kernels contain approximately 60% oil, or about 6% of the air-dry weight of the whole fruit.

TABLE VI

Oil Content of Mbocayá Pulp and Kernels

Authority	Pulp		Kernel	
	Moisture, %	Oil, %	Moisture, %	Oil, %
Grimme (11)	......	......	Not recorded	58.9
Négri and Fabris (18)	......	......	......	ca. 70
Mehl and Cuevas [a]	18	16	14.8	58
Andrada (2)	19.4	23.8	......	......
Landmann (13)	Not recorded	30–32	Not recorded	55–65
Commercial firm [b]	8.7	25.7	3.2	60.5

[a] Quoted by G. T. Bertoni (4).
[b] Unpublished work, 1948.

Because of the gross anatomic similarity of the fruits of *A. totai* and *E. guineensis* various authors who have discussed the commercial exploitation of the former tend to compare it with the latter. These authors however fail to present quantitative data with respect to the components and oil contents of the fruits of the two palms, without which these comparisons are meaningless.

The principal components of the fruit of the African oil palm vary over a wide range depending on selection or type, soil and climatic factors, cultural conditions, etc., compared to the much narrower range of the uncultivated mbocayá palm (Table VII).

TABLE VII

Comparison of *A. totai* and *E. guineensis* as Sources of Oil (Fresh Fruit Basis)

Component	*A. totai*	*E. guineensis*
Hull (epicarp)		
% Whole fruit	18	[a]
Oil content, %	None	None
Pulp (mesocarp)		
% Whole fruit	45	[b]
Oil content, %	12–15	....
Hlll and pulp (pericarp)		
% Whole fruit	63	48–73
Oil content, %	8–11	44–73
Kernel		
% Whole fruit	9–10	6–13
Oil content, %	60	42–49

[a] Hull (rind) is too thin and soft to be separated from pulp.
[b] Pulp (mesocarp) cannot be separated from soft hull or rind (epicarp).

For the African oil palm the pericarp (outer hull and pulp) comprises 48 to 73%, and the nut 27 to 52% of the fresh mature fruit. The pericarp contains 44 to 73% oil, and the kernel, which comprises 6 to 13% of the whole fruit, contains 42 to 49% oil.

The fresh mature fruit of *A. totai* is composed approximately of 18% outer hull containing little or no oil, 45% pulp containing only 12 to 15% oil, and 9 to

10% kernel containing about 60% oil. The fruit of *A. totai* is a somewhat better source of kernel oil than is the African oil palm but a comparatively poor source of pulp oil. The average content of combined pulp and kernel oils, on a fresh fruit basis, is approximately 11% for the mbocayá palm compared to approximately 40% for the African oil palm.

Production. A great deal of effort has been expended in trying to develop satisfactory equipment for processing mbocayá fruit. Samples of fruit and nuts have in the past been submitted to various manufacturers of African oil palm processing equipment in Europe and seed-processing equipment in the United States, but none of the standard equipment was found satisfactory and none of the manufacturers was interested in modifying existing equipment for use with mbocayá fruit and/or nuts. However machines for hulling, depulping, cracking, and separating the various components of the mbocayá fruit were developed and built locally. These machines are ingenious though often poorly constructed, owing to lack of proper metals, and inadequate manufacturing facilities. Unfortunately the depulping machines operate successfully only with fruit dried to the approximate moisture content which is in equilibrium with the atmosphere. Natural drying of the whole fruit to this moisture content requires weeks and sometimes months, during which time the hydrolytic enzymes in the pulp split a large proportion of the oil into free fatty acids and glycerol. Generally only 40 to 60% of the recovered total lipids is neutral oil. The remainder is a mixture of fatty acids.

In order to obtain relatively neutral oil from the pulp, it would be necessary to process the fresh fruit directly from the trees, preferably by harvesting the whole bunches at maturity and processing them immediately as is done with the African oil palm. The common practice with the African oil palm is to harvest the bunches of fruit, sterilize them within a few hours after harvesting to destroy or inactivate the enzymes, mechanically strip the fruit, and press or centrifuge the pulp oil from the fruit after first cooking it with steam or water.

In the centrifugal process the water-oil mixture is separated from the nuts by centrifuging. The fiber is removed from the wet nuts, which are then dried and cracked, and the separated kernels are transported to oil mills. The water-oil mixture from the centrifuge is treated with steam or hot water and allowed to stand in tanks to separate most of the water. It is then washed with hot water, and the oil is centrifuged to remove the last small amount of water. In this way pulp oil with as little as 2 to 5% free fatty acid is obtained.

It was thought that the same process might be used with mbocayá fruit, but when samples were shipped to one manufacturer of African oil palm processing equipment in England, it was found that the pulp oil could not be separated by the centrifugal process. This firm reported that cooking the fruit with steam and water produced a water-oil emulsion which would not separate, partly because of the low oil content of the pulp and partly because of the presence of a mucilaginous substance which appeared to act as a strong emulsifying agent.

Rapid artificial drying of the whole fruit has been tried, but it is ineffective and costly. It is used however with the kernels after their recovery in the water-separation of shells and kernels.

Both the whole fruit and kernels are sold to the oil mills, some kernels are still separated by hand-cracking, but much larger amounts are produced mechanically at the hulling and cracking plants, more than 20 of which are located at strategic points in the mbocayá zone. The dry pulp from the defibering machines and the separated kernels produced by the cracking plants are shipped in bags to oil mills for extraction. Both materials are processed in continuous screw presses although one firm extracts dried mbocayá pulp in a continuous solvent extractor and some mills still use either hydraulic cage or box presses.

The composition of the various primary products and by-products produced in commercial processing of mbocayá fruit are given in Table VIII.

TABLE VIII

Composition of Commercial Samples of *A. totai* Products (14)

Constituent	Outer hull (Epicarp)	Pulp (Mesocarp)	Pulp Expeller cake	Shell (Endocarp)	Kernel	Kernel Expeller cake
	%	%	%	%	%	%
Moisture (H_2O)	6.65	4.31	5.26	6.84	3.17	7.44
Lipides (oil)	3.88	27.94	6.26	2.46	66.75	7.22
Nitrogen	0.74	0.67	0.98	0.31	2.02	5.50
Protein (N x 6.25)	4.62	4.18	6.12	1.94	12.62	34.38
Crude fiber	36.00	8.82	6.83	49.69	8.60	11.65
Sugars (total)	......	4.85	5.16	......	1.28	2.80
Ash	5.82	10.32	9.16	3.26	1.98	5.37
Potassium	2.18	2.18	2.75	1.02	1.36	1.55
Phosphorus	0.10	0.12	0.16	0.04	0.42	1.14
Calcium	0.07	0.09	0.10	0.04	0.08	0.27

Composition. Pulp Oil. It is difficult to discuss the composition of mbocayá pulp oil or to compare it with other pulp oils such as that from the African oil palm because the pulp of the mbocayá fruit contains a highly active fat-splitting enzyme, which attacks the oil soon after the fruit ripens and hydrolyzes it to free fatty acids and glycerol.

If the pulp oil is extracted and analyzed about the time that the fruit is ripe, it will be found to consist principally of neutral oil with about 2 to 2.5% free fatty acids. If however the fruit is stored or allowed to dry naturally over a period of weeks or months and the pulp oil is then extracted, it will consist of a mixture of 40 to 60% neutral oil and 60 to 40% free fatty acids.

Owing to the inadequacy of present processes and equipment it is not possible to process fresh mbocayá fruit. The fruit is generally allowed to lie on the ground to dry partially and then collected and stored for periods up to six months or more before it is processed (Figure 8), by which time the oil has largely been converted into free fatty acids.

Oil containing 40 to 60% free fatty acids cannot be refined and is of value only in the manufacture of soap, or for the production of distilled or fractionated fatty acids. Even for these purposes it is less valuable than neutral oil because during the enzymatic hydrolysis the glycerol is lost.

In Table IX comparative data are presented for some of the more important physical and chemical characteristics of the pulp oils of *A. totai* (mbocayá) and *E. guineensis* (African oil palm). The data reported by Landmann refer to oil extracted from fresh fruit. The two pulp oils differ materially in the composition of their respective fatty acid glycerides. The

TABLE IX

Characteristics and Composition of the Pulp Oils of *A. totai* and *E. guineensis*

Characteristic	*A. totai* (14)	*A. totai* (13)	*E. guineensis* [a]
Specific gravity, 40°C	....	0.9240	0.898–0.901 [b]
Refractive index, 40°C	1.4615 [c]	1.4582–1.4607	1.453–1.456
Titer value, °C	....	26.1–33.2	40–47
Iodine value	64.4	54.5–66.7	44–58
Unsaponifiable matter, %	0.81	0.27–0.55	0.8
Saponification value	197.0	200–209	195–205
Free fatty acids, % palmitic	41.2	1–....	[d]
Total fatty acids			
Iodine value	69.7	....	....
Thiocyanogen value	66.6	....	....
Saturated, %	20	....	39–50 [e]
Oleic, %	80	....	38–52 [e]
Linoleic, %	0	....	6–10 [e]

[a] American Oil Chemists' Society Standard for African palm oil.
[b] Measured at 37.8°C.
[c] Measured at 25°C.
[d] Trading in palm oil is based on free fatty acid content (see text).
[e] A. E. Bailey, Industrial Oil and Fat Products, 2nd ed., Interscience, New York, 1951, p. 158.

lower titer value and higher iodine value of the pulp oil from *A. totai* indicate a higher content of oleic acid, and a lower content of saturated acids in this oil, compared to that from the African oil palm.

The fatty acid composition of the pulp oil of the African oil palm is rather well known, but only limited compositional data are available with respect to the pulp oil of the mbocayá palm. These data (Table IX) indicate that mbocayá pulp oil is composed of glycerides containing 20% saturated acids and 80% oleic acid whereas African palm oil is composed of glycerides containing 39 to 50% saturated acids, 38 to 52% oleic acid, and 6 to 10% linoleic acid.

Kernel Oil. In Table X data are given for the more common chemical and physical characteristics of three samples of Paraguayan mbocayá kernel oil (14). Landmann (13) reported a range of properties for this oil which are given in Table XI, together with those for the better known American palm kernel oils of commerce, and for African palm kernel and coconut oils.

The outstanding difference in the characteristics of mbocayá kernel oil and the other palm kernel and coconut oils is the higher iodine value and lower melting point of the former. The higher iodine value of the mbocayá kernel oil indicates a higher content of oleic acid and a lower content of saturated acids than the other palm kernel oils. This is also reflected in the lower melting point and titer value. From the compositional data in Table XI it is seen that mbocayá kernel oil is unique among American palm kernel oils with respect to its content of saturated and oleic acids.

The higher content of oleic acid and lower content of saturated acids strikingly reflect the effect of climate on the composition of the mbocayá oils. All of the kernel oils except mbocayá in Table XI are products of tropical palms whereas *A. totai* is found abundantly in the South Temperate Zone. In fact, the mbocayá is the only *Acrocomia* which is indigenous to this climatic zone.

Utilization. Mbocayá pulp and kernel oils are suitable for the manufacture of soap. The kernel oil can be refined to produce an edible grade cooking oil.

TABLE X

Characteristics and Composition of *A. totai* Kernel Oil (14)

Characteristic	Villeta (1943)		Asunción (1943)
	Crude	Neutralized	Crude, filtered
Refractive index (25°C.)	1.4570	1.4579	1.4571
Iodine value	29.2	31.3	29.8
Thiocyanogen value	26.9	28.1	27.9
Saponification value	243.3	241..8	241.1
Unsaponifiable, %	0.40	0.32	0.38
Hydroxyl No.	4.9	4.2	6.5
Color, yellow/red [a]	70/6.72	70/6.12	70/20.79
Phosphorus, %	0.0032	0.0006	0.0036
Free fatty acids, % oleic	6.50	2.71	6.52
Free fatty acids, % palmitic	5.91	2.48	5.92
Free fatty acids, % lauric	4.61	1.93	4.63

[a] Lovibond color units measured in 135 mm. cell.

Some efforts have been made to blend it with stearine and soft (yellow) oils to make shortening, but the product leaves much to be desired.

The higher content of unsaturated acid glycerides, which the iodine value reflects, is advantageous in the culinary use of this oil because it insures that it will remain liquid at summer and tropical temperatures. For culinary use careful refining of the oil is essential. The finished oil must be free from traces of soaps and moisture otherwise slow hydrolysis occurs with the liberation of low molecular weight fatty acids and the development of disagreeable flavors and odors.

The higher unsaturation of mbocayá kernel oil compared to other palm kernel oils is a disadvantage only from the point of view of its resistance to oxidative stability (rancidification), especially in the hot months of the year. As a class, palm kernel oils contain little natural antioxidant compared to cottonseed, peanut, and other soft or yellow oils.

Summary

The mbocayá palm (*Acrocomia totai* Mart.) is one of a number of oil palms found in Latin America

TABLE XI

Characteristics of Various Palm Kernel Oils and Coconut Oil [a]

Characteristic	Mbocayá (13)	American palm kernels					African palm kernel	Coconut
		Babassu	Tucum	Murumuru	Ouricuri	Cohune		
Iodine value	28.0–30.2	15.5	9–14	11	15	10–14	16–23	7.5–10.5
Saponification value	239–246	247	230–250	242	257	250–255	248	250–264
Density (60°C.)	0.915–0.920 [b]	0.893	0.893	0.893	0.898	0.893	0.892	0.893
Refractive index 60°C	1.451–1.453 [c]	1.443	1.443	1.445	1.440	1.441	1.443	1.441
Unsaponifiable, %	0.2–0.4	0.2–0.5	0.3	0.3	0.3	0.4	0.4	0.1–0.3
Melting point, °C	20.0–23.0	22–26	30	32	18	24	26	21.8–23
Titer, °C	19.7–21.0	23	27	......	......	21	......	20–24
Reichert-Meissl value	6.2–7.6	5–7	4	3	6	7	5–7	6–8
Polenske value	10–14	10–12	6	......	18	14	10–12	15–18
Saturated acides, %	67–68(14)	82.5–85.3	84.3	88.8	84.7	89.2	80.8	91.2–91.7
Oleic acid, %	29–31(14)	11.9–16.1	13.2	10.8	13.1	9.9	18.5	5.7–7.5
Linoleic acid, %	2–4(14)	1.4–2.8	2.5	0.4	2.2	0.9	0.7	0–2.6

[a] Except for mbocayá kernel oil, data are from A. E. Bailey, Industrial Oil and Fat Products, 2nd ed., Interscience, New York, 1951.
[b] Measured at 20°C.
[c] Measured at 40°C.

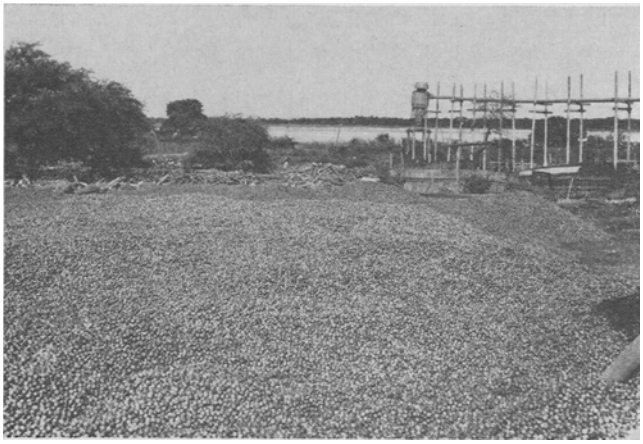

FIG. 8. Mbocayá fruit stored on ground outside of oil mill to dry prior to processing.

which is exploited for its pulp and kernel oils. Since the products of many of these palms are consumed locally or are exported to neighboring countries or Europe, they are little known in the United States.

The mbocayá is one of these palms which has been exploited commercially for its kernel oil for about 50 years and for a lesser time for its pulp oil. The kernel oil is similar in composition to that of other American oil palms but is unique in being more unsaturated and having a lower melting point which clearly reflects the more temperate environment in which this palm thrives.

Paraguay contains 6 to 7 million of these palms which produce annually an estimated 55,000 to 120,000 metric tons of fruit, only a part of which is processed for oil. In recent years production of kernel oil has varied between 2,000 and 2,700 metric tons and pulp oil between 500 and 1,100 metric tons, all of which has been consumed locally or exported to Argentina. Processing mbocayá fruit presents many difficulties not encountered with most oilseeds but which are similar to those encountered in processing most American oil palm fruits.

This is the first comprehensive report in English on the mbocayá palm and its economic importance.

REFERENCES

1. Anon. El Cocotero O Mbokayá. Dirección de Tierras y Colonias (Paraguay), Informaciones para los Agricultores. pp. 10-11, 1923.
2. Aranda, Santiago. El Cocotero o "Mbocayá," *Acronomia totai* Mart., Revista de Agricultura y Ganadería (Asunción) *1* (5), 32-35 (1938).
3. Bailey, L. H., Acrocomia—Preliminary Paper. Gentes Herbarum IV (Fasc. XII), 452-461 (1941).
4. Bertoni, Guillermo T., El Mbocayá o Coco del Paraguay (*Acrocomia totai* Mart.). Revista de Agricultura (Asunción) *1*, 36-50 (1941).
5. Bomhard, Miriam L., "What Palms Grow in Louisiana," Louisiana Conservation Review, Winter 1938-39.
6. Bray, C. T., and Elliot, F. L., Analyst *41*, 298-302 (1916).
7. Covas, G., and Ragonese, G., Las palmeras argentinas del genero "Acrocomia." Ministerio de Instrucción Pública y Fomento Provincia de santa Fé, Instituto Experimental, de Investigación y Fomento Agrícola-Ganadero Pub. Tec. No. 27, pp. 12-14 (1941).
8. Eckey, E. W., "Vegetable Fats and Oils," Reinhold Publishing Corporation, 1954, p. 344 *et seq.*
9. Espinosa, S., Arístides, B., and Mendaro, Ernesto, La Explotación de Cocoteros en el Paraguay, Ministerio de Agricultura y Ganadería, (Asunción) pp. 68 (1952).
10. Gorostiaga, J. Bernardino, Ministerio de Industria y Comercio (Asunción) Resolución No. 517, November 19, 1953.
11. Grimme, C., Ueber einige seltene Oelfruchte, Chem. Revue 7, 156-157 (1907).
12. Junelle, Henri, Les Palmiers à huiles d'Amérique, Les Matieres Grasses, *12*, 5507-5510 (1920).
13. Landmann, Werner, Die Paraguay—Cocopalme, Seinfen-Ole-Fette-Wasche *77*, 403-404 (1951).
14. Markley, Klare S., El Aceite de Coco, Ministerio de Agricultura y Ganaderia, Asunción, STICA Bol. No. 114, pp. 36 (1952).
15. ————, La Palma "Mbocayá," *idem.* Stica Bol. No. 162, pp. 20 (1953).
16. ————, The Mbocayá or Paraguayen Cocopalm (*Acrocomia Totai* Mart.), Economic Botany, in press.
17. Ministerio de Industria y Comercio (del Paraguay), Resolution No. 992, October 6, 1954.
18. Negri, G. de, and Fabris, G., Sull'olio di Mbocayá del Paraguay, Giorn. farm. Trieste, No. 12, 359-361 (1896). (Abst. Chemische Revue, No. 6, 82, 1897).
19. Nogueira, J. Bondar, and Machado, Raul D., Glossário Palmeiras Oleaginosas e Ceríferas, Instituto de Òleos, Ministério da Agricultura, Rio de Janeiro, pp. 37 (1950).
20. Ortiz, Gregorio, El Mbocayá, Ministério de Economia, Cartilla Agro-Pecuaria (Asunción) No. 10-11, 11-15 (1939).
21. Peterson, Lyall E., Aceite de Coco en el Paraguay, STICA Special Report No. 3 rev. (Asunción) pp. 25, 1945; see also Vegetable Oils in Paraguay, STICA Commodity Report No. 2 rev. (Asunción), 1945.
22. Range, Federico H., Las Grandes riquezas inexplotadas del Paraguay (Investigaciones y Estudios)—El Coco o Mbocayá, Revista Agropecuaria (Asunción), *2* (2), 40-43 (1930).

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Isomerization of Polyunsaturated Fatty Acids and Their Esters by Sodium Amide in Liquid Ammonia[1]

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ALTHOUGH AMIDES of the alkali metals have been used extensively as reagents in numerous inorganic and organic reactions (1, 2, 3), their reaction with the fatty acids or derivatives has only been given limited attention. Khan *et al.* (4) used sodium amide in liquid ammonia in dehydrobromination of dibromostearic acid to stearolic acid. Attempts by the authors to apply the method for preparation of the diacetylenic derivative of tetrabromostearic acid were not successful. Consequently the study of the effect of sodium amide on a substance having a methylene-interrupted unsaturated system seemed to be necessary before tackling the problem of preparing polyacetylenic compounds. Because polyacetylenic fatty acids are unavailable, the polyethenoid fatty acids, linoleic and linolenic acids and their esters, were used in this study.

The alkali amides are the caustic alkalis of the ammonia system. One might expect some resemblance between the actions of the alkali amides and of the alkali hydroxides upon the polyunsaturated fatty acids. The alkali hydroxides at high temperatures are known to cause migration of the double bonds resulting in a conjugated system, the character of the products being dependent to a large degree on the concentration of the alkali reagent, the temperature of the reaction, and the ratio of the reagent to sample size. With the alkali amides in liquid ammonia one might expect greater effect on the polyunsaturated fatty acids under comparable conditions due to the basicity

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