

Reaction of Monomeric Adipic Anhydride with Aniline.—One cubic centimeter of anhydride was added to about eight cubic centimeters of aniline with stirring. Reaction was immediate and much heat was evolved. The excess aniline was dissolved in dilute hydrochloric acid. The solution was diluted to 200 cc. and filtered. The crude product was dried and weighed; m. p. 152–153°; yield 80%. The monoanilide of adipic acid has previously been prepared by heating $C_6H_5NHCOCH(COOH)(CH_2)_3COOH$.⁶

Recrystallization from water did not raise the melting point. The crude compound was completely soluble in hot water (absence of dianilide). A similar experiment was carried out and worked up in smaller volume; m. p. (crude), 151–153°; yield, 87%.

Anal. Calcd. for $C_{12}H_{16}O_4N$: C, 65.12; H, 6.80; neutralization equiv., 221. Found: C, 64.76, 64.86; H, 6.81, 7.01; neutralization equiv., 222, 223.

Summary

The monomeric and polymeric forms of adipic anhydride have been prepared, the former for the first time, and they have been shown to be mutually interconvertible. The reactions of the compounds with aniline have shown the monomer to be a seven-atom ring and the polymer a long chain or large ring. Diphenyl adipate is described.

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BRAZIL NUT OIL

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Data pertinent to the composition of the oil in the seeds of the Brazil nut tree, *Bertholletea excelsa*, are few. A statement by Andes¹ that this oil consists of stearin, palmitin and olein, and several reports by others² on a few of its more common chemical and physical constants appear to represent the published information on its chemical composition.

This oil finds a limited use in the arts in this zone but in the country of its origin it serves the inhabitants much the same as olive oil does elsewhere, that is, for alimentary purposes, for soapmaking and, to some extent, as a fuel for lamps. The nut meats contain approximately 70% of oil, more than one-half of which may be removed merely by expression in a hand press.

In view of the situation which obtains as above noted, and the ambiguity surrounding the methods of recovery of the oil used by others, it seemed worthwhile to re-investigate the chemical and physical characteristics of

⁶ Dieckmann, *Ann.*, 317, 62 (1901). The melting point given is 152–153°.

¹ Andes, "Vegetable Fats and Oils" (translated by Salter), Scott, Greenwood and Co., London, 1902, p. 187.

² De Negri and Fabris, *Z. anal. Chem.*, 33, 563 (1894); De Negri, *Chem.-Ztg.*, 22, 961 (1898); Merrill, *Maine Agr. Expt. Sta. Bull.*, 65, 111 (1900); Grimme, *Analyst*, 36, 21 (1911); Niederstadt, *Ber. deut. pharm. Ges.*, 35, 145 (1902).

both the expressed product and that recoverable from the residues by solvent extraction, and to make an analysis of the latter. The presentation of these data is the object of this communication.

I. Preparation of Materials

The oil in the meats³ from twelve kg. of fresh Brazil nuts was expressed in a small, manual press rather than one of the hydraulic type because it had been demonstrated by experimental trials that a cleaner product and one better adapted for chemical analysis without a preliminary refining process is obtainable by using this method of recovery. The residual meat pulp was then extracted in percolators with low-boiling petroleum ether, the final portions of which were in turn removed from the oil in the presence of carbon dioxide. A dark brown oil was recovered from which, in distinction to that obtained by expression, no glycerides separated when stored in the refrigerator (5–10°). The expressed oil possessed, after filtration, a pale yellow color and a taste suggestive of the nut itself.

II. Analysis of Oils

(a) **Chemical and Physical Characteristics.**—The more important chemical and physical characteristics (Table I) of both the expressed oil and that recovered from the residual meat pulp were determined by recog-

TABLE I
CHEMICAL AND PHYSICAL CHARACTERISTICS OF BRAZIL NUT OIL

	Expressed oil	Residual oil
Specific gravity 25°/25°	0.9150	0.9143
Index of refraction 20°	1.4678	1.4683
Titer test	...	33.3 ^a
Iodine number (Wijs)	99.92	95.21
Saponification number	194.0	198.00
Ester number	193.9	193.8
Reichert–Meissl number	0.0	0.31
Polenske number	0.0	0.32
Free fatty acids (per cent. oleic)	0.006	0.02
Acetyl number	12.3	12.3
Soluble acids (per cent. as butyric)	0.87 ^a	0.56
Insoluble acids (per cent.)	94.16 ^a	93.88
Unsaturated acids (per cent.) corrected	73.00	70.10
Saturated acids (per cent.) corrected	20.29	21.36
Iodine number of unsaturated acids	129.18	127.92
Saponification no. of unsaturated acids	199.6	201.2
Unsaponifiable matter	0.64	0.68

^a Grateful acknowledgment is made to C. A. Tarnutzer and W. W. F. Enz who determined the titer test of the residual oil and the soluble and the insoluble acids of the expressed oils, respectively.

³ The average of five determinations of the (ethyl) ether extract of these meats was 68.67%.

nized procedures.⁴ Separation of the saturated from the unsaturated acids was effected by the lead salt-ether method⁵ after which corrections were made⁶ for the small amount of unsaturated acids contaminating them when this procedure is used, and for the unsaponifiable matter accompanying the insoluble acids.

Glycerides of fatty acids of low molecular weight are absent, or at least present in very small amount, a situation pertinent also to sterols and hydroxylated compounds. The low acidity suggests the probable absence of any very active fat splitting enzymes in the nut. Its iodine number assigns this oil to the semi-drying group.

(b) **Unsaturated Acids.**—Bromination⁷ of the unsaturated acids led to the formation of no hexabromide, the derivative of linolenic acid. Appreciable quantities of the tetrabromide (m. p. 14.5°; Br, 53.58%) of linoleic acid were obtained. The bromine content (39.73%) of the dibromide fraction showed that the latter was contaminated with a small amount of the linoleic derivative. Using the former value and the theoretical iodine numbers of oleic and linoleic acids, the percentage composition of the whole was then calculated⁸ with the following results.

TABLE II
COMPOSITION OF THE UNSATURATED ACID FRACTION OF THE RESIDUAL OIL

Acid	In oil, %	Glycerides in oil, %	Total, ^a %
Oleic	51.26	53.57	55.64
Linoleic	18.84	19.69	21.65

^a This column includes the unsaturated acids present with the saturated.

The same acids were qualitatively identified, both by bromine content and melting point, in the unsaturated fraction of the expressed oil.

TABLE III
RESULTS OF ANALYSIS OF METHYL ESTERS OF THE SATURATED FATTY ACIDS

Fraction	Boiling range, 3 mm.	Wt., g.	Iodine no.	Sapon. no.	Mean mol. wt.	Unsatd. acids, g.	Myristic acid, g.	Palmitic acid, g.	Stearic acid, g.
1	145-150	3.52	11.87	213.9	259.34	0.33	1.18	1.84	..
2	150-157	25.56	12.42	208.8	266.20	2.48	3.21	18.60	..
3	157-165	12.51	19.74	205.6	269.35	1.93	0.36	9.63	..
4	165-168	10.58	35.63	197.0	281.55	2.95	..	4.28	2.85
5	168-175	8.28	30.66	193.2	289.62	1.99	..	1.85	4.07
Res. ...		2.30	59.68	167.2	390.50	1.18
Total	4.75	36.20	6.92

⁴ Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., 1925, 2d ed., pp. 281-285.

⁵ Gusserow, *Arch. Apoth.-Vereins nord Teutschland*, 27, 153 (1828); Varrentrapp, *Ann.*, 25, 197 (1840).

⁶ Jamieson, *J. Assoc. Official Agri. Chem.*, 11, 303 (1928).

⁷ Eibener and Muggenthaler, *Farben-Ztg.*, 18, 131 (1912).

⁸ Baughman and Jamieson, *THIS JOURNAL*, 42, 157 (1920).

(c) **Saturated Acids.**—Separation of the methyl esters⁸ of the saturated acids into five fractions whose boiling range was 145 to 175° (3 mm.) (Table III) was followed by the calculation of the mean molecular weight of each from saponification and iodine numbers, the latter serving as a measure of the degree of contamination by unsaturated acids. These values lay between 259.3 and 289.6, indicating the presence of esters in the C₁₂ to C₁₈ group. Myristic, palmitic and stearic acids were subsequently identified by their melting points.

These data lead to the following statement of the percentage composition of the saturated acid fraction.

TABLE IV

COMPOSITION OF THE SATURATED FRACTION OF THE RESIDUAL OIL

Acid	%	Percentage in oil	Glycerides in oil
Myristic	7.94	1.70	1.79
Palmitic	60.48	12.92	13.55
Stearic	11.57	2.47	2.58

The same fatty acids were qualitatively identified by means of their melting points in the corresponding fraction of the expressed oil.

Summary

The chemical and physical characteristics of the expressed and the residual portions of a specimen of Brazil nut oil have been determined. The statement¹ that this oil contains stearin, palmitin and olein has been confirmed. To this list have been added myristin and linolein.

The percentage composition of the residual oil was found to be as follows: myristin, 1.79; palmitin, 13.55; stearin, 2.58; olein, 55.64; linolein, 21.65; unsaponifiable matter, 0.68; residues and undetermined, 4.11.

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THE ACIDITY OPTIMUM OF YEAST HEXOSEDIPHOSPHATASE¹

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The hexosediphosphoric acid ester and the enzyme which splits it into fructose and phosphoric acid were discovered by Harden and Young. It has been shown that the enzyme is present in practically all kinds of yeast and also in the *Coli* bacteria. It is present in different organs of the animal body, as well as in many higher plants. Although a great many papers have dealt with yeast hexosediphosphatases, we have but very little information concerning its optimum *PH*.

¹ The writer's sincere thanks are due to Professor H. v. Euler and to the Stockhoms Högskola for the opportunity to make this study.