The hydrocarbon XI (50 mg.) was oxidized with potassium dichromate (60 mg.) in acetic acid (2 cc.) by boiling for ten minutes. The quinone was precipitated by water, then treated with ethanol and recrystallized from high-boiling petroleum ether as short red rods, m. p. 178° (XII).

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.7; H, 5.5. Found: C, 84.4; H, 5.7.

When the hydrocarbon XI (0.8 g.) was heated with selenium (0.4 g.) to 310–320° for twelve hours, and the mass extracted with boiling xylene, an oil, b. p. 260–265° (0.02 mm.), was obtained, which on recrystallization from isopropanol yielded yellowish rods, m. p. 137–138°, identical with the starting material, and a minute amount of small blocks, which adhered to the wall. This second substance was separated and yielded from an acetic acid solution a picrate of m. p. 165° (red rods). Its amount, however, was not sufficient for analysis.

Decarboxylation of IX with Copper.—Five grams of the aromatic anhydride IX and basic copper carbonate (5 g.) were heated in quinoline (35 cc.) for half an hour. Then benzene (100 cc.) was added and the solution washed with excess dilute sulfuric acid. On concentrating the benzene solution, a small amount of crystals separated; from butyl acetate as beautiful prisms, m. p. 292–293° (Xa or b).

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.7; H, 4.8. Found: C, 85.4; H, 5.1.

Summary

1. The central position of 1,2,3,4-dibenzphenanthrene in the system of carcinogenic hydrocarbons is discussed.

2. 6-Isopropenylchrysene is used in the Diels–Alder reaction for the attempted synthesis of 1″-methyldibenzphenanthrene. This route led finally to the tetrahydro stage (XI) of the desired aromatic hydrocarbon.

3. An hypothesis has been advanced for the influence of aliphatic side-chains on the activity of carcinogenic hydrocarbons.

4. A series of 6-alkenyl- and 6-alkylchrysenes is synthesized, related to 1″-methyl-1,2,3,4-dibenzphenanthrene, for carcinogenic tests.

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Puerto Rican Fatty Oils. IV. Expressed Tropical Almond (Talisay) Oil

BY CONRADO F. ASENJO AND JOSÉ A. GOYCO

The tropical almond tree (*Terminalia Catappa* L.) is indigenous to the East Indies but is also found widely distributed in Puerto Rico and many other tropical countries. The kernels of the fruit are edible and yield nearly 55% of a fixed oil by extraction; by expression the yield is only 35%. This oil is known in the Philippines as Talisay oil and in India it is called Indian almond oil.

Oudemans[1] reported that tropical almond oil consisted principally of olein, palmitin, and some traces of stearin. Grimme[2] gave the range of its characteristics. Cruz and West[3] examined a sample of ether extracted oil from Philippine kernels and found it to consist of the glycerides of oleic (40.85%), linoleic (22.91%), myristic (1.00%), palmitic (28.47%), stearic (3.99%), and arachidic (0.75%) acids. Except for this last study, no other quantitative studies of the composition of the oil seem to have been carried out.

The present investigation was undertaken to supply information with regard to the composition of the expressed almond oil from Puerto Rican kernels. The sample expressed in the laboratory of the School was used immediately in this investigation. It had a very light yellow color and an excellent odor and taste. It was found suitable for the manufacture of edible fats, cosmetics and pharmaceutical products.

Material.—Only ripe fruits were collected, either yellow or purple in color according to the degree of ripeness, and these came from trees in San Juan and in the neighboring town of Toa Baja. The fruit was ovoid in shape, measuring 5 to 6 cm. in length and 3 to 4 cm. in width at its axis. Their average weight per fruit, as collected, was 22.7 g. but, after drying out in a circulating air oven at a temperature of 50 to 60°, they weighed only 5.5 g. each. The dried fruit consisted of 50% fibrous covering, 42% husk, and 8% kernel. Upon analysis the dried kernel gave the following results:

Moisture, %	4.92
Fat (ether extract), %	54.60
Proteins (N × 6.25), %	27.87
Crude fiber, %	2.49
Ash, %	1.06
Nitrogen-free extract, %	9.06

Preparation of the Oil.—The oil was expressed from the dried kernels in a Carver press, using a maximum pressure of 15,000 lb. per sq. in. The oil yield was 35%. Filtration

(1) Oudemans, *J. prakt. Chem.*, **100**, 409 (1867), through Wehmer, "Die Pflanzenstoffe," Gustav Fischer, Jena, 1931.

(2) Grimme, *Chem. Rev. Fett-Harz.-Ind.*, **17**, 233 (1910), through Wehmer, ref. 1.

(3) Cruz and West, *The Philippine J. Sci.*, **48**, 13–19 (1932).

was the only operation required for its purification and the oil thus obtained had a faint but agreeable almond taste.

Physical and Chemical Examination.—The physical and chemical properties of the oil were determined by the usual procedures,[4] unless otherwise stated, and the results recorded in Table I.

TABLE I

CHARACTERISTICS OF TROPICAL ALMOND OIL FROM PUERTO RICO

Specific gravity 25°/25°	0.9024
Refractive index 20°	1.4639
Saponification value	187.6
Iodine no. (Hanus)	71.32
Acid value	7.39
Unsaponifiable matter, %	0.65
Unsaturated acids, % (cor.)	52.92
Saturated acids, % (cor.)	40.96
Iodine no. of unsaturated acids (Hanus)	120.70
Reichert-Meissl no.	0.08
Polenske no.	0.12
Acetyl value	4.67
Peroxide no.[5]	0.61

Unsaturated Acids.—The unsaturated acids were separated from the saturated acids by the lead salt–ether method. On bromination by the usual procedure, no hexabromostearic acid separated from the ether solution of the brominated product at −10°. This indicated the absence of linolenic acid. On the other hand, tetrabromostearic acid, m. p. 114°, was obtained in appreciable amounts from the petroleum ether solution, indicating the presence of linoleic acid. As the iodine number of the unsaturated acid fraction was 120.7, the percentage of linoleic and oleic acids was calculated by Lewkowitsch's formula[6] with the results given in Table II.

Saturated Acids.—The methyl esters of the saturated acids were prepared by the procedure described by Hilditch.[7] When free of moisture and solvents, the esters were fractionally distilled at 2.5 mm. pressure. Five fractions and a residue were obtained and the composition of each was determined, by the Baughman and Jamieson method.[8]

In order to test the correctness of these data, the acids were isolated from their different fractions by saponifying the esters, acidifying with hydrochloric acid, washing the liberated fatty acids with water until free from chlorides, and fractionally crystallizing from 95% ethyl alcohol. The anilides of the acids thus obtained were also prepared.

Myristic Acid (m. p. 53.8°).—From fractions 1 and 2 an acid melting at 54.5° was obtained. Its anilide melted at 84°. Myristic acid anilide melts at 83.4°.

Palmitic Acid (m. p. 62°).—From fractions 1, 2, 3, 4, 5, and the residue an acid melting at 63° was obtained. Its anilide melted at 90°. Palmitic acid anilide melts at 89.5°.

Stearic Acid (m. p. 69.2°).—From fractions 3, 4, 5, and residue an acid melting at 69.8° was obtained. Its anilide melted at 93°. Stearic acid anilide melts at 92.6°.

TABLE II

UNSATURATED AND SATURATED ACIDS IN EXPRESSED TROPICAL ALMOND OIL FROM PUERTO RICO

Acids	In unsatd. acids, %	In satd. acids, %	In oil, %	Glycerides in oil, %
Linoleic	33.77	...	17.87	18.58
Oleic	66.23	...	35.05	36.63
Myristic	...	1.58	0.65	0.69
Palmitic	...	89.16	36.52	38.31
Stearic	...	9.25	3.79	3.96

In concluding, the writers wish to express their thanks to the Department of Agriculture and Commerce of Puerto Rico for the grant-in-aid to carry on this work; also to Dr. D. H. Cook, head of the Department of Chemistry, for his encouragement and coöperation, and to Miss Julita Margarida-Mora, for her technical assistance.

Summary

The characteristics and composition of expressed tropical almond (*Terminalia Catappa* L.) oil have been determined.

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(4) Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., 4th ed., 1935, pp. 404–429.

(5) French, Olcott and Mattill, *J. Ind. Eng. Chem.*, **27**, 274 (1935).

(6) J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Macmillan & Co., Ltd., London, Vol. 1, 1921, p. 574.

(7) T. P. Hilditch, "The Chemical Composition of Natural Fats," John Wiley and Sons, New York, N. Y., 1941, pp. 371–372.

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