[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUW UNIVERSITY]

The Composition of the Seeds of *Asimina triloba*

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The mature fruit of *Asimina triloba* (common name papaw) required for this investigation was collected from woodlands in Putnam County, Indiana, about October 1, 1937, and the seeds were extricated from the pulp almost at once and allowed to air dry at room temperature. Each fruit contains from two to twelve flat, oblong, dark brown seeds, the average weight of which is 0.7 g. The air-dried seeds were ground carefully and dried at 100–110° for an hour in a carbon dioxide atmosphere. The loss in weight indicated a moisture content of 5.1%. The dried material was then extracted quantitatively with petroleum ether (b. p. 30–60°) and found to contain about 38% of a reddish-brown fatty oil. The unextracted residue was a slightly gray powder.

Experimental

Analysis of the Fatty Oil of Papaw Seed.—The usual physical and chemical characteristics of this oil were determined by standard methods[1] and are as follows: sp. gr. (25°/25°), 0.9296; ref. ind. (Abbe 25°), 1.4728; iodine no. (Hanus), 113.5; sap. value, 194.0; mean mol. wt. satd. acids, 307.9; mean mol. wt. unsatd. acids, 308.2; iodine no. unsatd. acids, 117.8; iodine no. satd. acids, 14.0; unsatd. acids (basis of oil) (by the lead-salt method) (corrected %), 85.5; satd. acids (basis of oil) (corrected %), 5.6; unsap. matter, %, 0.80; Reichert–Meissl no., 1.05; acid value, 6.4; acetyl value, 18.11.

Composition of the Unsaturated Acids.—The unsaturated acids (270 g.) were converted into the methyl esters and distilled at 4 mm.: yield 228 g.; b. p. 175–182°. The narrow boiling point range indicated that the mixture contained acids with the same number of carbon atoms.

Two and one-half grams of the unsaturated methyl esters was reduced catalytically with hydrogen. The product was saponified and the acid thus produced, recrystallized once from 95% alcohol, melted at 68–70°. The unsaturated acids were thus shown to consist of only eighteen-carbon-atom acids.

Linolenic and more highly unsaturated acids were found to be absent by adding bromine to a cold ether solution of the unsaturated acids. Another sample was dissolved in petroleum ether, cooled to −5° and bromine added slowly with stirring. A precipitate formed, was filtered off and recrystallized once from glacial acetic acid. The melting point of the product was 112.5–113.5°. This indicated qualitatively the presence of linoleic acid.

The ozonolysis method of Riebsomer and Johnson[2] was applied to 175 g. of the unsaturated methyl esters, and the methyl esters from this process fractionally distilled from a modified Claisen flask with the following results: at a pressure of 14 mm., the fractions had boiling points and weights of (1) 53–57°, 7.4 g.; (2) 57–88°, 4.7 g.; (3) 88–99°, 15.8 g. At a pressure of 4–5 mm., the fractions had boiling points and weights of (4) 60–121.5°, 21.8 g.; (5) 121.5–127.5°, 54.8 g.; (6) 127.5–155°, 30.0 g.; (7) 155–167°, 11.9 g.; (8) 167–177°, 9.4 g.; undistillable, 15.4 g.

Fractions 3 and 4 were put together and redistilled into three fractions which are designated as fractions 3a, 3b, and 3c. At a pressure of 14.5 mm., these fractions had boiling points and weights of (3a) 85–91°, 5.4 g.; (3b) 91.5°, 21.1 g.; (3c) residue, 11 g.

For the examination of the various fractions densities were determined at 20°, converted to densities at 4°; refractive indices were determined at 20° using the Abbe refractometer. The refractive index and density of fraction 1 were 1.407, 0.8858. The ester was saponified and the acid distilled, b. p. 106–107° at 18 mm.; found for the refractive index and density of the acid, 1.4150, 0.9211; reported for caproic acid, 1.4138, 0.927. The anilide prepared from this acid melted at 94.5–95°. Mixed m. p. of known caproic anilide (m. p. 96°) was 94.5–95.5°. These data established the identity of fraction 1 as methyl caproate.

Fractions 2 and 3a were small and each boiled over a wide range. Their refractive index, density and saponification equivalents all indicated them to be a mixture of methyl caproate and methyl pelargonate found in fraction 3b.

For fraction 3b the refractive index and density were 1.4210 and 0.8792. The ester was saponified and the acid distilled, b. p. 142–144° at 18 mm.; neut. equiv. acid, found 157.0; calculated for pelargonic acid, 158.1; refractive index and density: 1.4309, 0.905; reported for pelargonic acid; 1.433, 0.907. The anilide prepared from this acid melted at 55–55.5°. Reported for the anilide of pelargonic acid 56°. These data indicated this fraction to be methyl pelargonate.

Fraction 3c.—The b. p. of fraction 3c and its saponification equivalent (137.6) indicated it to be a mixture of the methyl esters of pelargonic and azelaic acids.

The refractive index and density for fraction 5 were 1.4361, 0.9974; reported for dimethyl azelate, 1.436, 1.005. The ester was saponified and the acid recrystallized from water. It melted at 106.5°; mixed m. p. with known azelaic acid (m. p. 106.5°) showed no depression; neut. equiv. of the acid 95.1; calculated for azelaic acid 94.1. Fraction 5 was thus shown to be dimethyl azelate.

In a similar manner, fraction 6 was demonstrated to be essentially dimethyl azelate.

Fractions 7 and 8 were relatively small and boiled over large ranges. Saponification equivalents, refractive indices, and density determinations indicated them to con-

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[1] Jamieson, "Vegetable Fats and Oils," Monograph Series No. 58, The Chemical Catalog Co., Inc., New York, 1932.

[2] Riebsomer and Johnson, THIS JOURNAL, **55**, 3352 (1933).

sist largely of dimethyl azelate admixed with the methyl esters of some 18 carbon monobasic acids which had not been cleaved by ozonolysis.

The three significant fractions for establishing the composition of the original unsaturated acids are 1, 3c, and 5, which were shown to contain, respectively, caproic, pelargonic, and azelaic acids.

Using the same reasoning as employed by Riebsomer and Nesty[3] these products were taken to mean that the only acids present in the unsaturated acids were oleic and linoleic. This is another case in which the double bonds in the natural occurring linoleic acid are found in the 9, 10, and 12, 13, positions, which is in accord with previous findings.[3]

The iodine number of the unsaturated acids was 117.8, which makes it possible to calculate the percentage of oleic and linoleic acids.

	In unsatd. fraction	In oil % acid	In oil % glyceride
Oleic acid	69.5	59.4	62.1
Linoleic acid	30.5	26.1	27.1

The Saturated Acids

The neutral equivalent of the saturated acids (307.9) indicated that the mixture contained some acids with more than 18 carbon atoms. Twenty grams of the saturated acids was converted into the methyl esters and were fractionally distilled at 4 mm. using a modified Claisen flask. The fractions had boiling points, weights, and saponification equivalents of (1) 160–175°, 12.5 g., 208.0; (2) 175–190°, 5.5 g., 317.7; residue 1.5 g.

The saponification equivalent of fraction 1 suggested a mixture of methyl palmitate and methyl stearate. This material was redistilled into three fractions. The first 1.2 g. of distillate (fraction 1a) was collected, the next 6.5 g. (fraction 1b) was collected, and the last 2.0 g. to distil was collected separately (fraction 1c). Fraction 1a was saponified and the acid recrystallized three times from ethyl alcohol. The m. p. of the acid was 60–61°. Mixed m. p. with palmitic acid was 61–62°; the m. p. of the anilide 88–88.5°. Mixed m. p. with known anilide of palmitic acid showed no depression. Fraction 1c was saponified and recrystallized from alcohol. The m. p. of the acid was 67–69°. Mixed m. p. with stearic acid 68–70°. These data were interpreted to mean that fraction 1 consisted of palmitic and stearic acids.

Fraction 2 (b. p. 175–190°) was saponified and, after three crystallizations of the acid from ethyl alcohol, a small amount of acid was left with a m. p. of 68–70°. A mixed m. p. with stearic acid showed no depression. The saponification equivalent (317.7) of this fraction indicated that another acid with a molecular weight greater than that of stearic acid was present, but it was not isolated from this fraction.

The residue (1.5 g.) was saponified, the acid dissolved in ethyl alcohol, decolorized with charcoal, and allowed to crystallize. On the second crystallization 0.3 g. of an acid was isolated; m. p. 76–77°. A mixed m. p. with an authentic specimen of arachidic acid (m. p. 76–77°) showed no depression, from which it was concluded that arachidic acid was present.

These data do not permit a very accurate calculation of the percentages of the saturated acids, but if we assume fraction 1 to be a mixture of palmitic and stearic acids, fraction 2 to be a mixture of stearic and arachidic acids, and the residue to be largely arachidic acid it is then possible to obtain the percentages shown in the accompanying table. These assumptions are admittedly not entirely valid, especially since no account has been taken of the small amount of unsaturated acids present.

	In satd. fraction	% acid	% glyceride
Palmitic acid	41.5	2.3	2.4
Stearic acid	31.8	1.8	1.9
Arachidic acid	26.6	1.5	1.54

Glycerol was shown to be present by conversion into the tribenzoate.

Estimation of Nitrogen, Crude Fiber, and Ash Content of the Seeds.—A Kjeldahl nitrogen determination on the ground dried seeds showed 0.1805% of nitrogen present. This would correspond to 1.128% of protein.

Crude fiber was determined on the dried meal after extraction of the oil. The percentage of crude fiber calculated on the basis of the dried seeds was 20.0%.

The ash content calculated on the basis of the dried seeds was 1.3%.

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Summary

1. The seeds from *Asimina triloba* have been analyzed.

2. These seeds contain about 38% of a fatty oil which consists of the glycerides of oleic, linoleic, palmitic, stearic, and arachidic acids.

3. The protein, crude fiber, and ash content of the seeds have been determined.

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[3] Riebsomer and Nesty, This Journal, **56**, 1784 (1934).