+0.1 volt (to the saturated calomel electrode) in the absence of oxygen at a large, quiet mercury electrode for seven and one-half hours. When hydrogen sulfide was passed through this solution after electrolysis, a black precipitate formed, showing the presence of soluble mercury in the solution. Also a portion of this electrolyzed solution was analyzed at the dropping mercury electrode and a cathodic wave was obtained which was not at all similar to the cathodic wave given by cystine (see Fig. 6), but corresponded to the reversible reduction of mercury from a complex compound. From the evidence obtained we feel justified in concluding that the product of the anodic reaction of cysteine at the dropping mercury electrode is a mercurous cysteinate of the composition HgSR.

This is the first case in the literature indicating that dissolved mercurous mercury can exist as Hg^+ instead of as Hg_2^{++}. In agreement with the literature we conclude from polarographic investigations carried out in this Laboratory with mercurous nitrate solutions that at mercurous ion concentrations greater than 10^{-5} *M* practically all of the mercury is present as Hg_2^{++}. However, it should be realized that with decreasing total mercurous ion concentration the equilibrium $Hg_2^{++} \rightleftarrows 2Hg^+$ is greatly shifted to the right. The mercurous ion concentration of the mercurous cysteinate can be calculated to be of the order of 10^{-20} *M* and at this small concentration practically all of the mercurous mercury may be present as Hg^+.

Summary

1. Cysteine can be determined with the dropping mercury electrode in a medium of 0.1 *M* perchloric acid. The diffusion current was found proportional to the concentration of cysteine. The diffusion coefficient of cysteine was calculated to be 3.10×10^{-5} cm.²/sec. at 25°. The half-wave potential in the above medium (pH = 1) was found to be −0.05 volt (to the saturated calomel electrode) and independent of the cysteine concentration.

2. At pH values greater than 2 the anodic waves were quite irregular. Over a wide range of potentials a small constant current was obtained which was smaller than the diffusion current. This abnormality is attributed to the formation of a film of HgSR.

3. The anodic waves of cysteine at the dropping mercury electrode do not correspond to the formation of cystine but rather to the formation of a mercurous compound, HgSR. The anodic reaction is given by the equation

$$RSH + Hg \rightleftarrows HgSR + H^+ + e$$

At a platinum electrode the anodic waves of cysteine occur at a potential about 0.6 volt more positive than at the mercury electrode and correspond to the formation of cystine.

4. Evidence is obtained that at mercurous ion concentrations of the order of 10^{-20} *M* practically all of the mercurous mercury is present in solution as Hg^+ and not as Hg_2^{++}.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUW UNIVERSITY]

The Composition of the Fatty Oil from *Carya Cordifornia* Nuts

BY J. L. RIEBSOMER, ROBERT LARSON AND LAWRENCE BISHMAN

Some studies have been made on the physical properties of oils from *Carya amarya* and *Carya ovata* nuts[1] but no work has been reported on *Carya cordifornia*. The quantity of *Carya cordifornia* oil available is relatively small, which accounts for the lack of interest. The nuts from these trees are from two to four centimeters in diameter. The shell is hard and in color quite similar to the English walnut. The meat from these nuts has a bitter taste and even animals refrain from eating them. This bitter material is not extracted with the oil.

Experimental

The nuts used for this analysis were collected in central Indiana in November, 1938. The nuts were ground (shell included), dried and extracted with petroleum ether (b. p. 30–60°). The moisture content of the ground nuts was 4.1%, and the petroleum ether extract which was a reddish brown oil was 27% calculated on the basis of the dried nuts.

The physical and chemical characteristics of the ex-

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[1] Peterson and Bailey, *J. Ind. Eng. Chem.*, **5**, 739 (1913).

tracted oil are listed in Table I. Standard methods of analysis as given by Jamieson[2] were used.

TABLE I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF *Carya cordifornia* OIL

Specific gravity (25°)	0.9319
Refractive index (Abbe 20°)	1.4712
Iodine number (Hanus)	77.5
Saponification value	189.1
Mean molecular weight saturated acids	271.5
Mean molecular weight unsaturated acids	317.0
Iodine number unsaturated acids	89.6
Iodine number saturated acids	29.4
Unsaturated acids (basis of oil) (cor. %)	86.0
Saturated acids (basis of oil) (cor. %)	11.8
Reichert–Meissl number	2.5
Acetyl value	37.2
Acid value	10.5
Unsaponifiable matter, %	0.67

The procedure for the determination of the acids present in this oil was exactly the same as used previously.[3] Accordingly most of the procedure will not be repeated here.

Unsaturated Acids.—The unsaturated acids were isolated using the lead salt–ether method. Their methyl esters were prepared in the usual manner and distilled at 4 to 5 mm. pressure. The boiling range of the main portion was 160 to 170°.

Bromination of samples of the unsaturated acids indicated the absence of linoleic, linolenic and other more highly unsaturated acids.

Three grams of the unsaturated methyl esters was reduced using platinum as the catalyst. The reduced product was saponified and produced only stearic acid, m. p. 67–68°; mixed m. p. with known stearic acid, 68–69°. This experiment proved the unsaturated acids to be essentially 18 carbon atom acids.

Sixty grams of the methyl esters was ozonized and the methyl esters produced from this process were distilled in the usual manner. Only two of the fractions need be considered here because all others boiled over wide ranges and were obviously intermediates or otherwise unimportant. One of these fractions, b. p. 74–79° at 6 mm. pressure, weight 7.6 g., was saponified, and the acid produced was shown to be pelargonic: $n^{20}{}_D$, 1.4310 (reported pelargonic acid, 1.433); $d^{20}{}_4$, 0.9103 (reported 0.907); neut. equiv., 156.4 (calcd., 158.1); anilide, m. p. 56° (reported 57°).

The second significant fraction boiled at 122–128° at 6 mm. The refractive index and density of this fraction were compared with dimethyl azelate: $d^{20}{}_4$, 0.9994 (reported, 1.005); $n^{20}{}_D$, 1.4360 (reported, 1.436). The ester was saponified and the acid produced melted at 105°, mixed m. p. azelaic acid (m. p. 106.5°) showed no depression. Neut. equiv., 93.2 (calcd., 94.1). This fraction was thus shown to be azelaic acid.

The presence of pelargonic and azelaic acids among the products of ozonolysis indicated the presence of oleic acid. On the basis of all the data obtained, iodine number, bromination, reduction and ozonolysis, oleic acid was the only unsaturated acid present in the oil. If other acids were present their quantity must have been very small.

Saturated Acids.—The mean molecular weight of the saturated acids fraction as obtained from the lead salt–ether separation was 271.5, which indicated a mixture of palmitic and stearic acids. About 25 g. of the saturated acids was converted to the methyl esters and fractionally distilled at 3 mm. The fraction boiling at 150–160° was saponified and the acid crystallized from methyl alcohol. M. p. 59°; mixed m. p. palmitic acid 61°. Neut. equiv., 255.5 (calcd. for palmitic acid, 256.2). Anilide, m. p. 86° (reported for anilide of palmitic acid, 87.5°). This fraction was apparently slightly impure palmitic acid.

The fraction boiling at 173–185° was saponified and crystallized from methyl alcohol, m. p. 67.5°; mixed m. p. stearic acid 68.5°. Neut. equiv., 286.2 (calcd. stearic acid, 284.3). Anilide, m. p. 95° (reported for anilide of stearic acid, 93.6°). These data indicated the presence of stearic acid. No other saturated acids could be isolated from the mixture.

Assuming the mixture to be palmitic and stearic acids and using the neutral equivalent of the saturated acids (271.5), a calculation of the percentages of the saturated acids was made: % palmitic acid in oil, 6.4; % stearic acid in oil, 5.4.

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Summary

1. The physical and chemical characteristics of the oil from *Carya cordifornia* nuts have been determined.

2. The oil contains the glycerides of oleic, palmitic and stearic acids and a small amount of unsaponifiable matter.

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[2] G. Jamieson, "Vegetable Oils and Fats," American Chemical Society Monograph 58, Reinhold Publishing Corp., New York, N. Y., 1932.

[3] Riebsomer and Nesty, THIS JOURNAL, **56**, 1784 (1934).