

acid. All areas for the mixtures refer to the area per molecule of the acid, without reference to the amount of paraffin oil present.

From Fig. 2 it is obvious that at areas at which no lenses are visible, if the molecules of acid were to be oriented as in a condensed film, the total area would be more than sufficient to allow every molecule of the paraffin oil to be in contact with the water, but it is not suggested that the orientation is of this type. The presence of the oil causes these films to occupy larger areas, and Myers and Harkins have shown that larger amounts of oil expand the film at low pressures, but more greatly condense it at high pressures.

Thus it appears that uniform mixed films composed of fatty acids and liquid hydrocarbons may exist but these films are transformed at definite film pressures to composite films with lenses of hydrocarbon oil.

An investigation of these phenomena is in progress. An important feature revealed in this work is that the appearance of the lenses does not give rise to a discontinuity in the pressure-area curves.

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Protein Content of the Bark of Black Locust, *Robinia Pseudacacia*

BY D. BREESE JONES AND SAMMIE PHILLIPS

The observations here recorded relate to the surprisingly large quantity of protein in the bark of the common black locust tree. Protein is a well-recognized constituent of most plants and animal tissues, but as far as known the black locust is the only tree from the bark of which protein has been isolated and studied.

In 1899, Power and Cambier¹ demonstrated that the protein of the black locust tree was responsible for the poisoning of horses which had gnawed the bark of this tree. Later, other investigators²⁻⁴ found that hypodermic injections of a solution of this same crude protein preparation produced an alteration of the kidneys producing a nephritis, and that even in great dilutions it agglutinated the red corpuscles of the blood of

(1) F. B. Power and J. Cambier, *Pharm. Rundschau*, **8**, 29 (1890).

(2) C. Lau, "Über vegetabilische Blut-Agglutinine," Inaugural dissertation, Rostock, 1901, p. 64.

(3) R. Kobert, *Landw. Vers.-Sta.*, **79-80**, 97 (1913).

(4) P. Ehrlich, *Klin. Jahrb.*, **6**, 315 (1898).

many different animals. Several instances are recorded⁵ where both people and animals have been poisoned by the bark of the locust tree.

In the work of the authors referred to only the crude protein coagulum was used. No attempt was made to study the chemical and physical properties of the bark proteins or to determine the amount of protein in the bark. In 1925, Jones and Gersdorff⁶ found that the dried inner bark collected from two locust trees in Maryland contained 17.5% crude protein. This protein was found to consist chiefly of a globulin, albumin and a proteose. The physical properties and composition of the proteins isolated were similar to those of most vegetable and animal proteins. They contained practically the same assortment and proportions of amino acids as found in most proteins.

Occasion was recently had to examine the bark from a number of black locust trees grown in different localities. This bark was collected⁶ in Ohio and Indiana from trees ranging in age from seven to ten years. The outer brown, spongy portion of the bark was carefully removed. Only the inner, light colored portion was employed. The latter was allowed to dry by exposure to the air, and then was ground to a coarse powder in a mill. Moisture in the ground bark was determined by heating for twenty-four hours at 110°. Nitrogen in the samples was determined by the Kjeldahl method, and the crude protein calculated by multiplying the percentage of nitrogen by the conventional factor 6.25. The percentages given in Table I are based on moisture-free material.

The quantity of protein found covers a rather wide range. The average, 21.5%, is, however, considerably higher than that previously found in this Laboratory when working with the bark from the trees grown in Maryland. This difference may be due to the fact that the barks were collected at different seasons of the year. The bark from the Maryland trees was collected about the middle of August, while that from the

(5) D. B. Jones, C. E. F. Gersdorff and O. Moeller, *J. Biol. Chem.*, **64**, 655 (1925).

(6) The samples were collected under the supervision of Dr. Ralph C. Hall of the Bureau of Entomology and Plant Quarantine, to whom grateful acknowledgment is made. Some locust trees are seriously damaged by the locust borer. Other trees seem to be resistant to the attacks of this insect. Determinations of protein in the bark of resistant and susceptible trees were made with the idea that there might be a correlation between immunity to borer attack and the quantity of protein in the bark. No such correlation was found, however.

TABLE I
PROTEIN CONTENT OF THE BARK FROM 21 LOCUST TREES
GROWN IN DIFFERENT SECTIONS

Series R				
Samples of Series R were from borer-resistant trees.				
Sample no.	Source	Time collected	Age of tree, yrs.	Protein content, %
R ₁	Hopedale, Ohio	11-26-34	9	18.12
R ₂	Hopedale, Ohio	11-26-34	9	25.34
R ₃	Hopedale, Ohio	11-26-34	9	23.23
R ₄	Hopedale, Ohio	11-26-34	9	20.38
R ₅	Cambridge, Ohio	11-26-34	8	22.41
R ₆	Cambridge, Ohio	11-26-34	8	20.93
R ₇	Cambridge, Ohio	11-26-34	8	20.93
R ₈	Cambridge, Ohio	11-26-34	7	20.81
R ₉	Cambridge, Ohio	11-26-34	7	19.46
R ₁₀	Cambridge, Ohio	11-26-34	7	22.68
R ₁₁	Versailles, Ind.	11-5-34	13	21.41
				Average 21.43
Series S				
Samples of Series S were from borer-susceptible trees.				
S ₁	Minerva, Ohio	11-26-34	9	27.98
S ₂	Minerva, Ohio	11-26-34	9	22.22
S ₃	Minerva, Ohio	11-26-34	9	26.62
S ₄	Minerva, Ohio	11-26-34	9	24.99
S ₅	Minerva, Ohio	11-26-34	9	23.32
S ₆	Hopedale, Ohio	11-26-34	10	12.94
S ₇	Hopedale, Ohio	11-26-34	10	25.69
S ₈	Hopedale, Ohio	11-26-34	10	15.87
S ₉	Hopedale, Ohio	11-26-34	10	19.11
S ₁₀	Hopedale, Ohio	11-26-34	10	17.06
				Average 21.58

Ohio and Indiana trees was collected the latter part of November. It has been shown⁷ that soon before the leaves fall in the autumn their protein is transported to the parenchyma of the bark where it is stored during the dormant period.

(7) E. Schulze, *J. Landw.*, **52**, 323 (1904).

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The Existence of a Maximum in the Gas Solubility-Pressure Curve

By I. R. KRICHEVSKY

Basset and Dodé¹ have measured the nitrogen solubility in water at 18° and under pressure up to 4500 kg./sq. cm. They detected an excessively interesting phenomenon, that at pressures about 3000 kg./sq. cm. the nitrogen solubility passes through a maximum. Though their determinations are not particularly exact, nevertheless the existence of a maximum is a reality and can be predicted theoretically.

(1) Basset and Dodé, *Compt. rend.*, **203**, 775 (1936).

For a case of slightly soluble gases in solvents with small vapor pressure we² have deduced a thermodynamical equation

$$\log f_2/N_2 = \log K + \bar{V}_2 P / 2303RT \quad (1)$$

where f_2 is the fugacity of the gas, N_2 its mole fraction in the solution, K Henry's coefficient, \bar{V}_2 partial molal volume of the dissolved gas and P total pressure.

The solubility maximum corresponds to that pressure at which

$$\partial \ln N_2 / \partial P = 0 \quad (2)$$

Differentiating the equation (1) with respect to pressure and substituting \bar{V}_2/RT for $\partial \ln f_2 / \partial p$, where \bar{V}_2 is gas volume, we can readily find that at the maximum solubility

$$V_2 = \bar{V}_2 \quad (3)$$

The partial molal volume of the water-dissolved nitrogen at 18° is 32.7 cc.² For lack of data we shall accept that the partial molal volume of nitrogen does not depend upon pressure. Extrapolating data of Amagat³ for nitrogen compressibility we found that at 18° the pressure of 3600 kg./sq. cm. corresponds to the volume of 32.7 cc., which is in a fairly good agreement with measurements of Basset and Dodé.

(2) Krichevsky and Kasarnovsky, *THIS JOURNAL*, **57**, 2168 (1935).

(3) Amagat, *Ann. chim. phys.*, **29**, 68 (1893).

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Mechanism of the Reduction of Unsaturated Compounds with Alkali Metals and Water

By CHARLES BUSHNELL WOOSTER AND KENNETH L. GODFREY

A number of valuable methods for reducing unsaturated organic compounds involve the use of a combination of an alkali metal or its amalgam with water or some other hydrolytic solvent, and the various interpretations which have been offered for these reactions are based on one, or the other, of two rival hypotheses. The earlier of these hypotheses attributes the reduction to "nascent" hydrogen liberated by the reaction between the alkali metal (or its amalgam) and the hydrolytic solvent.¹ In more general terms, this hypothesis requires that the actual reduction is effected by the *combination* and not by the metal alone. The more recent hypothesis attributes the

(1) Kekulé, *Ann. Suppl.*, **1**, 129 (1861); Herrmann, *Ann.*, **132**, 75 (1864); von Baeyer, *ibid.*, **269**, 145, 170, 174 (1892).