fixed in 3 per cent. potassium dichromate, which reacts to form a brown precipitate in cells which contain adrenalin.[3] In these specimens no alteration in the normal intensity or extent of this reaction could be observed.

In experimentally untreated normal mice, at certain stages of development, a wide band of tissue may be found between cortex and medulla which does not give the reaction with bichromate at any time, and which during the first part of its existence does not stain with Sudan III, in contrast to the overlying cortex. This band of tissue is definitely separated from the overlying cortex by cellular differentiation at the boundary. On the other hand, there is no connective tissue band between this intermediate tissue and the medulla, but the cell groups intermingle. The combined effect is strongly suggestive of a medulla which has lost part of its adrenalin. However, this does not seem to be the case, because one can follow the development of this intermediate zone of tissue from a very narrow inner band of cortex cells.

At two weeks of age in the mouse the zone develops very quickly, degenerates in the male before sexual maturity is reached, and degenerates in the virgin female during the first half of the reproductive period. On the degeneration of this inner zone the usual type of boundary between the medulla and the cortex is established. The apparent close connection of this zone with the adrenal medulla may be explained as a result of simple mechanical factors operating during its growth.

This reaction occurs normally in the mouse as a phase of development. An apparently similar sequence of events is found in the human adrenal during the first year of life. Analogous reactions in other species have not been reported.

It is this large cortex zone which Cramer seems to have described as "exhausted medulla." Although it may be possible to produce the zone experimentally by other means than adrenalin injections, it should be recognized as cortical rather than medullary tissue.

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[3] E. H. Miller. *Amer. Jour. Physiol.*, 75: 267, 1926.

STRUCTURE OF PLANT COMPOUNDS AND SOLUBILITY

During some recent work in plant analysis the writer had occasion to work with a number of organic acids and was surprised to find how readily certain carbohydrates, as well as other plant constituents, dissolved in cold formic acid of about 75 per cent. or more of acid. It is well known that the different sugars are quite soluble in water, and also that as the molecular weight increases and the structure becomes more complicated the solubility is decreased. Thus there is a lessened solubility among the carbohydrates in about the following order—dextrose, sucrose, raffinose, dextrins, starch, pectins, mucilage, gums (cherry), lignin, cellulose, etc. Hence, as the carbohydrate ladder is ascended from dextrose toward cellulose, each rung brings new structures not well understood. The term carbohydrates includes all the simple sugars and all substances which can be converted into simple sugars by hydrolysis. It is known that there is much variation in solubility even among starch grains. When some are boiled in water they break loose from their shells of amylo-pectin material leaving amylose in solution, and the shell coverings may be separated by filtration. Other starches do not even break open, but only swell and tend to form a gel structure.

Formic Acid Dissolves Starch Groups

Although water does not dissolve many of these carbohydrate compounds, it was found that formic acid dissolves not only sugars but also dextrin, starch, inulin, glycogen, agar, chlorophyll, glucosides, etc., together with some of the plant pigments usually found combined or associated with glucosides, as the blue from privet berries giving a wine-colored solution, the pigment from cotton-seed meal which gives the solution a very red color, and also chlorophyll from tomato leaf giving a blue-green solution. Formic acid does not dissolve much mucilage, cherry gum, lignin, cellulose, or proteins in the cold (unless very concentrated acid is used). When starch is dissolved in this acid it makes a clear syrupy liquid partly hydrolized as it gives a blue color with iodine solution shortly after dilution with water, but not after standing. Corn and potato starches are precipitated when the syrup is diluted with water, but inulin remains in solution.

Formic Acid in Relation to Photosynthesis

Erlenmeyer[1] in 1877 suggested that formic acid is the most probable intermediate compound in the production of carbohydrates by photosynthesis. He believed that the synthesis took place by a reduction of carbonic acid producing formic acid and hydrogen peroxide. Wislicenus[2] in 1918 concluded that the hydrogen peroxide produced as a by-product to formic acid probably brings about a further reduction in the plant, resulting in the production of formaldehyde in the presence of light and leaf pigments.

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[1] Erlenmeyer, *Ber. Deut. Chem. Ges.*, 10: 634–637. 1877.

[2] Wislicenus, *Ber. Deut. Chem. Ges.*, 51: 942–965. 1918.

It was shown by Spoehr[3] in 1923 that when formaldehyde vapor is mixed with air it is oxidized to formic acid; also that formic acid may be produced by the action of ultra-violet light upon carbon dioxide and water, and that further exposure of the acid to this light produced a non-volatile syrup which resembled the simple sugars in some of their properties. It is known, too, that when dextrose is heated with some mineral acids formic acid is one of the acids produced, as shown by the following equation:

$$C_6H_{12}O_6 \longrightarrow C_5H_8O_3 + H\ COOH + H_2O.$$

Thus dextrose not only yields formic acid as one of its decomposition products, but is probably a constituent in the chain of its construction. Since it is possible to produce formic acid by the action of light on carbon dioxide and water, and since some of the carbohydrates found in plants yield this acid on decomposition and are of such a structure as to be soluble in this acid, and possibly *only* in this acid, the formic acid theory of photosynthesis receives added support.

Peculiarities of Formic Acid

This acid is unique among the organic acids not only because it is the strongest, being about twelve times more highly ionized than acetic or others in the series, but also because it has properties of an aldehyde as well. When this acid comes in contact with a solution of silver, or mercury salt, a deposit of metal is produced similar to that formed when other aldehydes are added. Hence the solvent action of this acid on carbohydrates may be linked with the presence of aldehyde grouping in the carbohydrate.

Formic Acid and Insect Life

This acid may be produced also by insect life as well as by plants. It is said to be the cause of the irritation of the skin noticed when one is stung by a bee, ant or nettle plant; also it is often found to be a constituent of honey.

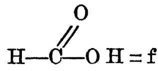
Structure of Carbohydrates as Related to Solubility in Formic Acid

It will be noted from a consideration of the different carbohydrates which are soluble in formic acid that this acid is quite selective in its solubilities. Thus sugars, dextrins, starches and glucosides, which are easily hydrolized, yielding aldehyde and ketone groups, are readily soluble in formic acid, whereas fats, proteins, gums, lignin and cellulose do not readily dissolve. This indicates that the starch structure is essentially different from the cellulose molecule even though they both produce *only* glucose residues on hydrolysis. It is known that while dextrose has five hydroxyl groups to six carbons in the molecule, starch, according to Irvine,[4] has but three; and cellulose, according to Malm and Clark,[5] has but one hydroxyl in twelve, which is chemically different from the rest and is capable of esterfication. They conclude that the cellulose molecule may therefore be expressed as a multiple of the unit $C_{24}H_{40}O_{20}$. Hence the solubility of carbohydrates seems to lessen about as the active hydroxyl groups decrease and the carbons increase.

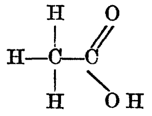
Polar and Non-polar Plant Structures

It is well known that plant compounds which contain the hydroxyl or carboxyl groups as sugars and organic acids are quite reactive and are often spoken of as polar compounds, whereas fats and cellulose would be representative of the inactive or non-polar compounds. This may partly account for the lack of solubility in formic acid of the germs and bran, etc., of the cereal grains; for the solubility of chlorophyll containing carboxyl groups; and for the insolubility of caratin from a carrot which is a hydrocarbon and is a non-polar compound.

A further reason for the great solubility of formic acid among the carbohydrates resides in its polarity. This acid with its single carbon atom would have two unsaturated linkages not present in those having two or more carbon atoms in the molecule. These relations may be represented as follows:



= formic acid;



= acetic acid.

Thus it is evident that this acid is a very polar compound capable of great activity on many semi-polar compounds and able to put them in solution.

It is hoped that this discussion will serve to make the properties of this unusual acid better known in order that it may be of service in several fields of science in making separations or identifications of various plant tissues, and thus through its selective solubility further our knowledge of the constituents of plants.

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[3] Spoehr, *Jour. Amer. Chem. Soc.*, 45: 1184–1187. 1923.

[4] Irvine, *Chem. Rev. 1*, 1: 41–71. 1924.

[5] Malm and Clark, *Jour. Amer. Chem. Soc.*, 51: 274–279. 1929.