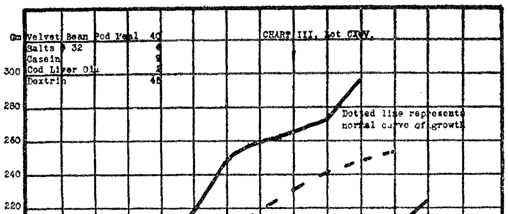
CONCERNING THE VITAMIN B CONTENT OF THE VELVET BEAN

THE question as to whether or not the seed of the velvet bean contains vitamin B in any appreciable quantity has recently been raised by Dr. E. R. Miller,[1] of the Alabama Station, and still more recently by Professor W. D. Salmon, of the South Carolina Experiment Station. In SCIENCE for September 29, 1922, Professor Salmon reports the results of certain experiments in which three groups of mature pigeons suffered ill consequences in a strikingly short period of time when they were fed ground raw velvet bean seed. The statement is also made that the results of certain experiments indicate at least a small quantity of the B vitamin in the velvet bean.

Sure and Read, in their paper reporting the "Biological analysis of the seed of the Georgia velvet bean" which appeared in the *Journal of Agricultural Research* for October 1, 1921, Vol. XXII, No. 1, called attention to the high degree of toxicity of the raw ground velvet beans when fed to rats. Young rats weighing from 40 to 90 grams existed only from 7 to 12 days on a diet composed solely of ground raw velvet bean seed and a liberal supply of distilled water. Miller[2] had previously pointed out that the toxicity of the velvet bean may be due to the presence of dihydroxyphenylalanine. In our paper we reported that the concentration of vitamin B in the seed, exclusive of the tough seed coats and also the seed pods, was low. In a recently completed study of the biological value of velvet bean meal (*i. e.*, the beans and pods ground together) the writer has found that the velvet bean meal carries a good concentration of the B vitamin, even after autoclaving for one hour at 15 pounds pressure. This is shown in the growth curves given in the figure.



This chart shows the growth of young rats on a ration carrying 40 per cent. autoclaved velvet bean meal as the only source of vitamin B. This ration contained all the other dietary essentials in satisfactory amounts.

These experiments show that vitamin B is relatively abundant and stable towards heat in the thick seed pods of the velvet bean, but is of rather low concentration in the seed.

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THE AMERICAN CHEMICAL SOCIETY

(Continued)

DIVISION OF ORGANIC CHEMISTRY. III.

New methods of splitting pyrimidines. The action of hydrogen peroxide and of sodium pentacyano-aquo-ferroate on thymine: OSKAR BAUDISCH and LAWRENCE W. BASS. Previous experiments have shown that the system $FeSO_4 + NaHCO_3 +$ air splits thymine with the formation of urea, acetol and pyruvic acid. The observation was made that the same products are obtained, but in different quantities, by using hydrogen peroxide, either alone or with traces of ferrous salts. The splitting of thymine by sodium pentacyano-aquo-ferroate yields pyruvic acid alone or pyruvic acid with traces of acetol. These facts are important for explaining the mechanism of the reaction.

New methods of splitting pyrimidines. The action of iodine solution and sodium bicarbonate on thymine: OSKAR BAUDISCH and LAWRENCE W. BASS. By the action of an aqueous solution of iodine and potassium iodide in the presence

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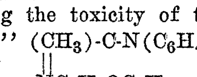
[1] Do velvet beans contain Vitamin B? Paper presented by Dr. Miller before the Division of Agricultural and Food Chemistry at the April (1922) meeting of the American Chemical Society, Birmingham.

[2] Miller, Emerson R., "Dihydroxyphenylalanine, a constituent of the velvet bean," *Jour. Biol. Chem.*, V. 44, No. 2, p. 481-486, 1920.

of sodium bi-carbonate, the pyrimidine ring can easily be split under mild conditions. In the case of thymine the products obtained are urea and acetol; no pyruvic acid is found. The fact that pyruvic acid is not formed is of special interest, since it was always present as a reaction product when the split was brought about by $FeSO_4 + NaHCO_3$ + air, by H_2O_2 alone or with ferrous salts, or by sodium pentacyano- aquoferroate.

The action of diazomethane on cyclic ureides: A. J. Hill and F. H. Case. With the object of throwing light on the linkage of the pyrimidine constituents in nucleic acids, both the former and the latter types of compounds are being investigated in regard to their behavior towards the methylating agent diazomethane. Uracil, thymine and 4-methyl uracil, suspended in ether solution and treated with diazomethane, dissolve completely and each yields the corresponding dimethyl derivative. On the other hand, cytosin dissolves but slightly and the insoluble residue appears to be a new crystalline modification of this compound. It has been necessary to synthesize the hitherto unprepared 2-oxy-6-methylamino pyrimidin in order to assist in the identification of the ether soluble product in the cytosine methylation.

Local anesthetics of the holocaine type: A. J. Hill and I. Rabinowitz. This investigation was undertaken for the purpose of increasing the efficiency and lessening the toxicity of the local anesthetic "holocaine,"



$$\underset{\underset{NC_6H_4OC_2H_5}{\|}}{(CH_3)\text{-}C\text{-}N(C_6H_4OC_2H_5)}$$

by systematic modifications of its molecular structure at the positions indicated by the bracketed portions of the above formula. In the types of compounds thus far prepared methyl has been replaced by aliphatic groups, such as ethyl and propyl, and by the aromatic benzyl. A new method has been developed for the synthesis of "holocaine," which depends upon the interaction of p-phenetidine and the hydrochloride of acetimino-ethyl ether.

The catalytic decomposition of glycerides: Francis L. Simons and Treat B. Johnson. Several simple triglycerides have been decomposed over ThO_2 at varying temperatures (350°-650°), and the composition of the products formed determined quantitatively. At the lower temperatures apparently a straight degradation of the glyceride into acrolein, fatty acid and small amounts of the di- and mono-glyceride takes place; higher temperatures favor the formation of more complex compounds. A new method of handling fatty acids (analytically) being developed in this laboratory by Dr. Donleavy has been given practical application in this work and found to work successfully. The investigation is still in progress and it is hoped that sufficient data will be uncovered to permit us to establish the general mechanism of these interesting decompositions.

The biochemical importance of the system: formaldehyde, ammonia and prussic acid: T. B. Johnson and H. W. Rinehart. A thorough investigation of the reactions occurring when formaldehyde, ammonia and prussic acid are allowed to interact is essential to an accurate understanding of the primary reactions taking place in plant growth. One substance formed by interaction of these three reagents is "methylene-aminoacetonitrile" $CH^2:NCH_2CN$. This is formed under conditions which are not well understood, and it has been reported in chemical literature that this substance can exist in isomeric modifications. Only one of them has received attention. Data has already been obtained which indicates that the isomerism is probably not physical isomerism. We find that the statements made regarding the molecular weight of these isomers is inaccurate. Furthermore, practically nothing has been published giving a true picture of constitution. We find that each compound is characterized by its crystalline habit. They are trimolecular compounds and are so constituted structurally as to reveal the presence of free cyanide groups. In many ways, they exhibit the properties of plant alkaloids. More work is in progress and an effort is being made to establish a constitutional formula.

The hydrogenation of several pyridine derivatives: T. B. Grave and E. Emmet Reid. Prolonged shaking with hydrogen under 3 atmospheres pressure in presence of platinum black hydrogenates 1-methyl-2-pyridone only to the tetra-hydro. The same has been found true of 2-amino-pyridine in a variety of solvents. When the hydrogenation is pushed further there is decomposition with elimination of ammonia. Tetrahydro-2-amino-pyridine is unstable and readily breaks up when set free from its salts by alkali. It gives tests for the primary amino group, but does not react with nitrous acid. 2-methyoxy-pyridine is hydrogenated directly to piperidine with loss of the methyoxy group.

The alkylation of benzene: T. M. Berry and E. Emmet Reid. Benzene has been alkylated by passing propylene in presence of aluminum chloride with high speed stirring. The isopropyl group is readily introduced in this way with the formation of mono and the poly-isopropyl-benzenes. The most of these up to the tetras have been isolated and identified. The isopropyl group can be introduced into toluene and napthalene by the same means.

Organic mercury compounds related to triphenylmethane dyes and azo dyes: E. R. Hanson, G. J. Leuck and F. C. Whitmore. Preliminary paper. Direct mercuration of triphenylmethane dyes has been found to be very difficult. The process takes place more readily in the aurin series than in the rosaniline series. A large number of soluble mercurated azo compounds have been obtained by coupling diazonium salts from aminobenzoic acids, sulfanilic acid, naphthionic acid and a number of amino dye intermediates with ortho mercurated phenol and with dimercurated para cresol. In the first case the coupling takes place in the para position, leaving the mercury group unchanged. In the second instance one of the mercury atoms is replaced during the coupling.

Reaction of organic mercury compounds with non-metal halides: Neal Thurman and Frank C. Whitmore. Preliminary paper. Of a very large number of halides studied the first to give clean-cut results was para toluene sulfone iodide which gives a good yield of para ditotlyl sulfone with para mercury ditotlyl. In most cases the organic mercury compound does not act with the halide except under conditions which lead to complete decomposition. Tertiary iodides yield organomercuric iodides and olefins.

The electrolytic reduction of maleic, fumaric and cinnamic acids, and the electrolytic production of amino salicylic acid: James F. Norris and E. O. Cummings. The fumaric and maleic acids furnish about 90 per cent. of the theoretical yield of succinic acid when reduced electrolytically. The yield of hydrocinnamic acid under the proper conditions is also about 90 per cent. of the theoretical. The product formed by condensing benzene diazonium chloride with salicylic acid was converted with a good yield into amino salicylic acid when titanium chloride was used as a catalyst. The production of this acid was accomplished more readily by reducing the diazonium compound with titanium chloride and regenerating the latter electrolytically.

The influence of environment on the reactivity of a chlorine atom: James F. Norris and Clifford Banta. The rates at which diphenyl chloromethane and several of its substitution products react with alcohol have been determined. The reaction was followed by the measurement of the conductivity of the hydrogen chloride formed as a result of the reaction. The compounds were selected because the reactions involved are reversible and proceed at such rates that the latter can be measured at 25 degrees. The velocity constants of the opposing reactions in the case of some of the compounds are as follows:

$(C_6H_5)_2CHCl + HOC_2H_5$ K_1 $(C_6H_5)_2CHOC_2H_5 + HCl$

	K_1 K_2	K_2
$(C_6H_5)CHCl$	$.0_31205$	$.001495$
p Chlor.	$.0_45176$	$.0_27240$
p Me	$.0_22491$	$.2657$
p Phenyl	$.0_41546$	$.0_21278$
o Chloro	$.0_51170$	$.05109$

Characteristics of two crystalline forms of glycine: C. A. Brautlecht and N. F. Eberman. Investigations of glycine have shown a number of physical and chemical differences. Emil Fischer, Ber. xxxviii, 1914 (1905) noticed that the plate and needle forms of glycine reacted differently to phosphorus pentachloride and acetyl chloride mixtures. He made no explanation of the difference. Ostromisslensky, in 1908, reported that one form of glycine precipitates one form of *1* asparagin from saturated solution, while the other does not. Some investigators consider glycine crystals as belonging to hemihedral division of the orthorhombic system, while others consider them as belonging to the monoclinic system. Various investigators then concluded that glycine might exist with the inner ammonium structure, especially when in solution. Further experimental evidence was therefore considered desirable to arrive at an understanding of the chemistry of glycine, a substance of basic importance both from the pure organic and biological chemical viewpoint. Following the suggestions offered by Falk and Seguira, *J. Biol. Chem.*, xxxiv, 29 (1918), who studied the action of bromine on the two crystalline forms of glycine, the authors of this paper report the results of melting temperature determinations of several samples of the two forms, alone and in mixtures, the action of heat, dry and moist hydrogen chloride, dry and moist sulfur dioxide, dry and moist bromine and acetyl and phosphorus chlorides on the two crystalline forms of glycine. The conclusions reached are that there is no chemical difference between the two crystalline forms of glycine in the dry state, and that in Fischer's experiments acetyl chloride, in presence of phosphorus pentachloride, reacted in a complicated manner.

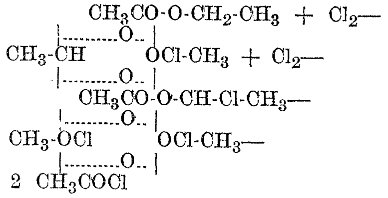
Some substituted aryldialkyl amine oxides: Lauder W. Jones and Elder B. Hartshorn. Meta and para nitro dimethyl aniline and para brom-dimethylaniline were oxidized by Caro's acid to the corresponding amine oxides, and isolated as sulfates. Other characteristic salts were prepared, the hydroiodides partially undergoing spontaneous intramolecular oxidation and reduction to the amine, iodine and water. Their stability seems to be a measure of the firmness with which the oxygen is bound to the nitrogen. The free bases prepared by the action of silver oxide on the hydrochloride do not react with methyl iodide to form stable addition products as do the trialkyl amine oxides.

Studies in cellulose chemistry (Part 8). Use of acetylene for the synthesis of cyclic acetals: HAROLD SANFORD HILL and HAROLD HIBBERT. By adding small amounts of conc. sulfuric acid and mercuric sulfate to a polyhydroxy derivative (glycols; glycerine) and passing acetylene into the mixture at temperatures ranging from 20° to 50°C. good yields of the corresponding cyclic acetals are obtained. The best results are found when very vigorous agitation is employed. This method is being applied to other poly-hydroxy derivatives.

Studies in cellulose chemistry (Part 9). Partition experiments in the formation of cyclic acetals: HAROLD SANFORD HILL and HAROLD HIBBERT. The method outlined in the previous abstract has been used to determine the nature of the partition in the formation of cyclic acetals comprising both five and six-membered rings. Using a mixture of one mole of a 1:2 and a 1:3 glycol and passing in only enough acetylene to combine with one of the glycols, it was found, in agreement with the previous work of Hibbert and Timm on this subject, that the tendency toward six-membered rings formation is much more pronounced than that of five.

Studies in cellulose chemistry (Part 10). The action of traces of iodine on organic esters: HAROLD HIBBERT. The study of polysaccharides is concerned with the properties of the hydroxyl and carbonyl groups, especially under the influence of catalysts. Unfortunately we are still quite in ignorance as to the mechanism of such fundamental reactions as the polymerization, condensation and halogenation of aldehydes, ketones and related compounds. Up to the present no explanation has been given to the mechanism involved in the ready transformation of aldehydes into esters under the influence of traces of aluminum alkylates (Tishchenke), a change evidently closely related to the Cannizzaro reaction. A consideration of the mechanism involved in such ester formation, as well as that relating to the halogenation of organic esters, leads to the conclusion that both are intimately related.

Studies on cellulose chemistry (Part 11). The action of chlorine on organic esters: RALPH S. MONTONNA and HAROLD HIBBERT. No satisfactory explanation has been given of the ready transformation of benzyl benzoate into benzoyl chloride under the influence of chlorine. Authors' experiments on the chlorination of ethyl acetate indicate the reaction takes place in the following stages:



Evidence is being accumulated with a view to showing that all alpha chlor-esters (III) exist as cyclic rather than as open chain compounds.

Tuberculinic acid—the nucleic acid of tubercle bacilli: ELMER B. BROWN and TREAT B. JOHNSON. Large amounts of tubercle bacilli, consisting of human and bovine types, have been subjected to analysis and hydrolysis and the nucleic acid purified and analyzed. An acid hydrolysis of this acid (tuberculinic acid) has revealed the presence of thymine and cytosine as normal pyrimidine constituents. Repeated examination has failed to reveal the presence of uracil. The usual purines, guanine and adenine are also present. An examination of the hydrolysis solution has produced evidence which proves that a hexane sugar functions in this nucleic acid molecule. Both formic and lævulinic acids have been identified, being produced in large amounts. Only very small amounts of furfuraldehyde are produced on hydrolysis.

Salts of pseudothioureas and their application in the identification of organic acids: J. J. DONLEAVY and T. B. JOHNSON. In the course of investigations dealing with the chemistry of fats, and the determination of structure of salts of pseudothioureas, it has been found that certain of these organic bases are characterized by their property of forming well-defined crystalline salts with the common organic acids. The salts so far examined are unique in that they are easily obtained in crystalline form, have definite melting points and serve admirably for purposes of identification. Thus far benzyl pseudothioureas has been the base which has received the most attention. It seems very probable that an analytical procedure may be developed through the use of these salts which will simplify our present methods of analyzing mixtures of organic salts.

The catalytic decomposition of formic acid: C. J. ENGELDER and B. B. WESTCOTT.

The electronic conception of valence and heats of combustion of organic compounds: M. S. KHARASCH and B. SHER.

CHARLES L. PARSONS,
Secretary