

# SCIENCE

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THE AMERICAN CHEMICAL SOCIETY AND  
SECTION C OF THE AMERICAN ASSO-  
CIATION FOR THE ADVANCEMENT  
OF SCIENCE

## II

### ORGANIC CHEMISTRY SECTION

*Julius Stieglitz, Chairman*

*Stereoisomeric Chlorimido Esters: W. S. HILPERT.*

The work is an elaboration and continuation of the work of Stieglitz and Earle, who in 1903 discovered the stereoisomeric chlorimido esters of meta-nitro-benzoic acid.

The new stereoisomers discovered are: methyl chlorimido p-nitrobenzoates, ethyl chlorimido p-nitrobenzoates, methyl chlorimido 4-methyl-3-nitrobenzoates, methyl chlorimido beta-naphtoates, ethyl chlorimido beta-naphtoates.

For each pair of isomers identity of structure was proven by chemical means; the impossibility of polymeric forms being present was substantiated by molecular weight determinations, and physical or crystal isomerism was shown to be absent by the fact that each of every pair of stereoisomers maintained its identity in all changes of physical conditions.

*The Applications of Physical Chemistry to Organic Chemistry: JULIUS STIEGLITZ.*

The author first called attention to the valuable aid given by physico-chemical methods in the study of isomerism, of stereoisomerism of the asymmetric type and of the "cis-trans" type, and of tauto-

merism, *i. e.*, in the study of organic compounds of the same composition but of different identity. Then it was shown how the mode of action of organic compounds may be analyzed by physico-chemical methods, the active component being found by properly planned determinations of velocities of action or of electromotive forces. Illustrations were drawn from the author's work, theoretical and experimental, on the theory of the catalytic action of acids, which showed that the accelerations produced by the catalyzing acid are simply due to the fact that the reacting component in such actions (esterification, saponification, inversion, amidine formation, etc.) is a positive ion whose *mass* (concentration) is *increased* by the addition of the acid. In the oxidation of aldehydes by silver nitrate in alkaline media (or of glucose by alkaline copper solutions), it was shown that the alkali is used to increase the concentration of the *reducing component of the aldehyde*, *e. g.*,  $(\text{NuO})\text{CH}$ , a methylene derivative with a bivalent carbon atom holding a free positive and a free negative charge. The alkali by suppressing the silver ion has a retarding effect on the oxidizing power of the silver nitrate. The demonstration was made with Ostwald's chemometric device.

*The Condensation of Nitromalonic Aldehyde with Acetonyl Acetone:* W. J. HALL.

From earlier work upon the condensation of nitromalonic aldehyde with acetone and its derivatives it may be inferred that two molecules of the aldehyde would condense with one molecule of acetonyl acetone and give a dinitro-dioxy-diphenyl. This result is accomplished only in the presence of a large amount of the condensing agent, otherwise but one molecule of the aldehyde enters into the condensation and there results a 2-acetonyl-4-nitro-

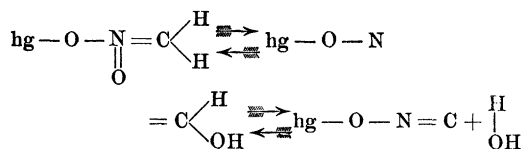
phenol. Both of these products, however, form but a small percentage of the total yield in condensation products. The third and largest portion arises from the condensation between one molecule of the aldehyde and one molecule of acetonyl acetone in which the two methylenic groups, between the two carbonyl groups, are found to react with the two aldehydic groups of the single molecule. In this way a fine carbon ring is formed which bears as substituents two acetyl groups and also a nitro group—a 1-nitro-3, 4-diacetylcyclopentadiene. This constitutes therefore a synthesis for derivatives of this class of homocyclic compounds. A number of similar condensations are already under investigation.

*The Conversion of Nitromethane into Fulminates:* LAUDER WILLIAM JONES.

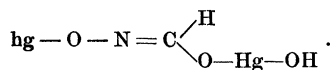
When a cold solution of mercuric chloride is poured into a cold solution of sodium isonitromethane, a white salt is precipitated, which Nef (*Ann.*, 280, 275) assumed to be mercuric isonitromethane. This salt has been isolated, and has been found to be nearly white and quite explosive. Its reactions show that it is undoubtedly mercuric isonitromethane. If this white salt is heated with water it passes very readily into mercuric fulminate, with the simultaneous formation of the explosive, yellow salt studied by V. Meyer and Rillet (*Ber.*, 5, 1030), Nef, and others.

The formation of formhydroxamic acid derivatives by the action of acyl chlorides upon sodium isonitromethane (*Am. Chem. J.*, 20, 25), and the successful transformation of formhydroxamic acid derivatives into fulminates by Biddle (*Ann.*, 310, 13), Nef (*Ann.*, 280, 317) and Wieland (*Ber.*, 40, 418) suggest an interpretation of the changes which mercuric isonitromethane undergoes in its conversion into fulminate.

( $\text{hg} = \frac{1}{2}$  an atomic weight of bivalent mercury.)

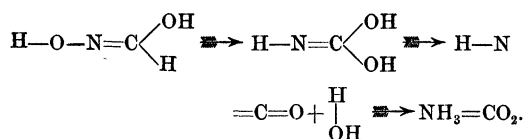


The yellow salt formed at the same time may be a basic mercury salt of formhydroximic acid,



This explanation was offered (*Ann.*, 20, 34) in view of the fact that the yellow salt, upon treatment with dilute hydrochloric acid, yielded some fulminate. Wohler (*Ber.*, 38, 1351) failed to obtain fulminate from this salt. Recently, a repetition of these experiments has yielded fulminate repeatedly.

If the reactions represented by the equations given above are assumed to be slightly reversible, it is possible to account for many of the singular changes of the fulminates. Thus, the change of fulminate into formhydroximic acid would account for the decomposition of fulminates into hydroxylamine and formic acid. By the Beckmann rearrangement, formhydroximic acid might be expected to pass into isocyanic acid, or into ammonia and carbon dioxide.



This would serve to clear up the behavior of fulminates towards acetyl chloride, ammonia, aniline, thiocyanic acid and certain other reagents.

In 1856 Kekulé represented fulminic acid as nitro acetonitrile,  $\text{CH}_2(\text{NO}_2)(\text{CN})$ . The chief experimental evidence for this formula lay in the fact that mercuric ful-

minate, under the influence of chlorine water, gave trichloronitromethane (chlorpikrine), and a small amount of chlorcyanogen. The formation of trichloronitromethane has never been explained; but its formation becomes self-evident in view of the above hypothesis, since mercuric isonitromethane in the presence of mercuric fulminate would be changed ultimately into trichloronitromethane, free fulminic acid, and mercuric chloride by the continued action of chlorine water. The presence of a small amount of chlorcyanogen may be accounted for by the presence of prussic acid, a substance very often formed by the breaking down of free fulminic acid.

#### *The Asymmetric Methyl Dialkylisoureas:*

RALPH H. MCKEE, Lake Forest University.

The isoureas of this series,  $\text{Alk}_2\text{N}-\text{COCH}_3=\text{NH}$ , were prepared by the action of methyl alcohol on the dialkylecyanamide in the presence of sodium methylate. They are strongly basic oils whose water solutions act similarly to ammonia on silver, mercuric and mercurous salts, but are unlike ammonia in that they do not affect copper or cobalt hydroxides. Decomposition of the dry hydrochlorides, or their solutions in water, gives methyl chloride and the urea ( $\text{Alk}_2\text{N}-\text{CO}-\text{NH}_2$ ) quantitatively. These isoureas readily condense with phenyl isocyanate, benzoyl chloride, etc., but are not affected by benzaldehyde, ethyl oxalate or ethyl malonate.

#### *Melting Points of Binary Mixtures of Ortho-Meta and Paranitraniline—A New Method for the Determination of these Compounds:* J. BISHOP TINGLE and H. F. ROLKER.

Binary mixtures of the three nitranilines have been made in steps of 2 per cent., and the melting points of these mixtures have been plotted against the composition. The curves given by the ortho-meta and meta-

para-mixtures are very smooth and of the same type; they rise regularly on each side of the entectic point to the melting point of the pure isomer. These curves are used for the determination of mixtures of unknown composition in the following manner: The substance under examination is divided into two portions, one of which is termed *A*; the other portion is mixed with a quantity of one of the pure isomers—say the meta compound, and is termed *A1*. The melting points of *A* and *A1* are determined simultaneously. That of *A* corresponds to a position on each of the two branches of the curve. If the m.p. of *A1* is lower than that of *A* the composition of the latter corresponds to the temperature marked on the ortho-branch of the curve, otherwise to that on the meta-branch. The curve given by mixtures of ortho- and paranitraniline is highly irregular and an attempt is being made to ascertain the reason for this.

*Intramolecular Condensation in the Phthalanilic Acid Series:* J. BISHOP TINGLE and H. F. ROLKER.

The work of Bishop Tingle and Cram<sup>4</sup> and Bishop Tingle and Lovelace<sup>5</sup> on this subject is being continued. Acids of the series RNH differ markedly in stability towards increase of temperature, and reactivity with amine as the group R varies. In some cases the action on an amine R, N.H<sub>2</sub> causes the formation of an amide; in others R is substituted by R, while with some acids substituted diamides are produced. Phthalanilic acid is stable in boiling aqueous solution, but in presence of a small quantity of aniline it is quickly converted into phthalanil. The action of alcohol on these acids has also been studied and a suggestion is made as to the cause of its "dehydrating" power in this case and in others.

<sup>4</sup> *Amer. Chem. Journal*, **37**, 598 (1907).

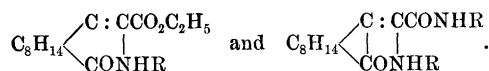
<sup>5</sup> *Ibid.*, **38**, 642 (1907).

*The Clarsen Reaction:* J. BISHOP TINGLE and ERNEST E. GORSLINE.

The authors' investigation of the mechanism of the Clarsen reaction and of the part played in it by ether and other catalytic agents such as quinoline and pyridine is being continued and extended so as to determine the influence on the condensation of ketones and esters of varying constitution. The results obtained so far are wholly incompatible with the Clarsen theory regarding the mechanism of the reaction, but are in excellent accord with that of Michael except in so far as it necessarily fails to take account of the influence of the ether, etc. An explanation is offered of the activity of the catalysis mentioned above. Evidence is being accumulated which tends to show that during the course of the Clarsen reaction at least two and possibly more different series of reactions take place side by side leading to quite dissimilar end-products.

*Action of Amines on Ethyl Camphoroxalate:* J. BISHOP TINGLE and L. F. WILLIAMS.

It has been shown by Bishop Tingle and Alfred Tingle<sup>6</sup> that ethyl camphoroxalate and amines yield compounds of the types



The ability to form one or other of these derivatives depends: (1) on the nature of the amine; (2) on the experimental conditions. A systematic investigation of the influence of these two factors is now in progress.

*Studies in Catalysis—The Formation of Guanidines:* JULIUS STIEGLITZ.

Ammonia acting on urea esters gives only very small yields of guanidines. The author's theory of the catalytic action of

<sup>6</sup> *Amer. Chem. Journal*, **21**, 256 (1899); **23**, 226 (1900).

acids (Congress of Arts and Science, St. Louis, IV., 278 (1904), *Am. Chem. Jour.*, January, 1907, etc.) suggested that probably the real reacting component is the positive urea ester ion and that the addition of an acid to the mixture would, by facilitating the ionization of the urea ester, lead to a perfect method of synthesis. Preparative as well as quantitative experiments carried out with Dr. R. H. Hall completely confirmed this view and brought, therefore, one more experimental confirmation of the theory of catalysis underlying the author's work.

*The Oxidation of M-Nitrobenzoylcarbinol:*

WM. L. EVANS and BENJ. T. BROOKS.

When benzoylcarbinol is acted upon by oxidizing agents it is found that there is obtained varying amounts of benzoylformaldehyde, mandelic, benzoylformic and benzoic acids, according to the agent used. Preliminary experiments, the results of which are herewith presented, are being conducted to determine the following points:

1. Are the same general reactions followed in the oxidation of these simple substituted sugars, like m-nitrobenzoylcarbinol, as were developed for benzoylcarbinol?

2. And also, what possible effect might introducing substituents into the ring have on the behavior of these substances towards oxidizing agents which were previously used with benzoylcarbinol?

The following results were obtained: (1) m-nitrobenzoylcarbinol gives with freshly precipitated mercuric oxide, freshly precipitated silver oxide and potassium permanganate alone or in the presence of alkalies, benzoic acid and carbonic acid exclusively; (2) m-nitrobenzoylcarbinol gives with cupric hydroxide and caustic alkalies only m-nitromandelic acid; (3) m-nitrobenzoylcarbinol gives with potas-

sium ferri-cyanide and alkalies both m-nitrobenzoic acid and m-nitromandelic acid.

Thus far, these preliminary experiments seem to follow the general interpretation previously given by one of us for the reactions of benzoylcarbinol.

*A Chemical Study of a Number of the Wild Fruits from Sylvan Beach, N. Y.:*

NICHOLAS KNIGHT.

The territory was formerly the lake bottom, and the soil is of so sandy a nature that it is unfit for purposes of agriculture. The fruit of the *Smilacina racemosa* and *Smilacina filifolia* were first investigated. It was necessary to pick the former while still green and to allow it to ripen slowly on the stems while under cover. Later on opportunity was presented for analyzing the fully ripened fruit that had matured normally. A glucoside in the fruit picked green changed to tannic acid in the ripe berries. In other respects the fruit of the earlier and later picking bore a striking resemblance, as likewise the fruits of the two species. The fruit of *Solanum dulcamara* from the same locality was also reported on.

*Bromination of Phenyl and Toly Ether:*

ALFRED N. COOK.

Phenyl ether yields a dibrom and tetrabrom derivative with iodine as a carrier. Ortho-, meta- and para tolyl ethers yield di- and tetrabrom derivative also with iodine as a carrier, as *per se*. The bromine evidently enters the nucleus even when heated to 150° C., and in direct sunlight, as indicated by the fact that the derivatives do not react with caustic potash, sodium carbonate or calcium carbonate and water even when heated under pressure. This is contrary to the well-known law. The halogen usually enters the side chain and not the nucleus in direct sunlight or at elevated temperatures.

*Mesoxalic Esters and their Reaction with Hydrazin:* RICHARD S. CURTISS and P. T. TARNOWSKI.

Methylmesoxalate may be obtained by saturating methylmalonate at 0° with N<sub>2</sub>O<sub>3</sub>. After forty-eight hours it is distilled in vacuo. A yield of 80–85 per cent. of (HO)<sub>2</sub>C=C(COOCH<sub>3</sub>)<sub>2</sub> can be crystallized from the oily distillate. Hydrazin hydrate and carbonate solutions react with OC=(COOH), forming gummy and resinous polymerization products. With carefully chosen conditions both the methyl and ethyl esters give white crystalline bodies.

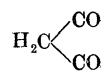
Owing to the ease of dissociation into hydrazin and mesoxalic esters, the question of an asymmetrical or a symmetrical hydrazin derivative was not settled. PCl<sub>5</sub> proves hydroxyl groups present. Benzaldehyde yields benzalazin and mesoxalic ester. Benzoyl chloride gives symmetrical dibenzoyl hydrazin. Acids and alcoholic solutions dissociate these derivatives into hydrazin and ester.

*Nitrosomalonic Esters:* RICHARD S. CURTISS.

The action of N<sub>2</sub>O<sub>3</sub> on malonic esters at low temperatures forms a number of unstable nitrogen derivatives. From the green oils thus obtained with ethyl malonate two potassium salts have been obtained: one (β) canary yellow, the other (α) nearly colorless. The molecular weight and potassium determinations show them to be salts of ethyl nitrosomalonate. The unstable nitroso ester formed by dilute acids on the salt is pale green; stains the cuticle like nitric acid; gives off nitrogen oxides in a desiccator, and is entirely different in its properties from the oxime of mesoxalic ester HON=C=(CO<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>. Saponification of the salt with alcoholic potash yields a chrome yellow potassium salt, which when treated

with dilute H<sub>2</sub>SO<sub>4</sub> and ether gives a yellow oil not at all like the stable crystalline oxime, HON=C=(CO<sub>2</sub>H)<sub>2</sub>. It is in fact extremely unstable. When air is allowed to enter the desiccator, after its ethereal solution has been freed of ethyl in vacuo, it heats up, liberates gases and puffs off white vapor, then flashes into flame, and leaves the desiccator filled with dense clouds of red oxides of nitrogen.

The study of these compounds as well as other nitroso and nitro derivatives of the group

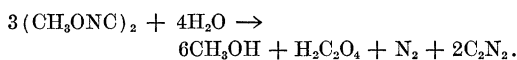


is in progress.

*A Peculiar Decomposition of the Esters of Formylchloridoxime:* H. C. BIDDLE.

In the action of caustic potash on methyl formylchloridoxime there are formed methyl cyaniminocarbonic and diiminooxalic esters, nitrogen, and the potassium salts of hydrocyanic, cyanic and oxalic acids.

The methyl fulminate naturally expected is not obtained. If formed at all, the fulminic ester probably condenses to the double molecule, which then dissociates in two directions, in one case giving rise to oxalic acid and methyl alcohol and in the other to cyanogen and alcohol, according to the equation:



The occurrence of cyaniminocarbonic and diiminooxalic esters is readily explained by the tendency of cyanogen to absorb alcohol in the presence of an alkali.

*The Constitution of Indigos and Related Compounds:* M. T. BOGERT, K. G. FOLK and J. M. NELSON.

Some recent work on indigos (chromophore CO·Ċ:Ċ·CO) is discussed on the hypothesis of the different colors being due

to differences in spatial configuration. The possibility of applying a similar explanation to compounds similarly constituted containing the grouping  $\cdot\text{CO}\cdot\text{C}:\text{C}$ , and also to some dibenzalacetone derivatives  $\cdot\dot{\text{C}}:\dot{\text{C}}\cdot\text{CO}\cdot\dot{\text{C}}:\dot{\text{C}}$ , is referred to.

*Phenylmalonic Nitrile*: JOHN C. HESSLER.

The silver salt of phenylmalonic nitrile is hydrolyzed almost immediately after its preparation, giving dimolecular and trimolecular phenylmalonic nitrile, as well as an oxidation product of unknown molecular weight. Phenylmalonic nitrile and the two polymers give this oxidation product when treated with chromic acid. The sodium salt of phenylmalonic nitrile gives the same substance when treated with bromine.

Dimolecular phenylmalonic nitrile gives a sodium salt and a silver salt. The silver salt reacts with alkyl iodides to give alkyl dimolecular phenylmalonic nitriles.

*The Catalysis of Imido Esters by Alkalies*:

HERMAN I. SCHLESINGER.

The parallel behavior of ordinary acid esters and acid imido esters when catalyzed by acids, as brought out by Hezty and his collaborators, is found also in their behavior towards alkalies. Imido esters were found to be catalyzed with a velocity proportional to the concentration of the hydroxyl ion.

*The Action of Alkalies on the Carbohydrates*: J. U. NEFF. Reported by title.

*Marrubiin*: H. M. GORDIN. Reported by title.

*Imido-hydantoïne*: JAMES B. GARNER. Reported by title.

*On the Salts of Tautomeric Compounds*: S. F. ACRER, R. F. BRUNEL, J. M. JOHNSON, G. H. SHADINGER and SIDNEY NIRDLINGER. Reported by title.

*The Hydrocarbons in the Lignites of the Northwest*: G. B. FRANKFORTER. Reported by title.

*Some Halides of Pinene*: G. B. FRANKFORTER and WALTER BADGER. Reported by title.

INDUSTRIAL CHEMISTRY SECTION

W. H. ELLIS, *Chairman*

*The Use of Carbon Tetrachloride as an Extractive in Commercial Analyses of Cotton-seed Meal*: CHAS. H. HERTY and F. B. STEM.

Carbon tetrachloride has been found to be an excellent extractive of cotton seed oil from the meal. As a substitute for the Soxhlet apparatus for extraction a simpler method is recommended. The meal is allowed to stand in contact with a definite volume of the extractive in an Erlenmeyer flask. One half of the extractive is then filtered off, the percentage of oil being determined in this filtrate from the weight of the residual oil after evaporation of the extractive. By extracting at 70° C. it is possible to get a complete extraction in 3¼ minutes.

*The Volatile Oils of Pinus Tæda and of Pinus echinata*: CHAS. H. HERTY and W. S. DICKSON.

The volatile oils distilled from specimens of the oleo-resins of *Pinus Tæda* (loblolly pine) and *Pinus echinata* (shortleaf pine) collected near Chapel Hill, N. C., have been studied. The results show these to be practically identical with the volatile oils of the more common long-leaf pine and Cuban pine. The chief constituent of each is pinene.

*A New Oxidizing Medium and its Function in the Blood and Muscle Elements*: J. E. SIEBEL.

\* This paper was placed in the industrial section under the title of "A New Oxidizing Agent." The

Experiments are quoted showing that alkaline bicarbonates may exchange carbonic acid for oxygen, which latter is thereby converted into an active modification, thereby enabling such bicarbonate solution to be used for oxidizing purposes, notably also as the negative element in electric batteries constructed by the author in which sugar, oleates, alcohol and other nutrient combustibles are oxidized, yielding a full equivalent of electricity without dissipation of energy. It also appears that alkaline carbonates present in the serous liquids of the human system act as a transmitter of oxygen from the oxyhemoglobin of the red corpuscles to the oxidable matter in the muscle elements, thereby activating or transferring the oxygen into the active modification.

As foreshadowed in a paper on electrodynamics of nutrition read at the former meeting, it is shown that the sarcois elements of the contractile disks of the voluntary muscle fiber represent the electrodes of batteries in which nutrients or their derivatives are oxidized by the active oxygen transferred to them by the bicarbonates, thereby causing contraction by the mutual attraction of the parallel electric currents regulated by simple contrivances fully explaining the interior mechanism of the concert action of voluntary muscles, nerves and nerve centers. Calculations are presented showing that currents of very low voltage and amperage suffice for these performances.

It is also found that the order in which, according to Atwater, different substances are preferred and replace each other in nutrition, viz., alcohol, sugar, fat, proteids, is the same as that in which they furnish the greatest amount of electromotive force in batteries constructed by the author in analogy to the supposed muscle batteries.

author subsequently added some biochemical data and presented it before the section.

*Wood Turpentine and their Relation to Gum Turpentine*: W. C. GEER. Reported by title.

*The Deposition of Arsenic upon the Vegetation of Smelter Regions*: W. D. HARKINS. Reported by title.

*Determination of Small Quantities of Monocarbonate in Bicarbonate of Soda*: J. D. PENNOCK and D. A. MORTON. Abstract misplaced.

*The Criteria of Deterioration in Flesh Foods*: W. D. RICHARDSON. Reported by title.

*Transparent Soot: a Supercooled Solution*: W. D. RICHARDSON. Reported by title.

*Examination of Crude Petroleum for Comparative Purposes*: DAVID T. DAY. Reported by title.

*Long-leaf Pine Oil*: J. E. TEEPLE. Reported by title.

*Microscopic Detection of Free Magnesia in Portland Cement*: ALFRED H. WHITE. Reported by title.

*Analysis of Turpentine by Fractional Distillation with Steam*: W. C. GEER. Reported by title.

BIOLOGICAL CHEMICAL SECTION IN JOINT  
SESSION WITH AMERICAN SOCIETY OF  
BIOLOGICAL CHEMISTS

*R. H. Chittenden, chairman and president Organic Soil Constituent*: OSWALD SCHREINER and EDMUND C. SHOREY.

The authors reported on a crystalline organic compound which had been isolated from several unproductive soils. The compound when tested by physiological methods is harmful to plants and appears to be the cause of the unproductivity in these soils. It can be obtained by extracting the soil with dilute soda solution, acidifying, filtering from the voluminous precipitate of humus bodies produced and

shaking the filtrate with ether. The ethereal solution contains the compound, and this is obtained in a crystalline form by evaporating the ether over water. When pure, the compound is white, melts at 98–99° and has the composition and other properties of dioxystearic acid prepared by oxidation of elaidic acid.

*Toxic Substances Arising During Plant Metabolism:* OSWALD SCHREINER and M. X. SULLIVAN.

For the purpose of studying the factors underlying the decrease in yield of plants grown successively on the same soil, wheat and cowpea were grown on different soils until the yield of the plants became poor. Water extracts of these soils proved to be poor media for the respective plants. On shaking the extract with carbon black and filtering, they became far better media for plant growth. It must be concluded then that the soil extracts contained something actually deleterious to the plant since the carbon black made from natural gas acts merely as an absorbing agent.

From wheat-sick soil there was obtained by steam distillation a crystalline body which is toxic to wheat. From cowpea-sick soil in the same manner a crystalline body was obtained which is toxic to cowpea but not to wheat.

*The Chemical and the Physiological Properties of a Solution of Hydrochloric Acid and Sodium Chloride:* AMOS W. PETERS.

The influence of neutral salts, *e. g.*, NaCl, extends to both chemical properties of solutions and to correlated physiological functions. The killing concentration of HCl for protozoa is lowered by the addition of a concentration of NaCl which is practically harmless when used alone. This effect can be explained by the increased acidity of the mixed solution, according to Arndt, Euler and others.

Colorimetric comparisons with methyl orange, and inversion tests by the polarimetric method, made with the dilute solutions of these experiments, favored this hypothesis, whether the solutions were made with redistilled water or with the original culture liquids. The increased velocity of inversion due to NaCl disappeared when the acid products of the reaction demonstrated by Kullgren increased.

*The Endo and Ekto-invertase of the Date:* A. E. VINSON.

The invertase of the date remains insoluble in all ordinary solvents throughout its green stages, but becomes readily soluble on ripening. The change in the behavior of the invertase toward solvents coincides very closely in point of time with the passage of the tannin into the insoluble form. Tannin in relatively large amounts does not retard the action of date invertase either in the extract or in the pulp. Soluble tannin, however, hinders the solution of date invertase in water, but the invertase can be extracted by glycerine, provided the glycerine is added at the same time the tannin is added. Green date invertase can not be extracted by crushing and macerating the green fruit with glycerine, therefore the invertase is not rendered insoluble, under the conditions of the experiment, by the escape of soluble tannin on crushing the tannin cells. This conclusion is confirmed by the behavior of the invertase in the tannin-free portion of the date after the tannin-bearing tissues have been completely removed. There is no direct connection between the change in the state of the tannin and that of the invertase.

The inversion of cane sugar by the green date pulp is not accomplished by the living protoplasm liberating a soluble ferment from a preexisting insoluble zymogen or

by rendering active a proferment. The rate of inversion by equivalent amounts of green and ripe pulp of the same variety are practically identical. Protoplasmic poisons—picric acid, chromic acid and formalin—retard the action of green and ripe pulp, but to approximately the same degree. If the living protoplasm were in any way connected with the inversion, the retardation would be greatly intensified in the presence of protoplasmic poisons. Green date tissue is not rendered inactive by soaking in ether, chloroform, acetone, etc.

The press juices of the green date contain most of the water in the fruit and large amounts of soluble substances which are usually retained by the healthy and unbroken semipermeable *hautschicht*. These juices and extracts are invariably free from invertase until the fruit ripens, although the press residues are always very active.

Treatment of the tannin-free green date tissue with chloroform, ether, toluol and acetone does not alter the behavior of the invertase towards solvents. Moreover the invertase is not liberated by heat. This treatment should destroy the semipermeable nature of the protoplasmic wall. From these observations the theory of the impermeability of the cell wall for the invertase of green date is untenable.

Enzymic action will take place whenever either enzyme or material to be acted upon is soluble; that is, molecular contact must be established. Tannin removes the invertase of ripe dates from solution, but inversion is not checked unless the precipitate is filtered off. Date extracts precipitated by lead subacetate still invert cane sugar, but on removing the precipitate inversion is stopped. It is thus possible to invert sugar by means of invertase artificially rendered insoluble.

In the place of impermeability of the

cell wall to the enzyme, the writer proposes the following theory. It is highly probable that green date invertase and possibly other endoenzymes are held in an insoluble combination by some constituent of the protoplasm. In some cases this combination may be broken down and the enzyme pass into solution while the protoplasm is living, but in others the combination may persist even after the death of the protoplasm. The enzyme may be rendered soluble also by external chemical or physical influence. On maturity of the tissues the enzyme is generally liberated, possibly by autodigestion or other profound change in the protoplasm.

In order to establish the impermeability of the cell wall to the enzyme in any given case it must be shown that the enzyme is in solution in the cell sap and not held in combination by the protoplasm.

*On the Occurrence of a Phytin-splitting Enzyme in Animal Tissues:* E. V. McCOLLUM and E. B. HART, Chemical Laboratory of the Wisconsin Experiment Station.

The authors have examined the influence of blood and of water and glycerine extracts of liver, kidney and muscle upon the sodium salt of anhydroxymethylenediphosphoric or phytic acid prepared from wheat bran. The sodium phytate was digested at 40° C. for one or two days with blood and with the tissue extracts, and the phosphoric acid in the mixture estimated by the method of Hart and Andrews<sup>\*</sup> for determining inorganic phosphoric acid in the presence of phytin. These values were compared with those obtained with blood and the extracts alone. The results indicate that blood and the liver of calves possess the power of cleaving sodium phytate with the formation of phosphoric acid. Muscle and kidney as well as the enzymes of the digestive tract do not alter phytin.

<sup>\*</sup> *Amer. Chem. Journal*, 30, 470 (1903).

*Bacterial Growth and Chemical Changes in Milk kept at Low Temperatures:* M.

E. PENNINGTON, United States Department of Agriculture, Bureau of Chemistry.

Bacteria in milk increased in numbers at a temperature of  $-0.55^{\circ}\text{C}$ . Bacterial growth at the end of a week was pronounced. There was a steady increase in the number of organisms for five or six weeks and at their maximum they numbered hundreds of millions. Occasionally they passed the billion mark per cubic centimeter. This occurred in spite of the fact that, though the milk was never solidly frozen, after ten days to two weeks it was a mass of small ice crystals. Neither odor nor taste indicated the high bacterial content and a curd was not produced even on heating, until the very end of the experiment.

There were present at all times during these experiments acid-forming, liquefying and neutral organisms. Acid formers were in lower and the liquefying organisms in higher proportion than is commonly found. Certain species, such as *B. formosus*, *B. solitarius* and *B. Ravenel*, were especially resistant to cold and frequently were the predominating species, or almost in pure culture at the end of the experiment.

Storage at this temperature ordinarily cuts down the number of organisms developing at  $37^{\circ}\text{C}$ ., the maximum number being found when the plates were kept at  $20^{\circ}$  or  $0^{\circ}\text{C}$ . The acidity increases to such an extent that sometimes 100 c.c. of N/10 sodium hydrate are required to neutralize 100 c.c. of milk, but this acidity has not caused a curd.

A chemical study of the proteid of milk in cold storage showed that the casein was rapidly digested, until finally more than 30 per cent. of it was changed to soluble compounds. Caseoses, amido acid and, probably, peptones increase, apparently at

the expense of the digested casein. The rapidity with which this digestion takes place varies in different samples, but at the expiration of two weeks it is pronounced.

*A Demonstration of a Method (with apparatus) of showing the Electric Charge of Colloids:* A. B. MACALLUM. Reported by title.

*On the Action of Nitric Acid on Nucleic Acids:* WALTER JONES. Reported by title.

*The Improbability of a Radiotropic Response:* C. STUART GAGER. Reported by title.

*Glycocoll as a Product of Uricolysis:* LYMAN B. STOOKEY. Reported by title.

*A Study of the Influence of Potassium Cyanide on the Excretion of Nitrogenous Substances in the Urine of Dogs:* WILLIAM H. WALKER. Reported by title.

Transmitted by Charles L. Parsons, secretary of Section C.

B. E. CURRY,  
Press Secretary

NEW HAMPSHIRE COLLEGE

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THE AMERICAN CHEMICAL SOCIETY  
CHICAGO MEETING

THE meeting of the American Chemical Society in Chicago was attended by some 350 chemists and was one of the most successful in its history. One hundred and thirty papers were presented at the meeting, including several important addresses of general interest, which required the society to meet in six subsections.

The reelection of Marston T. Bogert as president was announced and of H. P. Talbot, Louis Kahlenberg, A. E. Leach, Wm. D. Richardson and W. Lash Miller as councilors at large.

The meeting was marked by enthusiasm throughout and the announcement that the