compounds with acenaphthene, fluorene, allylamine, benzylamine, *p*-chloro-aniline and dimethyl-α-naphthylamine were obtained by mixing hot saturated solutions of the constituents and allowing the mixtures to cool slowly.

Camphylamine and α-naphthylamine were dissolved in dil. hydrochloric acid and mixed with hot saturated solutions of trinitro-*m*-cresolate in water. The menthylamine and piperazine derivatives were prepared from hot aqueous solutions. *p*-Bromo-aniline was dissolved in water and added hot to an alcoholic solution of the cresol, while alcohol was used for both solutions in the cases of *p*-iodo-aniline, *o*-anisidine, *o*-phenetidine, pseudocumidine, triphenyl-guanidine and α-naphthol. The hexamethylenetetramine and β-naphthol compounds were prepared by mixing hot aqueous solutions.

Our thanks are due to the Wolcott Gibbs and C. M. Warren Funds for grants which defrayed part of the expenses of the investigation.

Summary

The temperature of explosion of an endothermic organic explosive substance is a natural constant.

Addition compounds between 19 aromatic amines and phenols and trinitro-*m*-cresol have been prepared and their explosion temperatures determined.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON CELLULOSE CHEMISTRY

IV. PROPERTIES OF GAMMA-DELTA-DIHYDROXY-CARBONYL DERIVATIVES AND THEIR BEARING ON THE POLYMERIZATION OF POLYSACCHARIDES

BY HAROLD HIBBERT AND JOHN ARREND TIMM[1,2]

RECEIVED JULY 7, 1923

The suggestion was made by one of us some years ago[3] that cellulose was probably derived from an anhydro glucose of the type of Formula I and this was termed the cellulose nucleus.

In a later paper[4] a comprehensive review was made of the reactions to which any formula for cellulose must conform and opportunity was taken to emphasize the importance of the role played by the hydroxyl groups in the γ,δ positions to the —CHO radical.

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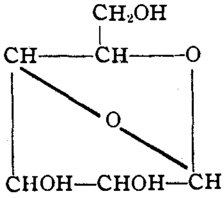
[1] This paper is constructed from Part II of a dissertation presented by John Arrend Timm in June, 1922, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

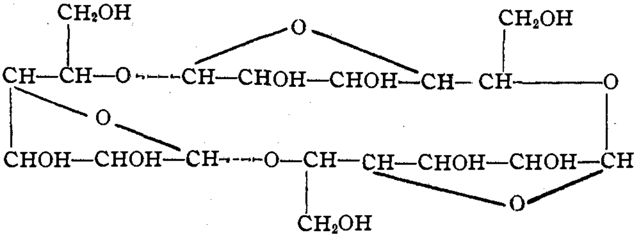
[2] Communicated to the Cellulose Section, American Chemical Society, Birmingham, Alabama, April, 1922.

[3] Hibbert, *Chem. Met. Eng.*, **22**, 838 (1920).

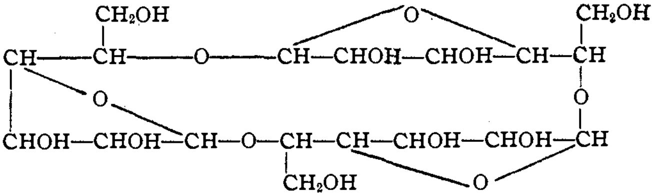
[4] Hibbert, *J. Ind. Eng. Chem.*, **13**, 256, 334 (1921).

The question as to whether cellulose is merely a polymerized form of the above nucleus or consists of a closed ring containing (x) anhydro glucose molecules, as shown in Formula II, was left open, no definite information being available at that time as to the magnitude of (x).


I


II

That this view was clearly expressed is evident in the current literature.[5] In view of Irvine's recent comments[6] it should be pointed out that no claim has ever been made other than that the cellulose molecule in all probability consists of a large ring of anhydro glucose molecules, each connected to the other through the aldehydic and δ-hydroxyl oxygen linkages, respectively. This view was put forward at a time when no experimental data were available to either confirm or disprove such a theory and it is only through the brilliant series of investigations carried out by Irvine and his collaborators and pupils that the matter is now approaching a settlement, the evidence submitted strongly favoring the constitution of cellulose as represented by Formula III.


III

It is of interest that their work should confirm the speculations first put forward by one of us[4] as to the mode of linking of the anhydro glucose units and of the fundamental importance of the γ,δ-hydroxyl groups in the glucose molecule.

If, as previously assumed, the polymerization of anhydro glucose to cellulose is fundamentally related to the behavior of, and dependent on, the loss of water from the δ- and aldehydic hydroxyls, then presumably other γ,δ-dihydroxy-carbonyl derivatives should exhibit the same behavior, and this is now found to be the case.

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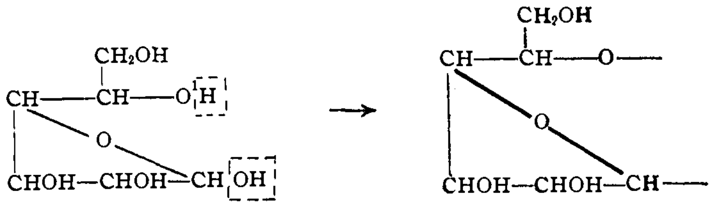
[5] Cross and Dorée, "Researches on Cellulose," Longmans, Green and Co., Part IV, **1922**.

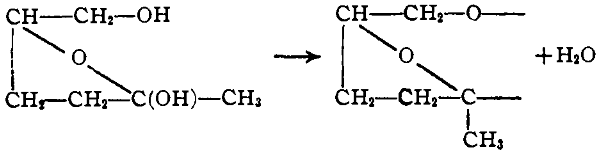
[6] Irvine and Hirst, *J. Chem. Soc.*, **123**, 527 (1923).



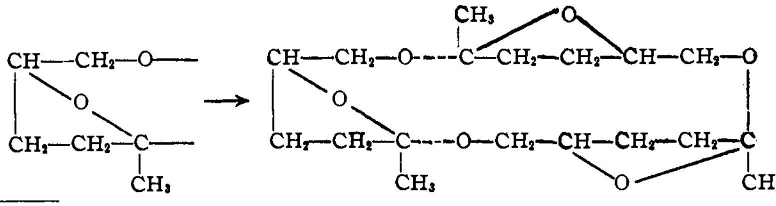
Polymerization of γ,δ-Dihydroxybutyl-methyl Ketone.—γ,δ-Dihydroxybutyl-methyl ketone ($CH_2OH—CHOH—CH_2—CH_2—CO—CH_3$) was first prepared by Traube and Lehmann[7] and is a pale yellow, viscous liquid which distils without decomposition at 190° under a pressure of 20 mm. Its mode of synthesis leaves no doubt as to the position of the hydroxyl groups relative to the carbonyl (CO) radical. When this ketone is heated at 120–130° in the presence of a trace of mineral acid (concd. sulfuric acid) for a few minutes, water is evolved and the liquid becomes more and more viscous, the dark-colored, very viscous product solidifying to a hard, compact resin at room temperature. This reaction also proceeds in the presence of this catalyst at room temperature, though much more slowly.

A determination of the amount of water evolved, and an analysis of the resin, show that the latter is derived from the dihydroxy ketone by the loss of one molecule of water from each molecule of the ketone. Assuming that the ketone possesses the butylene oxide structure[8] the changes taking place may presumably be represented as follows:

(a)



(b)



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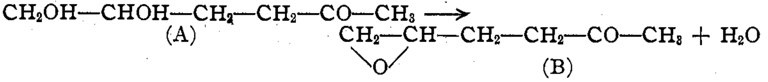
[7] Traube and Lehmann. *Ber.*, **34**, 1971 (1901).

[8] The constitution of dihydroxybutyl-methyl ketone has not yet been definitely established. A decision as to whether it contains (a) a butylene or (b) an amylene oxide ring can presumably be reached by employing the technic developed by Irvine. Thus by converting it into the methyl ketoside, followed by methylation, hydrolysis, and oxidation (a) should yield a 1:4 diketone, while (b) should give a ketonic acid. This work is in progress as well as the synthesis of the corresponding aldehyde ($CH_2OHCHOHCH_2CH_2CHO$), an examination of whose properties is expected to yield further valuable information. The senior author courteously requests that he may be left undisturbed in the prosecution of this work for a limited period.

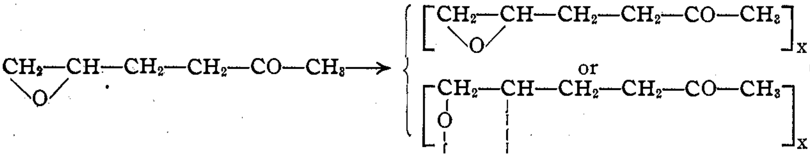
the reaction thus representing an *intramolecular cyclic acetal condensation.* Such a reaction would seem to be of considerable importance when considered in the light of its bearing on the formation of inulin from fructose, starch and cellulose from glucose, etc.

There is one other explanation as to the course of the above reaction, namely, the primary splitting off of water to give an ethylene oxide ring,



$$\underset{(A)}{CH_2OH{-}CHOH{-}CH_2{-}CH_2{-}CO{-}CH_3} \longrightarrow \underset{(B)}{\underset{\diagdown O \diagup}{CH_2{-}CH}{-}CH_2{-}CH_2{-}CO{-}CH_3} + H_2O \quad (1)$$

followed by polymerization to the resinous product,



$$\underset{\diagdown O \diagup}{CH_2{-}CH}{-}CH_2{-}CH_2{-}CO{-}CH_3 \longrightarrow \left\{ \begin{array}{c} \left[\underset{\diagdown O \diagup}{CH_2{-}CH}{-}CH_2{-}CH_2{-}CO{-}CH_3 \right]_x \\ \text{or} \\ \left[\underset{\overset{|}{\underset{|}{O}}}{CH_2}{-}\underset{|}{CH}{-}CH_2{-}CH_2{-}CO{-}CH_3 \right]_x \end{array} \right. \quad (2)$$

That this does not occur was proved by the direct synthesis of B from allyl acetone by treating the latter with hypochlorous acid to give the chlorohydrin and then removing hydrochloric acid with formation of the oxide, which was first prepared in this manner by Kablukow,[9] (B). On warming with a drop of concd. sulfuric acid, this oxide shows no tendency to polymerize, prolonged heating resulting only in charring.

The results thus obtained provide valuable experimental support for previous speculations relative to the role played by hydroxyl groups in the γ and δ positions to the carbonyl radical and of their function in the polymerization processes leading to the formation of polysaccharides. The importance of these groups is being further emphasized by Irvine and his school in connection with the properties of the γ sugars as related to vital problems such as the abnormal metabolic changes taking place in cases of diabetes.

Experimental Part

Preparation of γ,δ-Dihydroxybutyl-methyl Ketone.—The ketone was prepared by the method of Traube and Lehmann[7] by heating together epichlorohydrin and the sodium salt of ethyl aceto-acetate. The sodium salt of 1-chloro-2-hydroxypropyl-ethyl aceto-acetate, first formed, decomposes, yielding sodium ethylate and α-acetyl-δ-chloro-γ-valerolactone. The lactone, on boiling with a dilute solution of potassium carbonate, yields the γ,δ-dihydroxybutyl-methyl ketone.

Method.—Twelve g. of sodium was dissolved in absolute alcohol and 70 g. of aceto-acetic ester added. The mixture was cooled to 0° and 50 g. of epichlorohydrin, dissolved in 50 cc. of absolute alcohol, was added drop by drop in the course of about two hours. The alcohol was then evaporated under reduced pressure and the residue treated with 500 cc. of 5% sulfuric acid. The oily layer which separated was dried over sodium

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[9] Kablukow, *J. Russ. Phys.-chem. Soc.*, **1**, 502 (1887); *Ber. Ref.*, **21**, 55 (1888).

sulfate and, on fractionation under reduced pressure, yielded 40 g. of the lactone, b. p., 163° (12 mm.), which corresponds to that obtained by Traube and Lehmann.

Forty g. of α-acetyl-δ-chloro-γ-valerolactone was boiled with 0.5 mole of potassium carbonate in the form of a 5% aqueous solution for 5 hours. The oil gradually dissolved with evolution of carbon dioxide. After removal of the water under reduced pressure at about 25°, the remaining oil was dissolved in absolute alcohol, the solution filtered from the potassium chloride, dried over sodium sulfate, and the alcohol removed by distillation. The remaining oil, on fractionation, yielded 8 g. of γ,δ-dihydroxybutyl-methyl ketone, b. p., 158–160° (7–8 mm.) [b. p., 189–191° (20 mm.)], which is in agreement with that found by Traube and Lehmann).

Conversion of Dihydroxybutyl-methyl Ketone into its Anhydro Derivative.—Prepared as outlined above, the dihydroxy ketone is a pale yellow, viscous liquid which distils under diminished pressure without decomposition if all traces of acid are carefully removed. It also undergoes no apparent change after standing at room temperature for months. However, when it is heated under atmospheric pressure in the presence of traces of concd. sulfuric acid at about 125°, dehydration followed by resinification takes place.

Fifty g. of dihydroxybutyl-methyl ketone was mixed with 0.05 g. of concd. sulfuric acid and the mixture heated to 150°. The liquid rapidly became very viscous, water was evolved and after 2–3 minutes it solidified on cooling to a hard resin. This was pulverized, dried for two hours at 100°, and analyzed.

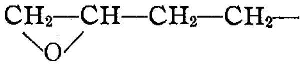
Analyses. Calc. for $C_6H_{10}O_2$: C, 63.11; H, 8.84. Found: C, 62.86, 62.91; H, 9.01, 9.11.

The analysis indicates that the product has been formed by the loss of one mol. of water from each molecule of the dihydroxybutyl-methyl ketone ($C_6H_{12}O_3 = C_6H_{10}O_2 + H_2O$), a conclusion confirmed by the direct weighing of the water evolved during the resinification process.

This was carried out by placing a known weight of the ketone in a small glass-stoppered tube (about 8 cc. in capacity, 10 cm. long and 1 cm. in diameter). This was fitted with a narrow inlet and outlet tube, the latter being connected to a weighed U-tube containing concd. sulfuric acid; 0.01 g. of concd. sulfuric acid was then introduced, the stopper inserted and the mixture heated to 120–130° in a current of dry air for about 6 hours to constant weight.

Analysis. Subs., 0.7956: H_2O obt. 0.1177; actual loss in weight of ketone product, 0.1337 g., or 16.8%. Calc. for 1 molecule loss of water: H_2O, 13.64%. Found: 14.79.

There is apparently some slight secondary decomposition brought about by the long continued heating under these conditions.



Preparation of γ-Ketobutyl-ethylene Oxide. $\underset{\diagdown O \diagup}{CH_2—CH}—CH_2—CH_2—CO—CH_3$.—This was made according to Kablukow's method[9] from allyl acetone.

Allyl Acetone.—Allyl acetone was obtained by condensing allyl bromide with the sodium salt of aceto-acetic ester[10] and saponifying the allyl-ethyl aceto-acetate, thus formed, with dil. potassium carbonate solution.

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[10] Wolff, *Ann.*, **201**, 46 (1880).

Mehrling's[11] method of hydrolysis with barium hydroxide was found unsatisfactory. The following modified procedure gave satisfactory results, but the yield was never high because of the formation of by-products.

One hundred g. of allyl-ethyl aceto-acetate was boiled for 20 hours with 300 cc. of a 5% potassium carbonate solution, the mixture being thoroughly agitated throughout. The product was then steam distilled, the upper allyl acetone layer in the distillate separated and the aqueous layer extracted with ether. The ether extract was dried over sodium sulfate and finally distilled. Yields of about 35% allyl acetone (b. p., 129–134°) were usually obtained.

Allyl Acetone Chlorohydrin.—The hypochlorous acid solution was prepared according to the method of Bamberger and Lodter.[12]

Two hundred g. of bleaching powder was suspended in water and allowed to stand for 24 hours in the dark at 40°, 115 g. of sodium carbonate was then introduced and the suspension thoroughly shaken. It was then filtered by suction and 160 g. of pulverized boric acid added to the filtrate.

To 100 cc. of this solution, 10 g. of allyl acetone was slowly added in the course of one hour, the mixture being agitated and the temperature kept below 0°. The solution was also protected from direct light. After standing for 12 hours another 200 cc. of the hypochlorous acid solution was added and the solution allowed to stand under the same conditions for an equal length of time. It was then extracted with ether, dried over sodium sulfate, the ether removed, and the remaining oil fractionated under reduced pressure; yield, 8 g.; b. p., 113° (20 mm.), which corresponds to that obtained by Kablukow.[9]

Conversion of the Chlorohydrin into the Oxide.—Eight g. of allyl acetone chlorohydrin was heated with 200 cc. of 5% potassium carbonate solution on a water-bath for 16 hours and then at the boiling point on a sand-bath for 10 hours. The solution was cooled, extracted with ether, dried, and the ether removed by distillation. No residue remained. The mother liquor was then carefully neutralized with hydrochloric acid and the water evaporated on a steam-bath. A viscous oil remained which was dissolved in alcohol, filtered, and dried over sodium sulfate; the alcohol was then removed, and the residue distilled under diminished pressure. The oxide was obtained as a colorless, mobile liquid; b. p., 169° (81 mm.); yield, about 2 g.; the boiling point recorded by Kablukow was 162–167° at 80 mm. When a portion of the oxide was heated with a drop of concd. sulfuric acid no indication of any polymerization could be observed, but prolonged heating resulted in some charring.

The authors desire to acknowledge gratefully the kind assistance rendered them for the purchase of supplies in the form of a grant from the Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Attention is drawn to the important role played by the γ- and δ-hydroxyl groups in the conversion of carbohydrates to polysaccharides.

2. It is found that the simplest γ,δ-dihydroxy-ketone, namely, γ,δ-dihydroxybutyl-methyl ketone, readily undergoes dehydration and polymerization in the presence of a trace of mineral acid. The change corre-

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[11] Mehrling, *Ann.*, **264**, 323 (1891).

[12] Bamberger and Lodter, *Ann.*, **288**, 81 (1895).

sponds to a loss of one molecule of water from each molecule of the dihydroxy ketone.

3. The polymerization taking place is probably closely related to that occurring in the formation of inulin from fructose.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TRIHYDROXY-METHYL-ANTHRAQUINONES. I

BY G. D. GRAVES[1] WITH ROGER ADAMS

RECEIVED JULY 23, 1923

Hydroxy-methyl-anthraquinones and their methyl ethers occur widely, either in the free state or as glucosides, in the leaves, bark and roots of various plants, forming natural drugs and coloring matters. Six natural trihydroxy-methyl-anthraquinones have been reported in the literature, the most important being emodin, found in *Cascara sagrada*, *Frangula*, rhubarb and other plants. The probable structures which have been suggested for a few of these anthraquinones contain two hydroxyl groups in one ring, with the methyl and remaining hydroxyl in the other. A study of a practical method of synthesis of this type of substituted anthraquinones has been undertaken with the ultimate object of synthesizing the natural products.

In general, the best method available for the preparation of substituted anthraquinones with definite structures is the condensation of phthalic anhydride or its derivatives with benzene derivatives to form substituted benzoyl-benzoic acids; these can then be dehydrated to give anthraquinones. To prepare the desired trihydroxy-methyl-anthraquinones it was proposed to condense dimethoxy-phthalic anhydrides with the cresols, to dehydrate the resulting benzoyl-benzoic acids, and to demethylate the anthraquinones.

But few condensations involving methoxy-phthalic anhydrides have been reported. Bistrazycki[2] condensed 3,4-dimethoxy-phthalic anhydride (hemipinic anhydride) with anisole by means of aluminum chloride, using benzene as a solvent. The same anhydride was condensed by Weizmann[3] with veratrol, pyrogallol-trimethyl ether and *o*-xylene, using aluminum chloride with carbon disulfide as a solvent. Simonsen condensed this anhydride with *o*-cresol by means of aluminum chloride in acetylene tetrachloride.[4] With the exception of the condensation product of hemipinic anhydride with anisole, the exact structure of the resulting products

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[1] This communication is an abstract of a thesis submitted by G. D. Graves, DuPont Fellow for 1922–1923, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Bistrazycki, *Ber.*, **31**, 2796 (1898).

[3] Weizmann, *J. Chem. Soc.*, (a) **91**, 1626 (1907); (b) **93**, 435 (1908); (c) **105**, 2748 (1914).

[4] Simonsen, *ibid.*, **119**, 1339 (1921).