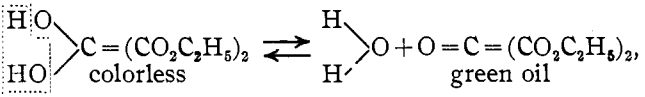
tion into water and the green keto ester takes place around 60°–70°



and reassociation with loss of color occurs a few degrees lower.

Methyl alcohol was mixed in molecular proportions with the ethyl keto ester at —15° and behaved in every way like ethyl alcohol under these conditions. Attempts to purify the thick, colorless syrup by crystallization and distillation failed for the same reasons as mentioned above.

Molecular quantities of benzyl alcohol were likewise mixed at —13° with ethyl oxomalonate. Here also, there was an intense reaction indicated by the evolution of considerable heat and the gradual loss of color of the mixture. The thick oil likewise dissociated when heated into its constituent parts, nor could it be crystallized.

The very characteristic appearance of the reactions, as well as the products, in these keto ester condensations with alcohols leaves no doubt in our minds that these unstable compounds are the primary addition products of the alcohol upon the keto group. $ROH + O=C=(CO_2R)_2 \longrightarrow$  They are perfectly analogous to the product formed by ethyl alcohol on methyl oxomalonate. This was obtained first as a colorless glycerol-like syrup, then in the crystallin state, and was readily dissociated, with reappearance of color, into alcohol and methyl oxomalonate when gently heated.[1]

URBANA, ILL.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE STEREOCHEMICAL CONFIGURATIONS OF THE SUGARS FUCOSE AND RHODEOSE.[2]

BY C. S. HUDSON.

Received January 18, 1911.

From the fact that certain varieties of kelp (*Fucus*) yield methylfurfural when distilled with acid, Bieler and Tollens[3] concluded that a methylpentosan is present in these plants. Günther and Tollens[4] hydrolyzed kelp with dilute acid and obtained from it by way of the hydrazone a crystallin sugar which they named *fucose*. Analysis proved it to be a methyl pentose, $CH_3.C_5H_9O_5$, and Laniewsky and Tollens[5] found its

[1] Curtiss and Spencer, THIS JOURNAL, 31, 1055.

[2] Read at the Minneapolis meeting of the American Chemical Society.

[3] *Ber.*, 22, 3062; *Ann.*, 258, 110 (1889); cf. Maquenne, *Compt. rend.*, 109, 603–6 (1889).

[4] *Ber.*, 23, 2585–6 (1890).

[5] *Ber.*, 33, 141 (1900).

molecular weight by the cryoscopic method to agree with this formula. Müther and Tollens[1] oxidized fucose to the monobasic fuconic acid and lactone and Tollens and Rorive[2] by stronger oxidation produced dibasic *d*-trihydroxyglutaric acid. These facts show that fucose has the constitution $CH_3.CHOH.CHOH.CHOH.CHOH.COH$.

Votocek[3] isolated from the glucoside convolvulin by acid hydrolysis a crystallin methyl pentose and named it *rhodeose* from an older name for convolvulin, *rhodeoretin*. On further study of this sugar Votocek[4] noticed that the melting points of its phenylhydrazone, osazone and other derivatives were practically identical with those of the similar derivatives of Tollens' fucose; and as the sugars themselves have equal and opposit specific rotations (fucose $+75.5°$; rhodeose $-75.5°$), he concluded that they are optical antipodes, similar to *d*-glucose and *l*-glucose. The proof of this interesting and unusual occurrence of antipodal sugars in nature was shadowed by one disagreement, however, for Votocek's rhodeose phenylosazone melted about 20° higher than did the substance which Tollens had described as being fucose phenylosazone. This disagreement was later removed by Votocek[5] who prepared some fucose phenylosazone and found it to melt at the same temperature as did his derivative of rhodeose; about the same time Tollens[6] repeated his work and found that his earlier preparation of fucose phenylosazone contained much hydrazone, and that a new preparation of pure fucose phenylosazone melted at the temperature of Votocek's derivative of rhodeose.

Both Votocek and Tollens have studied the constitution and configuration of these methylpentoses. The former[7] obtained the alcohol, rhodeitol, by reduction of rhodeose with sodium amalgam and found that it is not oxidized by Bertrand's[8] sorbose bacillus. By oxidation of rhodeose with nitric acid he prepared *l*-trihydroxyglutaric acid. From these facts he obtained the configuration of rhodeose by the following reasoning. As *l*-trihydroxyglutaric acid is known to have the configuration

$$\begin{matrix} & OH & OH & H & \\ COOH & . & C & . & C & . & COOH \\ & H & H & OH & \end{matrix}$$

, the structure of rhodeitol must be either (*a*)

$$\begin{matrix} & OH & OH & H & \\ CH_3CHOH & . & C & . & C & . & CH_2OH \\ & H & H & OH & \end{matrix}$$

or (*b*)

$$\begin{matrix} & OH & H & H & \\ CH_3CHOH & C & . & C & . & CH_2OH \\ & H & OH & OH & \end{matrix}$$

; and

[1] *Ber.*, **37**, 298–308 (1904).
[2] *Ibid.*, **42**, 2009–12 (1909); cf. Mayer and Tollens, *Ibid.*, **40**, 2434–40 (1907).
[3] *Z. Zuckerind. Böh.*, **24**, 248–57.
[4] *Ibid.*, **25**, 297–305; **27**, 15–27.
[5] *Ber.*, **37**, 3859–62 (1904).
[6] Mayer and Tollens, *Ibid.*, **38**, 3021–2 (1905)
[7] *Ibid.*, **43**, 469–75 (1910).
[8] *Ann. chim. phys.*, [8] **3**, 181.

that of rhodeose must be either (I) $CH_3.CHOHC \begin{matrix} OH\ OH\ H \\ .\ C\ .\ C.COH \\ H\ \ H\ \ OH \end{matrix}$ or (II)
$CH_3.CHOH.C \begin{matrix} OH\ H\ \ H \\ .\ C\ .\ C.COH. \\ H\ \ OH\ OH \end{matrix}$ Bertrand's sorbose bacillus has been found to oxidize only those alcohols in the structure of which the two carbon atoms nearest the CH_2OH group have similarly placed hydrogen atoms. As Votocek could detect no action of the bacillus on rhodeitol, he concluded that the latter cannot have the structure (*b*) and must therefore have (*a*). From this structure of rhodeitol (*a*) that of rhodeose (I) follows directly. The proof is interesting and suggestive, but most chemists will doubtless agree that in so far as it depends upon the non-action of the bacillus it is not as convincing as could be wished.

Tollens and his students, Mayer and Rorive,[1] have presented independent evidence on the constitution of fucose. Starting from the fact that the sugar yields *d*-trihydroxyglutaric acid by oxidation with nitric acid, it must be concluded that its constitution is limited to the antipodes of (I) and (II). A choice between these configurations was made by Tollens from the results of a study of the fucohexonic acids which result from fucose by the cyanide synthesis. If the antipode of (I) applies to fucose the two possible fucohexonic acids have the respective constitutions
$CH_3.CHOHC \begin{matrix} H\ \ H\ \ OH\ OH \\ .\ C\ .\ C\ .\ C.COOH \\ OH\ OH\ H\ \ H \end{matrix}$ and $CH_3.CHOH.C \begin{matrix} H\ \ H\ \ OH\ H \\ .\ C\ .\ C\ .\ C.COOH, \\ OH\ OH\ H\ \ OH \end{matrix}$
and should yield on oxidation *d*-mannosaccharic and *d*-saccharic acids having the constitutions $COOH.C \begin{matrix} H\ \ H\ \ OH\ OH \\ .\ C\ .\ C\ .\ C.COOH \\ OH\ OH\ H\ \ H \end{matrix}$ and
$COOH.C \begin{matrix} H\ \ H\ \ OH\ H \\ .\ C\ .\ C\ .\ C.COOH. \\ OH\ OH\ H\ \ OH \end{matrix}$ On the other hand, if the antipode of structure (II) applies to fucose the two fucohexonic acids from fucose should yield on oxidation $COOH.C \begin{matrix} H\ \ OH\ OH\ OH \\ .\ C\ .\ C\ .\ C.COOH \\ OH\ H\ \ H\ \ H \end{matrix}$ and
$COOH.C \begin{matrix} H\ \ OH\ OH\ H \\ .\ C\ .\ C\ .\ C.COOH, \\ OH\ H\ \ H\ \ OH \end{matrix}$ which are respectively *d*-talomucic and mucic acids. As Mayer and Tollens were unable to detect any mucic acid in the oxidation products, though mucic acid crystallizes very readily, they concluded that the antipode of configura-

[1] *Loc. cit.*

tion (I) applies to fucose. Votocek[1] has supplied the other side of the evidence by isolating, though in an impure condition, the acid potassium salt of saccharic acid from the oxidation products of the rhodeohexonic acids which result from rhodeose by the cyanide synthesis. He was unable to detect any mucic acid in these products and therefore concluded from a course of reasoning similar to that of Mayer and Tollens that rhodeose has configuration (I) and fucose the antipodal structure.

The purpose of this article is to show that the configuration of rhodeose and fucose can be obtained by a third, independent method which is based upon a recently found relation between the constitution and the optical rotatory power of the sugar lactones.[2] The description of the extensive evidence upon which this method is based will be found in detail in the former article. It may suffice to recall the principle upon which the method depends, namely, that the "lactones of dextrorotation have the lactonic ring on one side of the structure (in the customary symbols, the lower side), lactones of levorotation have it on the other, and the position of the ring shows the former position of the OH group on the γ-carbon atom." Writing the carbon chain of rhodeose $CH_3.CHOH.C\ .\ C\ .\ C.COH$

(1) (2) (3)

and referring to the fact that the rotation of rhodeonic lactone is $-76°$[3] it will be seen that the lactonic ring from the end carbon to its γ-carbon is above the carbon chain and consequently the hydrogen atom in the sugar is below atom (1). The rotations of the rhodeohexonic lactones were found by Krauz[4] to be $-35°$ and $-41°$, or in other words decidedly negative for both substances; consequently by similar reasoning the hydrogen atom in the sugar is to be chosen below carbon (2). The structure of rhodeose

OH OH |

is thus determined partially to be (III) $CH_3.CHOH.C\ .\ C\ .\ C.COH$.

H H |

If the specific rotation of the heptonic lactones from fucose or rhodeose were known, the configuration of the groups attached to carbon (3) could be decided. In the absence of these values another way must be followed. From the fact that rhodeose yields *l*-trihydroxyglutaric acid on oxidation its structure must be either I or II (see preceding), and as only structure I has the hydrogen atoms below carbons (2) and (3), as required by III, it must be selected for rhodeose. The structure of fucose is then the mirror image of I.

It will be noticed that a configuration of the group $CH_3.CHOH$, which

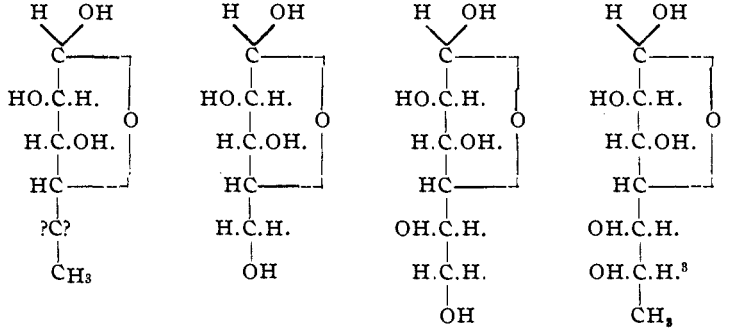
[1] *Ber.*, 43, 474 (1910).

[2] THIS JOURNAL, 31, 338–46 (1910).

[3] Votocek, *Z. Zuckerind. Böh.*, 25, 297 (1902). Müther and Tollens (*loc. cit.*) found the specific rotation of fuconic lactone to be $+71°$ to $+78°$, which agrees with the accepted antipodal relation between fucose and rhodeose.

[4] *Ber.*, 43, 486 (1910).

is an asymmetric one, is not indicated in I. The reason for this omission is that none of the facts which have been adduced to prove the structure of the other asymmetric groups has any bearing on the configuration of this one. Lately Tollens[1] has expressed the view that this group has the same structure in fucose that it has in *l*-galactose for the reason that the two sugars have nearly the same rotations, —75.5° and —81°. Votocek[2] does not consider this evidence of any weight. Regarding this question the following may be presented. The four sugars, fucose, *d*-arabinose, *l*-galactose and *l*-α-rhamnohexose have a large portion of their structure in common, as will be seen from the formulas, which are here printed in the γ-lactonic ring form.



Fucose. *d*-Arabinose. *l*-Galactose. *l*-α-Rhamnohexose.

The portions of the structures included by the lactonic rings are identical, but the portions below vary greatly, being in one case (*d*-arabinose) not even asymmetric. The specific rotations[4] of these sugars, or more correctly of the stable solutions which contain their α and β-forms in equilibrium, are, fucose —75.5°, *d*-arabinose —105°, *l*-galactose —81° and *l*-α-rhamnohexose —61°. These values are sufficiently alike, especially when they are reduced to the molecular rotations, to show that the common structure included within the lactonic rings is the principal factor in fixing the rotation, and that the latter depends only in a minor degree upon the groups below the rings. This conclusion is emphasized by a peculiar relation between the rotations of these sugars and those of their lactones. Fuconic lactone rotates +75°, *d*-arabonic +74°, *l*-galactonic +78°, *l*-α-rhamnohexonic +84°,[5] or in other words the lactones have almost identical rotations, which are of opposit sign from those of the sugars. This evidence shows again that the rotations

[1] *Ber.*, 40, 2438 (1907); 42, 2012 (1909).

[2] *Ibid.*, 43, 469–75 (1910).

[3] The configuration of this group follows from the structure of rhamnose. See THIS JOURNAL, 31, 345 (1910).

[4] Quoted from Lippmann's "*Chemie der Zuckerarten.*"

[5] For references see THIS JOURNAL, 31, 338–46 (1910).

of these sugars and their lactones are principally due to their common element of structure which is within the lactonic ring, and that the configuration, weight, etc., of the groups which they do not possess in common have only a minor influence on the rotatory powers. Since such is the case it is hardly possible to agree with Tollens that the configuration of any of the groups below the ring can be decided from the rotations of the sugars. The only way at present known by which the configuration of the doubtful $CH_3.CHOH$ group of fucose and rhodeose can be determined is from a knowledge of the sign of the rotation of the methyl tetronic lactones which should be yielded by these sugars. This method has been used in determining the configuration of the similar group in the related methyl pentose, rhamnose,[1] but the methyl tetronic lactones from fucose and rhodeose have not yet been prepared, and the difficulty of obtaining these rare sugars in quantity prevents me from attempting the preparation of these substances.

To summarize, the structure of the antipodal sugars fucose and rhodeose has been determined by three independent methods. In each of these the fact that fucose yields *d*-trihydroxyglutaric acid on oxidation, and rhodeose, *l*-trihydroxyglutaric, is used to limit the possible structures to forms I and II. A choice between these forms is then made, according to the first method (Votocek's) from the fact that Bertrand's sorbose bacillus does not attack rhodeitol, according to the second (Tollens' and Votocek's) from the fact that the oxidation of fucohexonic and rhodeohexonic acids does not yield crystallin mucic acid, and according to the third method, from the fact that rhodeonic and rhodeohexonic lactones are of strong negative rotations. The three methods give the same conclusion, namely, that rhodeose has the structure I and fucose the antipodal configuration. The configuration of the first asymmetric group of these sugars $CH_3.CHOH$ remains entirely undetermined, but could doubtless be decided from a knowledge of the rotatory powers of the methyl tetronic lactones from fucose and rhodeose, which however have not yet been prepared on account of the difficulty of obtaining the sugars.

WASHINGTON, D. C.

[CONTRIBUTIONS FROM THE DIVISION OF CHEMISTRY, HYGIENIC LABORATORY, U. S. PUBLIC HEALTH AND MARINE HOSPITAL SERVICE.]

LUCIFERESCEINE,[2] THE FLUORESCENT MATERIAL PRESENT IN CERTAIN LUMINOUS INSECTS.

BY F. ALEX. MCDERMOTT.

Received January 16, 1911.

In 1909, Dr. W. W. Coblentz,[3] of the U. S. Bureau of Standards, an-

[1] THIS JOURNAL, 31, 348.

[2] In my own notes I have adopted this name as representing the fluorescent