Thesis Approved

By

Philippos E. Papadakis

Major Advisor

A. G. Unseld

Dean
THE SYNTHESIS
OF A 13-CARBON CHAIN DIALDEHYDO-7-KETO UNSATURATED SUGAR BY DECARBOXYLATION OF 1,3-DICARBOETHOXY 1,3-
BIS (4',5'-O-ISOPROPYLIDENE-D-XYLOFURANOSYLIDENE] ACETONE AND BY HYDROLYSIS OF THE -O-ISOPROPYLIDENE GROUPS.

THE POLYMERIZATION
OF THE PRODUCT 1,3-BIS-D-(1-ALDEHYDO-XYLOSYLIDENE-5] ACETONE WITH DIETHYL ACETONEDICARBOXYLATE.

BY
SISTER MARY PHILIP OZDYCH, C.S.S.F.

A THESIS

Submitted to the Faculty of the Graduate School of the Creighton University in partial Fulfillment of the Requirements for the Degree of Master of Science in the Department of Chemistry

OMAHA, JUNE 1964
I wish to express my gratitude and appreciation to Dr. P. E. Papadakis for the suggestion of this investigation and for the valuable assistance and supervision he has given me throughout this period of research.
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>10</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>27</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>34</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>37</td>
</tr>
</tbody>
</table>
INTRODUCTION
At the onset of this paper, it seems to be essential and significant to briefly trace the history of the isopropylidene sugars and ascertain the position attained by this branch of carbohydrate chemistry since the close of the nineteenth century when Emil Fischer made his first contribution in this area.

This research does not actually deal with a detailed study of the isopropylidene derivatives of the pentoses and hexoses. One of these, diacetone glucose, has merely been employed as a starting material for the sugar polymerization. It is quite evident then, that in the introductory remarks reference will be made particularly to this derivative.

Monosaccharides and certain of their derivatives react with carbonyl compounds under the influence of acidic catalysts to form acetals or ketals, the most important reaction products being the acetone sugars. In most instances condensation takes place between the acetone and cis hydroxyl groups on contiguous carbon atoms in such a manner as to favor the introduction of the isopropylidene residues into the molecule.

---

Because α-D-glucopyranose has only two adjacent cis hydroxyl groups, one would tend to predict the formation of a mono rather than a di acetone derivative. This is not so because under the experimental conditions the α-D-glucopyranose rearranges to α-D-glucofuranose which affords two pairs of cis hydroxyl groups on carbons 1,2 and 5,6 as shown below.\(^2\)

The original process of condensing glucose with acetone was adopted by Fischer. He succeeded in preparing a new compound by converting the sugar into the "glucodimethylacetal" and thereafter treating this product with acetone containing hydrogen chloride. Fischer claimed that the mono derivative was an intermediate product in the formation of diacetone glucose.

Shortly after his activity in this region, Fischer began to turn to fields of inquiry other than carbohydrate chemistry because available methods of

---

3E. Fischer, *Ber.*, 28, 1145-1150 (1895).
investigation had failed to provide a solution to many fundamental structural problems. He felt he had reached the limit in the study of the constitution of sugars.

Before any structural investigation could be made into compounds like the sugars which contain many hydroxyl groups as well as reactive potential aldehydic or ketonic groups, it was obviously necessary to protect the hydroxyl groups in some way. This was recognized at the beginning of the century by James Irvine who made the association that Purdie's recently discovered methylation reaction provided a technique which could be applied to structural work in all branches of sugar chemistry. Irvine realized that the reactive hydroxyl groups of the sugars could be transformed into stable methyl ethers with the use of dry silver oxide and methyl iodide. He then outlined the whole field of carbohydrate chemistry and communicated his discoveries to Purdie. Together they initiated a vigorous attack on the structure of sugars and reported

---


their findings to the British Association for the Advancement of Science in 1902. 6

Irvine propounded long-term schemes of research on possible development of sugar derivatives for the use in chemotherapy. His investigations led to detailed studies of the isopropylidene derivatives. He showed that by methylation of the hydroxyls and subsequent hydrolysis of the acetone groups, these compounds could also be converted into a series of partly methylated sugars. 7 Further experiments by Karrer and Hurevitz 8 confirmed the fact that diacetoneglucose was a 1,2-5,6 isopropylidene compound.

As a result of his research, Irvine was able to tie many loose ends of Fischer's investigation together. He established proof that the condensation of the sugar and ketone led directly to the diacetoneglucose from which the mono compound could be prepared by partial hydrolysis of the diisopropylidene sugar. He explained that

---

the production of the monoacetone compound in the process described by Fischer was due to the presence of minute traces of acids, which, during the various manipulations involved in the isolation of the diacetone compound, remove the less stable acetone residue.

Fischer\(^9\) returned to the subject in 1915 and by an application of similar principles, prepared a number of partly acylated derivatives analogous to the methylated compounds.

After the original obstacles were overcome, sugar chemists were quick to recognize that the "acetone sugars" were compounds of great importance. These opened the way to the preparation of definite derivatives of sugars in which certain hydroxyl groups could be substituted while others remained open for further reactions. Hoping that these isopropylidene compounds would eventually play an important part in the synthetic development of sugars as did the glucosides, the chemists sought to develop improved methods for preparing them.

Criegee\(^10\) provided a substantial impetus to carbohydrate research by introducing a method to cleave

\(^10\)R. Criegee, *Ber.*, 64, 260 (1931).
glycols with lead tetraacetate. He recognized the value of this oxidation as a tool for locating the position of substituent groups in sugars and performed experiments to substantiate his theory.\textsuperscript{11}

Monoacetone glucose was among the first to be examined. Its oxidation was found to yield formaldehyde which confirmed the presence of a furanose ring in its structure. The major oxidation fragment was identified as 1,2-0-isopropylidene-5-aldehydo-D-xylopentadialdose. It was characterized subsequently by Iwadare\textsuperscript{12} and has recently been converted to a crystalline dimer.\textsuperscript{13} This compound plays a very significant role in the development of this research.

In 1954 Papadakis\textsuperscript{14} had successfully condensed monoaldehydo-O-isopropylidene dialdehyde sugars with 5-p-hydroxycyclohexanedione-1,3.

He predicted that diethyl acetonedicarboxylate, a 1,3-dicarbonyl compound, could also favor the formation

\begin{flushright}
\textsuperscript{11}R. Creigee, \textit{Ann. der Chemie}, 495, 211 (1932).
\end{flushright}
of long chain sugars. Its two methylene groups could condense with the aldehyde form of aldoses or dialdoses giving rise to such derivatives. In 1955 he reported that he had formulated a new method for the synthesis of long carbon chain sugars by condensing diethyl acetonedicarboxylate with 1,2-O-isopropylidene-D-xylo-pentadaldehyde.\textsuperscript{15}

In this report Papadakis predicted that hydrolysis of the isopropylidene groups in his condensation product could give rise to two aldehyde groups. This, in turn could open the way for a chain polymerization with diethyl acetonedicarboxylate resulting in sugars which might be of physiological, industrial and scientific interest and importance.

In an effort to verify the soundness of Doctor Papadakis's predictions, the study and experimentation outlined here has been undertaken. This paper is a report and discussion of the work accomplished.

\textsuperscript{15}Ibid., 20, 630 (1955).
The purpose of this experimental research was twofold:

1. To synthesize a 13 carbon chain dialdehydo-7-keto unsaturated sugar by decarboxylation of 1,3-dicarbethoxy 1,3-\textit{Bis (4',5'-0-isopropylidene-D-xylofuranosylidene)} acetone and by hydrolysis of the isopropylidene groups.

2. To polymerize the product 1,3-\textit{Bis-D-(1-aldehydo-xylosylidene-5)} acetone with diethyl acetonedicarboxylate.

The starting material, diacetone glucose (II), was prepared by the condensation of glucose with acetone under the influence of sulfuric acid as a catalyzing agent.\textsuperscript{16}

\begin{align*}
\text{HO-C-H} & \quad \text{H-C-O} \\
\text{H-C-OH} & \quad \text{H-C-O} \\
\text{H-C-OH} & \quad \text{H-C-O} \\
\text{H-C-OH} & \quad \text{H-C-O} \\
\text{H}_2\text{C-OH} & \quad \text{H}_2\text{C-O} \\
\text{O + 2CH}_3\text{COCH}_3 & \quad \text{H}_2\text{C-O} \\
\text{[H}^+] & \quad \text{H}_2\text{C-O} \\
\text{HO-C-H} & \quad \text{H-C} \\
\text{H-C-O} & \quad \text{H-C-O} \\
\text{H-C-O} & \quad \text{H-C-O} \\
\text{H-C-O} & \quad \text{H-C-O} \\
\text{H}_2\text{C-OH} & \quad \text{H}_2\text{C-O} \\
\end{align*}

(I) (II)

The use of concentrated sulfuric acid as a catalyst and dehydrant for acetonization of carbohydrates has

found general acceptance today though the neutralization with sodium carbonate is very time consuming. The reaction also proceeds well in the presence of copper sulphate, zinc chloride, and phosphorus pentoxide though not as well as in concentrated acids.

Since the isopropylidene derivatives are actually cyclic ketals, one would expect them to be readily hydrolyzed by aqueous mineral acids. This definitely is the case. Under proper conditions one of the groups may be much more easily removed than the other. This results in the formation of the monoisopropylidene sugar. Such are the conditions required for the conversion of diacetone glucose to the monoacetone derivative. Here the ketal in the 5,6 position is hydrolyzed more than forty times as rapidly as that in the 1,2 position.

In this experiment diacetone glucose was converted to monoacetone glucose (III) through hydrolysis of the


18 H. Fischer, Ber., 60, 485-490 (1927).


ketal in the 5,6 position with glacial acetic acid and a calculated amount of water at 50°C.

The third step in the synthesis entailed the preparation of 1,2-0-isopropylidene-5-aldehyde-D-xylo-pentodialdose by the oxidation of (III) with lead tetraacetate in a benzene medium according to the method described by Grosheintz and Fischer.\(^\text{21}\)

\[\text{HO} - \text{C} - \text{H} \quad \xrightarrow{\text{H}^+} \quad \text{HO} - \text{C} - \text{H} \]

\[\text{H} - \text{C} - \text{O}(\text{CH}_3)_2 \quad \text{H} - \text{C} - \text{O}(\text{CH}_3)_2 \]

(II) \quad (III)

\[\text{HO} - \text{C} - \text{H} \quad \xrightarrow{\text{Pb(C}_2\text{H}_3\text{O}_2)_4} \quad \text{HO} - \text{C} - \text{H} \]

\[\text{H} - \text{C} - \text{OH} \quad \text{H} - \text{C} - \text{OH} \]

(III) \quad (IV)

\[\text{H}_2\text{C} - \text{OH} \quad \text{H}_2\text{C} - \text{OH} \]

\[\text{H} - \text{C} - \text{OH} \quad \text{H} - \text{C} - \text{OH} \]

(II) \quad (III)

---

As had been stated in the introduction, this reaction was discovered by Criegee. In studying the oxidation of saturated alcohols by lead tetraacetate in cold acetic acid he found that only those alcohols containing two free adjacent hydroxyl groups were oxidized, yielding aldehydes or ketones. Criegee recognized its applicability to the carbohydrates with their numerous hydroxyls. Here, the cleavage of 1,2 glycols could provide a means for studying their structure. By oxidizing the two adjacent hydroxyls of (III), he confirmed the presence of a furanose ring in its structure and at this time simply identified the remaining fragment to be 1,2-0-isopropylidene-5-aldehyde-D-xylo-pentadialdose.

It was Iwadare's investigation into the dialdo-pentoses which led to the characterization of this derivative. He showed that (IV) reduced Fehling solution, a typical test for aldehydes, and that it formed the mono derivatives with phenylhydrazine (V) and semicarbazide (VI).

---

22 Iwadare, p. 40.
In 1957 Schaffer and Isbell reported that infrared spectroscopy failed to show any absorption corresponding to a free aldehyde group in the dialdehyde pentose. They therefore assumed that the aldehyde was "masked" by the formation of a dimer (VII).
The dimer formula was the result of aldol condensation using alkali for catalysis. Schaffer and Isbell prepared derivatives of the acetylated compounds to confirm this assumption and to justify the proposed structure of the dimer.\(^{23}\)

[For a time it was feared that this research work would be completely nullified by their findings. Doctor Papadakis promptly gave the assurance that under the experimental methods and conditions used, sufficient evidence was available to prove the existence of a monomer in the aldehydo form of the sugar.

The collective evidence is summarized below:

1. If there were no such available monomer, the aldol condensation\(^{24}\) between two molecules of 5-aldo-1,2-0-isopropylidene-D-xylo-penta-furanose could not take place.

2. If there were no such monomer, the cyanide reaction\(^{25}\) would have no feasible explanation and there would be no aldol condensation with nitromethane to give the nitro derivative.\(^{26}\)

3. If there were no aldehydo form of the monomer, Iwadare would have been unable to characterize the derivative and Papadakis could not have condensed it with diethyl acetonedicarboxylate to prepare a long carbon chain sugar.]

\(^{23}\)Schaffer and Isbell, p. 3864.

\(^{24}\)Ibid., 80, 756 (1958).

\(^{25}\)Ibid., 79, 3867 (1957).

\(^{26}\)Grosheintz and Fischer, p. 1478.
After the preparation of the syrupy dialdehyde pentose, the 13 carbon chain sugar (VIII) was synthesized by Papadakis’s method. 27

In the condensation, two moles of 1,2-0-isopropylidene-D-xylo-pentafuranose reacted with one mole of diethyl acetonedicarboxylate in benzene using piperidine as a catalyst to produce one mole of a product, C25H34O13, and two moles of water. Since the xylo-pentadialdehyde possessed only one functional aldehydic group, the condensation was assumed to have occurred between this aldehyde group at C-5 and the active methylene group of diethyl acetone dicarboxylate giving rise to structure (VIII).

At this point a 3,5-dinitrobenzoate of the 13 carbon chain sugar was prepared by reaction it with 3,5-dinitrobenzoyl chloride in an excess of pyridine according to the method described by Shriner. 28

\[
\text{O}_2\text{N} \quad \text{O}_2\text{N} \quad \text{O}_2\text{N} \quad \text{COCl} + \text{HOR} \rightarrow \text{O}_2\text{N} \quad \text{O}_2\text{N} \quad \text{O}_2\text{N} \quad \text{COOR} + \text{HCl}
\]

27 Papadakis, 20, p. 630.

Since there were two hydroxyl groups open for attack, it was expected that both would react. Analysis of the product of this reaction indicated that the derivative corresponded to formula (IX).

It seemed apparent that two dinitrobenzoyl groups were attached to the diacetone 13 carbon-chain sugar but that subsequently, an acetone group was lost by hydrolysis. This assumption may be supported by the fact that if by miscalculation this system lacked an excess of pyridine, the hydrochloric acid formed would not be completely neutralized. Later when the material was poured over crushed ice to remove the pyridine hydrochloride, the unneutralized acid, now diluted, could have had a hydrolyzing effect on one acetone group.
The preparation of the 3,5-dinitrobenzoate brought the preliminary work to completion. The next step was to hydrolyze the acetone groups still attached to the 1,2 and 1',2' carbons of the 13 carbon chain sugar.

The deacetonization was completed by using 0.1 N sulfuric acid. The final product was expected to have the structure:

\[
\begin{align*}
\begin{array}{c}
\text{H}_5\text{C}_2\text{O} \\
\text{OC}_2\text{H}_5 \\
\end{array}
\end{align*}
\]

Analysis showed that this was not the product. The question as to what could have happened soon became apparent. The desired hydrolyzate contained two carboxylic groups which could have been easily hydrolyzed by the acid. This is a general property of the esters and it is expressed by the following equation:

\[
\text{RCOOH}_1 + \text{H}_2\text{O} \xrightarrow{[\text{H}^+]} \text{RCOOH} + \text{R'}\text{OH}
\]

In this case the resulting compound would be:

\[
\begin{align*}
\begin{array}{c}
\text{OH} \\
\text{OH} \\
\end{array}
\end{align*}
\]
Prolonged heating in the acid medium may well have brought about the decarboxylation of the resulting \( \beta \)-ketonic dicarboxylic acid according to the following general reaction:

\[
\text{RCOCH}_2\text{COOH} \xrightarrow{[\text{H}^+]} \Delta \quad \text{RCOCH}_3 + \text{CO}_2
\]

The analysis seemed to justify the following as the correct formula for the new product, 1,3-Bis-D-(1-aldehydo-xylosylidene-5) acetone (X).

\[
\begin{align*}
\text{O} & \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{O} \\
\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\end{align*}
\]

\( (X) \)

It is commonly known that aldoses, as do aldehydes, react with phenylhydrazine to form phenylhydrazones. If an excess of phenylhydrazine is used, the reaction proceeds further to yield products known as osazones which contain two phenylhydrazine residues per molecule. A third molecule of the reagent is turned into aniline and ammonia.
With this fact in mind, an attempt was made to prepare a 2,4-dinitrophenylhydrazine derivative of (X) which, according to the theory, would contain five dinitrophenylhydrazine attachments as indicated in structure (XIII). Analysis indicated that an insufficient amount of 2,4 dinitrophenylhydrazine may have been used. This assumption seemed justifiable because upon further investigation of compound (X) it became evident that seven dinitrophenylhydrazine attachments were possible.

Structure (XI) by tautomerization of hydrogens may be converted to structure (XII) which will react with a greater proportion of phenylhydrazine than the former. 29

\[
\begin{align*}
\text{CHO} & \quad \text{CH} = \text{NNHC}_6\text{H}_5
\\
\text{CHOH} & \quad 3 \quad \text{C}_6\text{H}_5\text{NNH}_2
\\
\text{Aldose} & \quad \text{Osazone}
\end{align*}
\]

Thus, the reaction could definitely not have gone to completion and a derivative with structure (XI) may have resulted. This type of structure containing three molecules of water of hydration finds support in Brode's experimentation. He showed spectroscopically that hydrazones form hydrates.

In the final step, 1,3-[Bis-D-(1-aldehyde-xylosylidene-5)] acetone and diethyl acetonedicarboxylate were polymerized mole for mole with piperidine as a catalyzing agent. The overall procedure was the same as that used in preparing the 13 carbon chain sugar.

An aldol condensation may proceed in two steps:

1. The dimerization of molecules -

   \[
   \text{H}_3\text{C}-\text{C}^\ominus \stackrel{\ominus}{\text{H}} + \text{H}_3\text{C}-\text{C}^\ominus \text{H} \xrightarrow{} \text{H}_3\text{C}-\text{C}-\text{C}^\ominus \text{H}
   \]

---

2. The dehydration of aldol products -

\[
\begin{align*}
\text{H}_3\text{C} - \text{C} - \text{C} - \text{C} & \quad \text{H}_2\text{O} \quad \text{H}_3\text{C} - \text{C} = \text{C} - \text{C} \\
\text{OH} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

Similarly, in the aldol condensation of the diethyl acetone dicarboxylate with the 13 carbon unsaturated dialdehyde keto sugar (X) there could be a polymer represented by (XV) which is the repeating unit of the first step of the aldol condensation. Another polymer representing the second step could be represented by structure (XVI). Analyses seem to justify the existence of both, the first being soluble in water and the second in alcohol. Formulas (XV) and (XVI) are general type polymers in which, for simplification, all the hydroxyls are written on the same side.

The results of this research are but a small contribution to the already vast and rapidly growing field of carbohydrate chemistry. It is hoped that the experimentation and analyses reported here will serve to enhance interest in this area and encourage further investigation.

The primary purpose for undertaking a research of this type is ultimately to serve mankind. Perhaps a
definite application for such sugars will soon be found in industry and medicine. The knowledge gleaned through the above research will then have found its desired place and the efforts expended in its acquisition will be more than amply rewarded.
All melting points listed in the following procedure are uncorrected. All microanalysis was done by Galbraith Laboratories, Inc., Knoxville, Tennessee and Dow Chemical Laboratories, Midland, Michigan.

**PREPARATION OF DIACETONE GLUCOSE. (II)**

One hundred and four grams (0.39 mole) of anhydrous dextrose and 1.8 l of acetone were placed in a three liter, three necked flask fitted with a condenser, stirrer and a dropping funnel. About 88 ml. of concentrated sulfuric acid were slowly dropped into the flask. After five hours the acid was neutralized with a calculated amount of anhydrous sodium carbonate, filtered, and the filtrate evaporated to dryness. The residue was taken up in cold water, the solution extracted three times with benzene and the extract washed twice with a little water which was combined with the original aqueous layer. The combined aqueous extracts were extracted six times with chloroform; the chloroform extract, after dehydration over sodium sulfate, was evaporated to dryness. The melting point was 110°. The reported melting point was 110°-111°.

**PREPARATION OF MONOACETONE GLUCOSE. (III)**

The diacetone glucose was dissolved in a minimal amount of glacial acetic acid containing a calculated
amount of water. Hydrolysis was completed after heating over a water bath at 50° for fifteen minutes. After cooling, the product was filtered and recrystallized from ethyl acetate. The melting point was 161°-162°. The reported melting point was 159°-161°.

PREPARATION OF 1,2-0-ISOPROPYLDENE-D-XYLOPENTADI-ALDEHYDE. (VI)

A mixture of 100 grams (0.45 mole) of monoacetone glucose and 1.6 l of dry benzene was moderately stirred. To the boiling suspension 205 grams (0.46 mole) of lead tetraacetate were added in five equal portions at three minute intervals without further heating. Stirring was continued for one quarter of an hour at 70°. Any unreacted lead tetraacetate was reduced with a few drops of ethylene glycol. After cooling to room temperature the precipitate was filtered off and washed with benzene. The combined filtrates were extracted five times with 25 cc. portions of ice water. The combined aqueous extracts were kept at 0° and extracted eight times with 25 cc. portions of chloroform. A viscous syrup was obtained upon evaporation of the solvents under reduced pressure.
PREPARATION OF THE 13 CARBON CHAIN SUGAR. (VIII)\textsuperscript{15}

To a benzene solution of 40 grams (0.025 mole) of 1,2-0-isopropylidene-D-xylotrihydroxyglutaric dialdehyde, were added 18.9 ml. (0.125 mole) of diethyl acetonedicarboxylate and 5 drops of piperidine. The mixture was allowed to stand at room temperature overnight and then refluxed for an hour. After the benzene was evaporated, the remaining syrup was boiled twice in distilled water. The product was purified from the following two component mixtures according to the method of Papadakis: benzene-petroleum ether, ether-petroleum ether and alcohol-water. The viscous amber syrup which was obtained was dried and pulverized to an amorphous powder.

PREPARATION OF THE 3,5-DINITROBENZOYL CHLORIDE DERIVATIVE OF THE LONG 13 CARBON CHAIN SUGAR. (IX)\textsuperscript{20}

A mixture of 1.0 gram (0.0018 mole) of the sugar (IX), 0.92 grams (0.0036 mole) of 3,5-dinitrobenzoyl chloride with 0.32 ml. (0.0036 mole) of pyridine in a dry dioxane medium was kept at 0\degree for one hour. After standing at room temperature overnight the mixture was heated at 60\degree under reflux for one hour. The dioxane was removed under suction and the product poured over crushed ice. The sticky residue was washed with 10 ml. of 2.0\% sodium bicarbonate. Upon recrystallization from
ether-petroleum ether a white solid with a melting point of 150°-152° separated out.

Anal. Calcd. for C₃₆H₇₆O₂₄N₄: C, 47.57 H, 3.99 N, 6.16

Found: C, 47.45 H, 4.26 N, 6.06

PREPARATION OF 1,3-[BIS-D-(1-ALDEHYDO-XYLOSYLIDENE-5)] ACETONE 2H₂O. (X)

Hydrolysis was accomplished by heating with dilute acid. Five grams of the 13 carbon chain sugar (VIII) were dissolved in dioxane to which was added 50 ml. of 0.1N sulfuric acid. The mixture was heated under reflux on a water bath at 75°-30° for two and a half hours. The hydrolyzate was neutralized with barium hydroxide followed by filtration and evaporation to dryness. The residue was crushed and dissolved in hot water. The hot solution was filtered in order to separate the hydrolyzate from any unhydrolyzed 13 carbon sugar (VIII) which was insoluble in water. The solution was again evaporated to dryness and the hardened syrup was pulverized to an amorphous powder which softened at 93° and was completely melted at 110°.

Anal. Calcd. for C₁₃H₂₂O₁₁: C, 44.05 H, 6.21

Found: C, 44.85 H, 6.31
PREPARATION OF THE 2,4-DINITROPHENYLHYDRAZINE DERIVATIVE OF 1,3-BIS-D-(1-ALDEHYDO-XYLOSYLIDENE-5). (XIV)

A solution of 2,4-dinitrophenylhydrazine was prepared by adding 2.5 ml of concentrated sulfuric acid to 1.11 g (.0056 mole) of 2,4-dinitrophenylhydrazine. Water was added dropwise with swirling until solution was completed. This freshly prepared solution was added to 0.3 grams (.0008 mole) of the 13 carbon unsaturated dialdehyde keto sugar (X) in 95% ethanol. The mixture was allowed to stand overnight. The red colored precipitate was collected under centrifuge and recrystallized from 95% ethanol. It sintered at 224° and melted at 229°-235°.

Anal. Calcd. for C_{49}H_{44}O_{30}N_{24}: C, 40.60 H, 3.04 N, 23.20
Found: C, 40.48 H, 2.71 N, 23.76

PREPARATION OF THE LONG CHAIN POLYMER. (XV) or (XVI)

A quantity of 1.53 ml (.008 mole) of diethyl acetonediicarboxylate was added to 3 grams (.008 mole) of 1,3-[Bis-D-(1-aldehydo-xylosylidene-5)] acetone in a benzene medium. After five drops of piperidine were added to catalyze the reaction, the mixture remained at room temperature overnight. This was followed by heating under reflux in a water bath at 80° for one hour. After a second day of standing it was again heated for
the same amount of time. The solution was then filtered to remove a residue which precipitated out during the reaction and then evaporated to dryness. The hardened syrup was purified in the following manner: It was divided into two portions, one soluble in water and the other in 95% ethanol. A residue was precipitated from the former by the addition of 95% ethanol and from the latter by the addition of water. The residue was removed by filtration (analysis later proved that it was not the polymer). This purification process was repeated several times. The amber solution of the water soluble and alcohol soluble materials containing the polymer were treated with Darco in an attempt to remove the coloration but to no avail. This was followed by evaporation to dryness. The hardened amber syrups were pulverized.

The material from the first portion represented by (XV) softened at 72° and was completely melted at 85°. The material from the second portion represented by (XVI) melted at 78°-81°.

**Compound (XV).**

Anal. Calcd. for \((C_{22}H_{32}O_{14})_n\): C, 50.76 H, 6.15

Found: C, 50.86 H, 6.01

**Compound (XVI).**

Anal. Calcd. for \((C_{22}H_{28}O_{12})_n\): C, 54.54 H, 5.78

Found: C, 54.77 H, 6.07

Found: C, 55.44 H, 5.93
SUMMARY
Diacetone glucose was prepared by the condensation of glucose with acetone under the influence of sulfuric acid as a catalyzing agent. It was converted to monoacetone glucose through hydrolysis with glacial acetic acid and a calculated amount of water. The monoacetone glucose was oxidized with lead tetraacetate in a benzene medium to yield 1,2-o-isopropylidene-5-aldehyde-D-xylopentodialdose.

Condensation of diethyl acetonedicarboxylate with 1,2-o-isopropylidene-D-xylopentadaldehyde using piperidine as a catalyst, gave a derivative of an unsaturated 13 carbon chain dialdehyde-7-keto sugar.

A 3,5-dinitrobenzoate was prepared from the 13 carbon chain sugar and 3,5-dinitrobenzoyl chloride.

The compound, 1,3-[\text{Bis-D-(1-aldehydo-xylosylidene-5)}] acetone was prepared by the deacetonization of the isopropylidene groups and the decarboxylation of the resulting 4-ketonic dicarboxylic acid with 0.1N sulfuric acid.

A 2,4-dinitrophenylhydrazone was prepared from 1,3-[\text{Bis-D-(1-aldehydo-xylosylidene-5)}] and 2,4-dinitrophenylhydrazine.
In the final step 1,3-[Bis-D-(1-aldehydo-xylosyldene-5)] acetone and diethyl acetonedicarboxylate were polymerized mole for mole under piperidine catalysis.
Books


Periodicals


Criegee, Rudolf, Ber., 64, 260 (1931).

Fischer, Emil, Ber., 28, 1145-50 (1895).

Fischer, Hermann and Taube, Carl, Ber., 60, 485-90 (1927).

Freudenberg, Karl, Durr, Walter and Hochstetter, Henrich, Ber., 61, 1735 (1928).

Freudenberg, Werner and Brauns, Fritz, Ber., 55, 3233-3238 (1922).


Ohle, Heinz and Koller, Ilse, Ber., 57, 1566 (1924).


Pette, J.W., Ber., 64, 1567-1568 (1931).


Smith, Lennart and Lindberg, Johan, Ber., 64, 505-516 (1931).