A STUDY OF THE QUANTITATIVE FORMATION OF FURFURAL FROM d-LYXOSE

by

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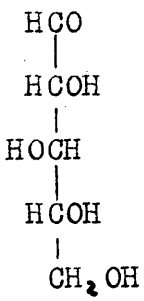
Acknowledgement

It is my wish to express sincere appreciation and gratitude for the valuable and stimulating assistance rendered by Professor Robert C. Hockett.

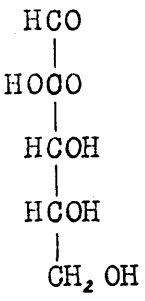
I INTRODUCTION

A. Discussion of Pentoses and Pentosans

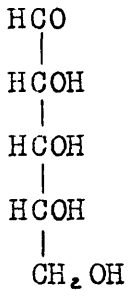
There are eight possible aldopentoses, that is, four pairs of optical antipodes. The d- forms of these pentoses may be represented by the following formulae:



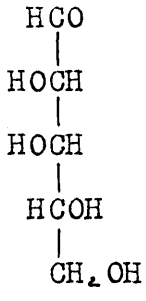
d-Xylose



d-Arabinose



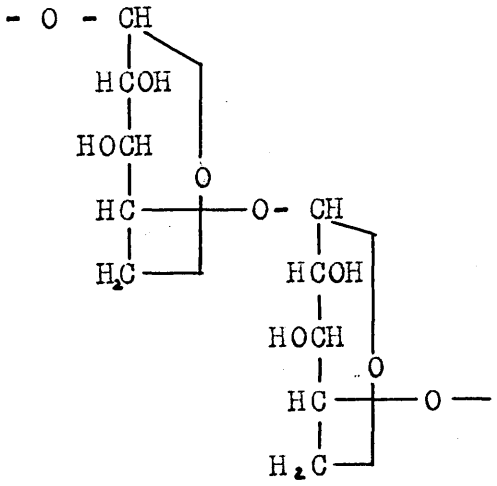
d-Ribose



d-Lyxose

Pentoses occur in nature as pentoses and also as "pentosans", condensation products of pentoses, long chain molecules consisting of pentose units bound togther by a glucosidic linkage analogous to cellulose which is a condensation product of the hexose d-glucose.

Pentosan Structure (Xylan)



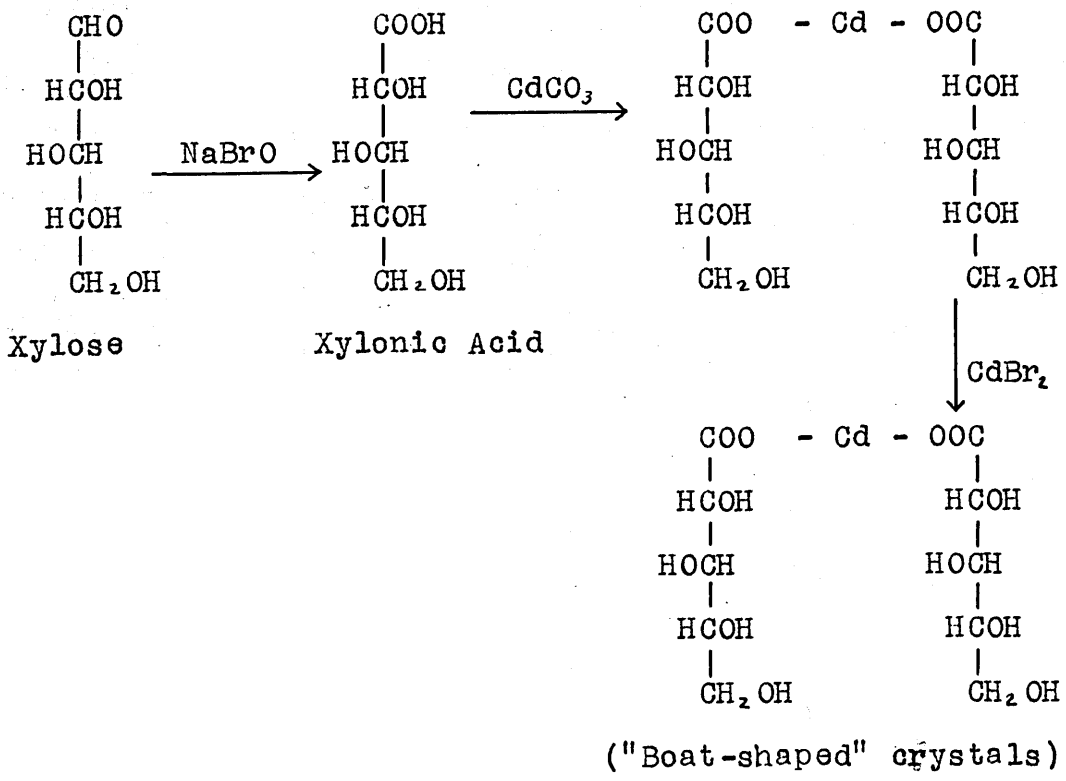
Pentoses and pentosans occur abundantly in natural materials along with cellulose, lignin, and various plant gums.

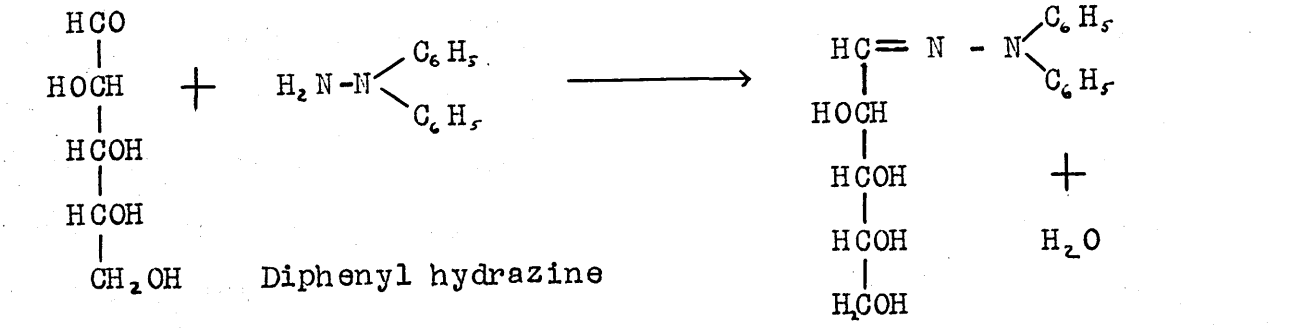
Therefore, their percentage determination is of significance to the agricultural chemist and of great importance in the cellulose industries. The d-form of xylose occurs most abundantly in nature usually as a polysaccharide. It is found in such materials as wood, straw, nutshells, oat hulls, corn cobs etc. Arabinose occurs widely in nature mostly as l-arabinose, a constituent of pectin, gum arabic, cherry gums and similar plant substances. d-Arabinose is found also in much lesser quantities, occurring in tubercle bacilli and barbaloin. d-Ribose has been detected in the nucleic acids of numerous plants but the amount of it compared to the quantities of arabinose and xylose existing in natural materials is relatively small. Lyxose has not as yet been discovered in nature. There are qualitative methods for detecting xylose and arabinose which are the two pentoses occurring most abundantly in natural materials. Xylose oxidized with sodium hypobromite forms xylonic acid which when treated with cadmium carbonate will form, on addition of cadmium bromide, a double salt with characteristic boat shaped crystals. Arabinose can be identified by reacting it with diphenyl hydrazine which produces a good crystalline hydrazone while xylose does not. (See page 3)

B. Evidence for the Occurence of Lyxose in Nature.

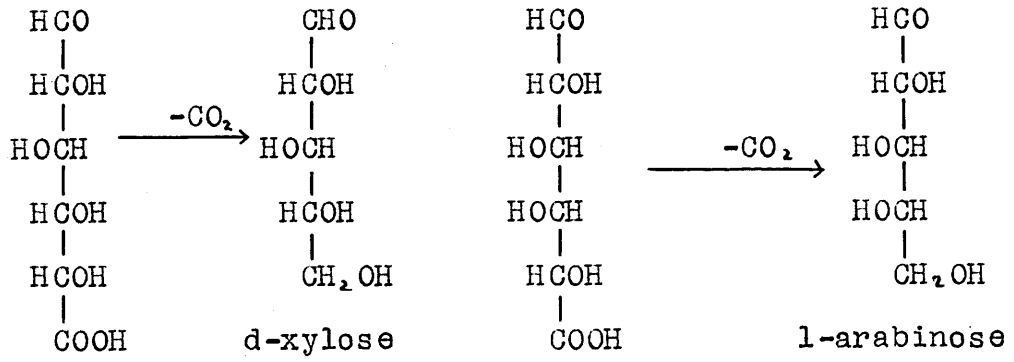
Although lyxose has not as yet been found present in nature, there is good evidence that it does exist, of course not in such large quantities as xylose and arabinose, but possibly in appreciable amounts. Frequently found associated with d-xylose

Identification of Xylose and Arabinose



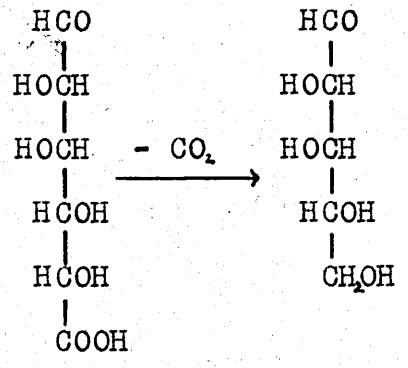


obtained from natural materials is the substance glucuronic acid, similarly the presence of galacturonic acid is detected in plant substances found to contain l-arabinose. It is seen that according to the structure of these two acids that a loss of carbon dioxide would result in the formation of d-xylose and l-arabinose respectively.



glucuronic acid galacturonic acid

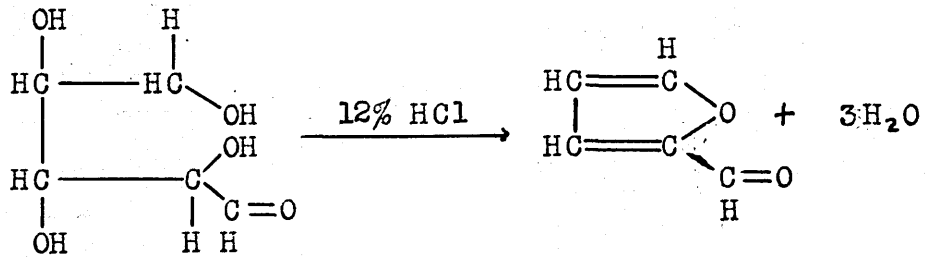
As the percentage of pentoses in a young growing plant is much smaller than in the later stages of its growth, it seems evident that the pentose content is gradually increased during the life period by a natural plant process in which the uronic acids break down with the evolution of carbon dioxide forming the pentoses corresponding to the acid structure. The fact that d-mannuronic acid, which would form d-lyxose on the loss of carbon dioxide, has been discovered present in nature in certain forms of seaweed (Nelson and Cretcher, J. Amer.Chem. Soc. (1929) 51, 1914) suggests that probably lyxose also occurs naturally. (X)



Mannuronic acid d-Lyxose

C. The Analytical Formation of Furfural.

The standard analytical method for the determination of pentoses or pentosans is based on the following reaction:



Pentose Furfural

When pentoses react with dilute acids (12-14% HCl used in standard procedures) the product is furfural. Under definite conditions of temperature, pressure, and with a specific type of apparatus this reaction possesses two important characteristics. First, the different pentoses form different characteristic yields of furfural, second, the amount of furfural formed is not directly proportional to the amount of pentose reacting. The fact that the yields of furfural are characteristic of the pentose reacting and that hexoses do not produce furfural by this reaction, make this a possible empirical method for determining the pentose or pentosan content of natural substances.

Furfural vs. Pentose Figure 1.

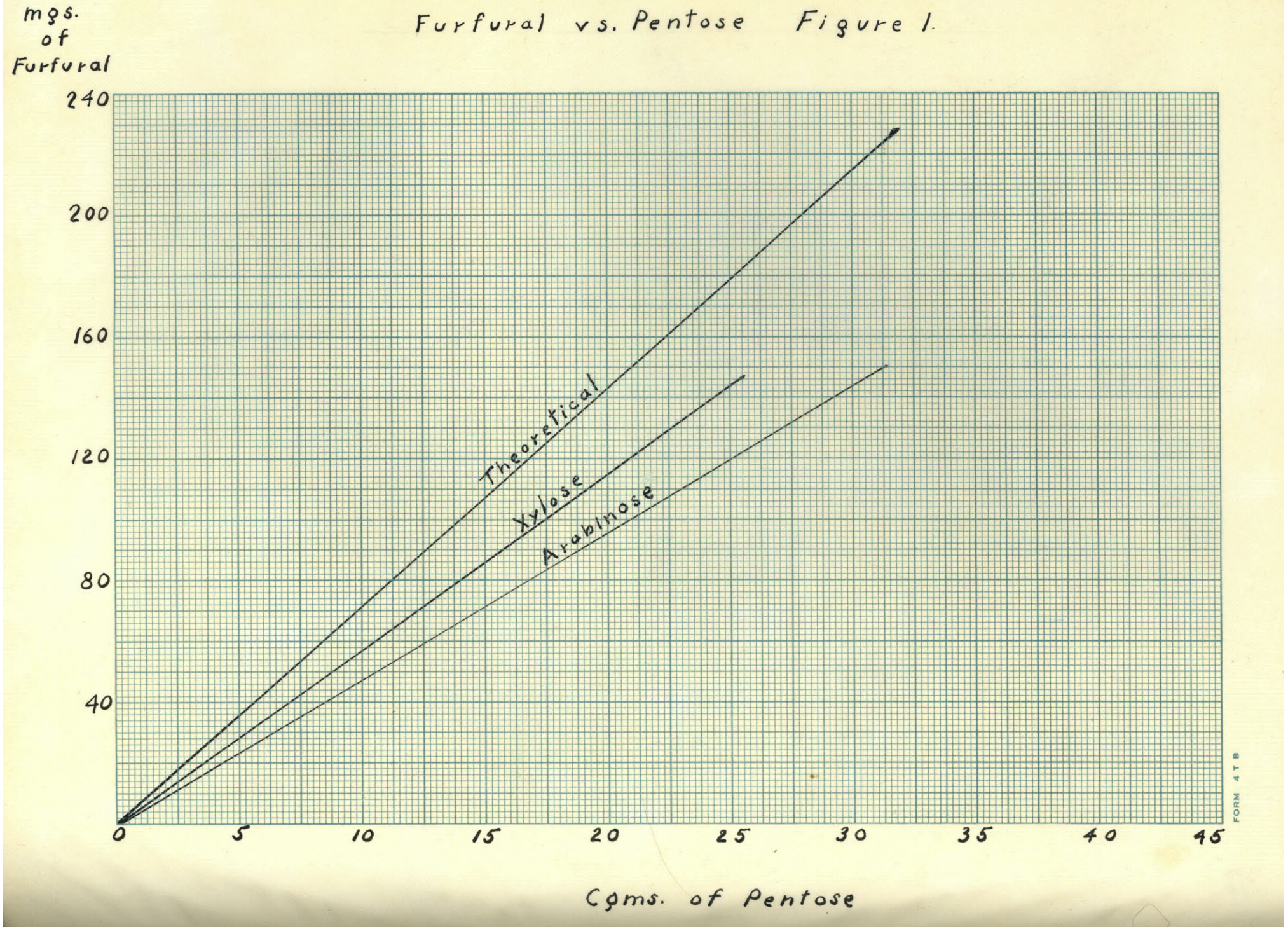


Figure 2

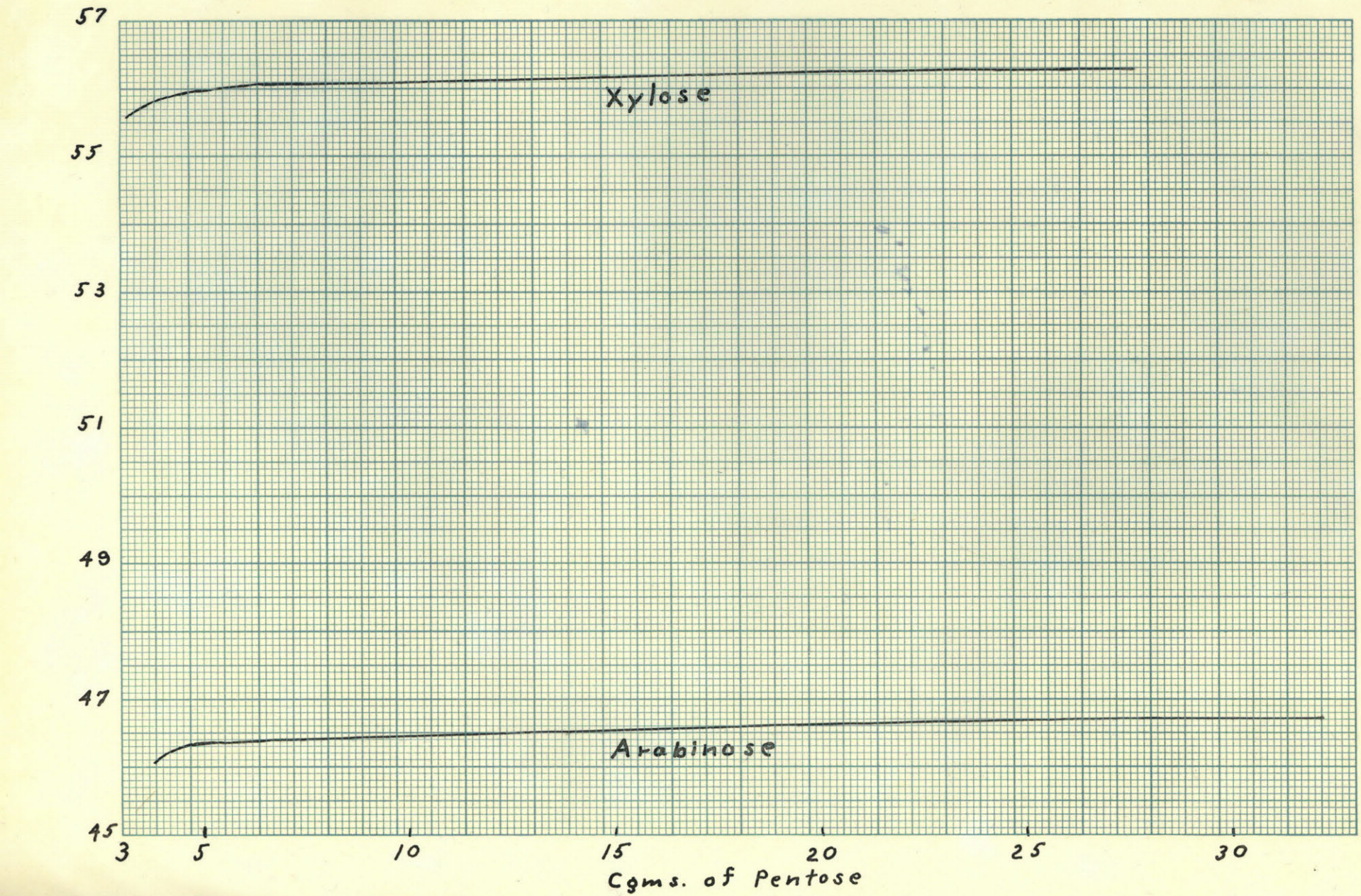

Furfural
Pentose
X 10²
57
55
53
51
49
47
45
Xylose
Arabinose
3
5
10
15
20
25
30
Cgms. of Pentose
FORM 4 T B

Figure (1) shows clearly that the yields of furfural are lower than theoretically expected and those of arabinose are different (less) than those of xylose. The lines in this graph although they appear straight, due to the scale of the graph, are actually curved because the formation of furfural is not a linear function of the of pentose used, the slope being greatest for small amounts of pentose. This effect is shown much better in figure (2), where the ratio of the amount of furfural produced to that of the pentose reacting is plotted against the amount of pentose used. By this method a truer conception is gained as to how the yield of furfural varies with the amount of pentose reacting. The standard procedure for the determination of pentoses consists in reacting the weighed sample material with dilute acid (usually hydrochloric acid) and distilling under defined conditions. The furfural in the acid-furfural distillate is then determined quantitatively by either gravimetric, volumetric, or colorimetric methods, which will be discussed in more detail later. Having obtained the weight of furfural, the weight of pentose or pentosan may be obtained by use of a formula, graph, or table of weights which have been derived empirically according to the procedure used.

D. Object of Thesis

As xylose and arabinose are the two pentoses occurring most abundantly in natural substances and most easily obtainable up until quite recent times, the literature contains data only on the quantitative formation of furfural from these two pentoses.

Since ribose has been found to exist in nature, and as previously pointed out there is good evidence for the probable existence of lyxose, it becomes of interest to see just how these would react under analytical treatment. It is possible that the presence of these two pentoses unaccounted for in a sample subjected to standard pentose analysis might introduce large deviations in the interpretation of the results. It is therefore the purpose of this thesis to investigate the formation of furfural from the pentose lyxose quantitatively and to obtain data as to the amount of furfural formed from different weights of lyxose when subjected to treatment according to the analytical standard procedure. Lyxose was selected instead of ribose because it was more conveniently available, due to the perfecting of methods of synthesis accomplished by Dr. Hockett and his co-workers. (XI)

E. Selection of a Method and Proposed Experimental Work.

The first problem to be considered was the selection of a method for the production and determination of the furfural. This involved the investigation of numerous important references obtained from several text-books dealing on the subject of pentose determination and obtaining a general survey of the various methods and reason for their existence. A thorough search of the Chemical Abstracts was made from the year nineteen-thirty up to the present time and important references investigated or their results recorded. Micro and colormetric

methods were eliminated because the literature showed them to be comparatively lacking in accuracy. A brief summary of some of the methods considered most important follows:

Tollen's Phloroglucinol Method

This is the original and so far the only method accepted as official by the Association of the Official Agricultural Chemists of America. In this method the pentose containing material is treated with 12% hydrochloric acid and the solution distilled at the rate of 30 ml. in ten minutes. The apparatus consists of a distillation flask with a dropping funnel inserted connected to a straight tube condenser. On collection of each 30 ml. of distillate, an equal amount of acid solution is added to the flask by means of the dropping funnel. After collection of 360 ml. of distillate, which consists of a solution of furfural and dilute acid, the process is discontinued. The determination of the furfural makes use of the reaction between furfural and phloroglucinol (in acid solution) which produces a dark flocculent precipitate, $C_{\alpha}H_{\delta}O_{4}$, (structure uncertain) and a molecule of water. This precipitate is extremely insoluble in dilute acid or water and can be weighed quantitatively, making a correction for the very slight amount that is soluble in the volume of distillate. This method represents a fundamental procedure in the formation of furfural, the other methods consisting mostly of modifications of this procedure. These modifications have arisen due to practical difficulties encountered by this method which will be described

in more detail later. However, one of the most important disadvantages is the occurrence in plant substances of interfering constituents that also form substances capable of producing precipitates with phloroglucinol. This and the disadvantage of the time involved in carrying out a determination are the important incentives behind most of the methods suggested. -- Abderholden's Arbeitsmethoden 1909, II, 130

Barbituric Acid Method

This is also a gravimetric method being merely a modification of Tollen's method where barbituric acid is substituted in the place of phloroglucinol in precipitating the furfural. This is suggested by Unger and Jäger in an attempt to cope with an interfering substance namely, hydroxymethyl 2 furaldehyde, which is sometimes present in the distillate obtained from some natural materials on analytical treatment and which forms a precipitate with phloroglucinol but not with barbituric acid. -- Z. Untersuch Lebensm. 66, (1933)

Thiobarbituric Acid Method

This is also a gravimetric modification suggested by Dox and Plaisance who use thiobarbituric acid in place of barbituric. It has been proven inadequate when small amounts of furfural are to be determined.--Acree, Bur. of Standards Jl. Research.(IX)

Jolle's Method

This is a volumetric method, the production of furfural differs from the procedure of Tollens in that it is distilled by steam in an attempt to avoid decomposition of the furfural

by acid fumes, and to eliminate the possibility of charring in the distillation flask. The distillate collected is neutralized and a measured amount of sodium bisulfite added. The excess is titrated with iodine (one tenth normal) using starch as an indicator, the difference giving the amount of bisulfite combined with the furfural and thus indirectly the amount of furfural present. This method is one of questionable accuracy and difficult technique. According to data presented by Acree, Bur. of Standards Jl. Reasearch, distillation by steam does not improve the yield of furfural. -- Sugar Analysis, C. A. Browne.

Bromine Oxidation Method

This consists of a volumetric method suggested by Kullgren and Tydén later modified by Powell and Whittaker. The furfural is obtained by the procedure of Tollen's and measured amounts of a standard bromide- bromate solution are added to samples of the distillate. After standing in the dark a short period ten percent potassium iodide solution is added and the free iodine produced titrated with sodium thiosulfate. The volume of thiosulfate serves as a measure of the bromine combined with the furfural, and accordingly the amount of furfural. This method is much more rapid than the phloroglucinol method and there is some evidence of excellent accuracy. -- Bur. of Standards Jl. Research - Vol. 8, (1932) 25

Bertrand Method

This is a volumetric method whose accuracy is more or less

in dispute. The furfural distillate obtained by the previously described Tollen's procedure is treated with Fehling's Solution producing cuprous oxide which is titrated with potassium permanganate solution. Satisfactory results have been obtained by this method. - Brodilnaya Prom. 11 No. 5 26-8 (1934) Zavodskoya Lab. 6 558-61 (1937)

The method selected was Tollen's Phloroglucinal Method. Reasons for this choice are as follows: It is the only pentose-pentosan determination method that is officially accepted by the Association of Official Agricultural Chemists of America, it is the method that was employed in making Kröber's Table (a table giving weights of furfural corosponding to various amounts of pentoses or pentosans) which is used universally in pentose determinations, it is the method that possesses the largest amount of supporting evidence that it is representative of the best attainable accuracy, erratic results due to interfering constituents found present in practical use are eliminated when pure pentoses are used, and finally the technique and apparatus required for this procedure are relatively simple.

The proposed experimental work consisted of two parts, the running of several determinations with duplicates on weights of pure pentoses (arabinose and Xylose) in order to ascertain reliability of the apparatus with an indication of the accuracy attainable and to develope an analytical technique, and the running of determinations on as many samples of lyxose as deemed

necessary to complete a graph similar to that of figure (1). As lyxose was potentially available in the form of calcium galactonate, the first step was the production of pure lyxose by a degradation process. Following this operation, the purification of samples xylose and arabinose was necessary.

II EXPERIMENTAL

A. Preparation and Purification of Reagents used

Preparation of d-Lyxose from Calcium Galactonate

Reagents: Calcium galactonate - (200 gms.)

Ferrous sulfate solution (0.0432 gms Fe/ml.)-(65.5ml.)

Barium acetate monohydrate solution (0.348 gms/ml)-(60 ml)

Hydrogen peroxide (27.5% - (240 ml.)

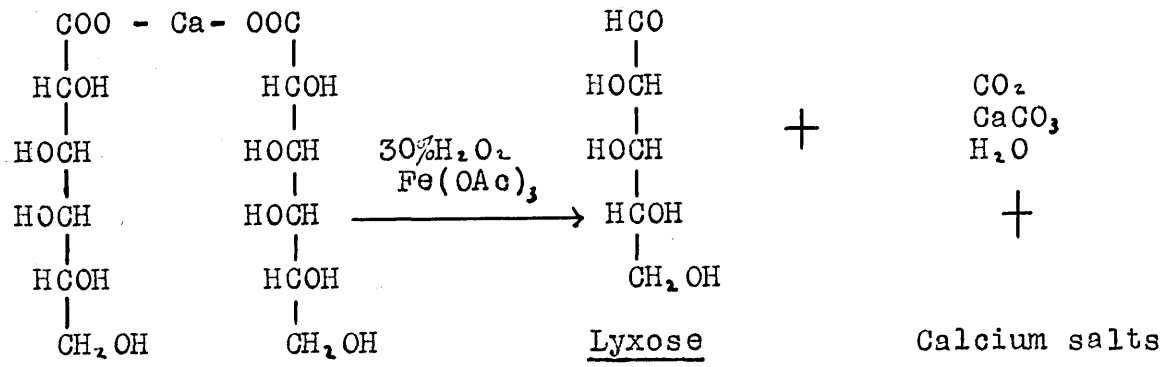
Methanol - (1865 ml.)

Ether - (670 ml.)

Absolute alcohol - (440 ml.)

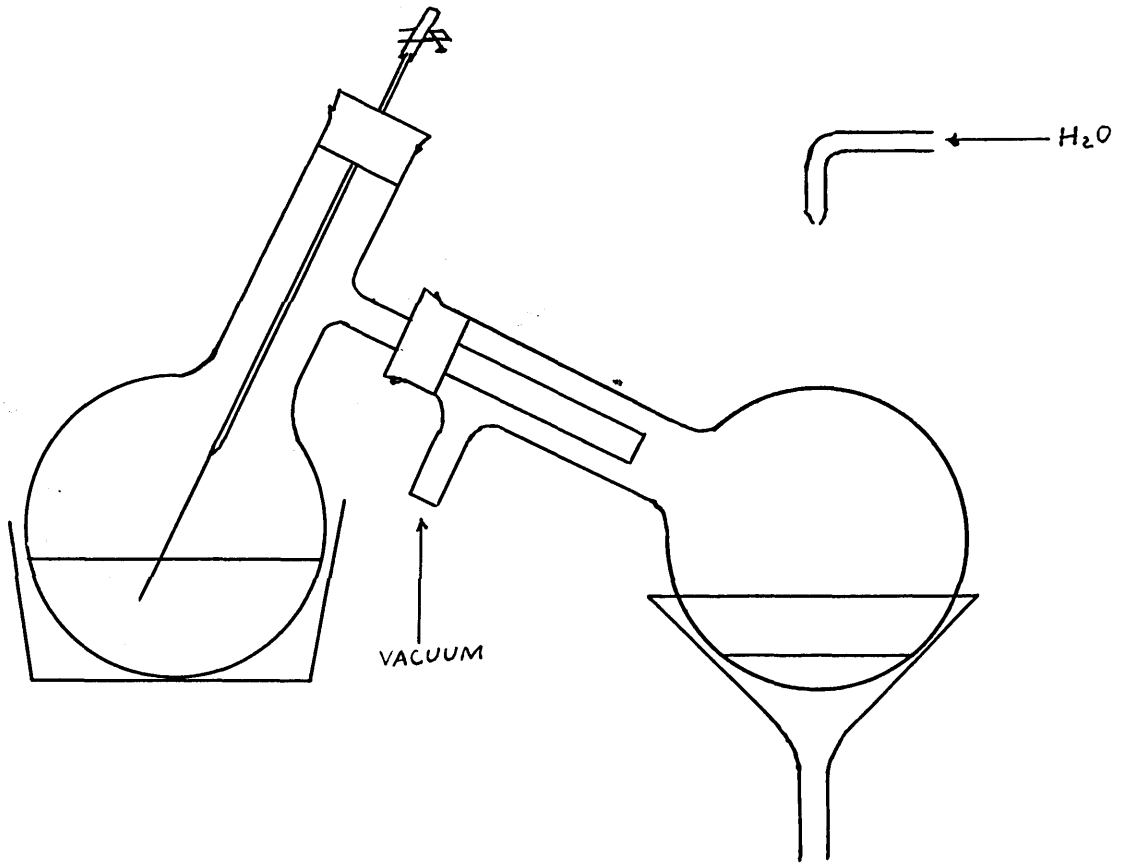
Acetone - (250 ml.)

Reaction:



Calcium galactonate — Lyxose — Calcium salts

Apparatus: A system for evaporating off solvent at low pressures was employed consisting of two three liter distillation flasks connected as shown by the following diagram.



Procedure:

Ferrous sulfate solution (65.5 ml.) was added to two liters of water in a four liter beaker. After stirring, 60 ml. of barium acetate solution was added producing a yellowish precipitate. To this solution was now added 200 grams of calcium galactonate, and with continual stirring the contents heated to the boiling point. Heating was then stopped and the precipitate allowed to settle. The supernatant liquid was then

filtered, by means of a Buchner funnel, through a filter paper coated with filtercel, and the filtrate was diluted with 250 ml. of water after washing the filter with 50 ml. of water. On reaching a temperature of 34° C., 120 ml. of 27.5% hydrogen peroxide (Albone) was added. This resulted in the copious evolution of gas, and a rise in temperature reaching a maximum of 56° in a few minutes. On cooling a second portion of hydrogen peroxide (120 ml.) was added and the resultant amber liquid allowed to stand over night. The following day a precipitate was noticed to have collected on the bottom of the beaker, and the entire solution was filtered through charcoal. The next operation was the evaporation of the solution under vacuum to a volume of 125 ml. to which was added 1500 ml. of warm methanol. On addition of the methanol a grayish flocculent precipitate resulted, which was collected on a carbon filter and washed with 300 ml. of methanol. To the clear filtrate 670 ml. of ether was added which produced a second grayish precipitate. This was again removed from the solution by filtration through a carbon filter. The complete methanol solution was now concentrated under vacuum to a thick, sticky sirup and then taken up with 300 ml. of absolute alcohol. To this solution was added 250 ml. of acetone which produced a third gray flocculent precipitate which was allowed to stand for a day and then removed by filtering through carbon. The filtrate was again reduced to a thick sirup in a vacuum and taken up this time with 65 ml. of methanol. After futile attempts to crystallize, the solution was evaporated down about 20 ml. by subjecting it to a current of air while

gently heating on a steam bath. Seed crystals were then added, and on placing the solution in the ice box over-night it was found to have completely solidified. The crystals removed by filtration were dried in the atmosphere and the specific rotation obtained using 0.4312 gms. of sugar. $[\alpha]_D^{25}$ -12.5°. Further drying was accomplished in a vacuum oven at 70° for two hours. The rotation obtained after this treatment was higher and considered satisfactory, $[\alpha]_D^{25}$ -13.3°, the value recorded in the literature is $[\alpha]_D^{25}$ -14.° The weight of d-lyxose obtained was 18.1 gms. having an uncorrected melting point range of 103.5°-104.° The yield was 12.9% based on the theoretical yield and 60.5% based on the possible yield.

Discussion: This preparation is a modification of Ruff's degradation making use of hydrogen peroxide in the presence of ferric acetate. (XII) The method used was that of R.C. Hockett and C. S. Hudson, which was originally used by them and described in the paper on "Improvements in the Preparation of d-Arabinose from Calcium Gluconate" (XI) It was suggested in this paper as a successful method for preparing d-lyxose. Ferric basic acetate is used as a catalyst and the many calcium salts appearing in the final solution are removed by precipitation with methanol, absolute alcohol, acetone etc., lyxose being one of the most soluble sugars in respect to methanol.

Purification of l-Arabinose

Procedure: The impure arabinose was tested for calcium salts by dissolving a small amount in a slightly alkaline solution and adding oxalic acid. No appreciable turbidity was observed. The

arabinose was dissolved in two-thirds its weight of water by heating on a steam bath and filtered hot through a charcoal filter. To this were added five times its volume of absolute alcohol and the solution seeded and placed in the ice chest. (Actually this procedure was carried out first using only ten grams therefore specific quantities are not mentioned. The specific procedure is recorded in the notebook.) Crystals were produced, but their form indicated impurity. These were recovered from the solution (48.1 gms) dissolved in 24 ml. of water and the hot solution filtered through carbon. To this solution 220 ml. of glacial acetic acid were added and the solution set aside to crystallize. The mother liquor of the alcohol crystallization was concentrated under vacuum to a sirup and taken up in 15 ml. of water. To this, 100 ml. of acetic acid was added and the solution allowed to crystallize. The total amount of l-arabinose procured from the acetic acid crystallization (33.5 gms) was again dissolved in water (22 ml.) and the hot solution filtered through carbon. To this filtrate, 215 ml. of absolute alcohol were added and the solution placed in the ice-box to crystallize. The crystals obtained were found to have a specific rotation $[\alpha]_D^{\cdot}$ 96.1° after drying for two hours in a vacuum oven at 70° C. Since the rotation of l-arabinose recorded in the literature is higher $[\alpha]_D^{\cdot}$ 105°, there is evidently an impurity present, However, other observers (Hockett, Goldman and Hudson) after subjecting l-arabinose, obtained from certain sources to a rigorous purification, also obtained a low value

for the optical rotation. Evidence collected by them as to the indentification of this impurity indicates that it is probably d-arabinose, and if such is the case, no futher purification need be attempted because the chemical properities of the antipodes are the same and would yield identical results in the analytical procedure to be undertaken. Assuming this no further purification was attempted.

Purification of d-Arabinose

Procedure: The impure arabinose (35 gmsl) found to have a rotation $[\alpha]_D = -102.5^\circ$ was dissolved in 15 ml. of hot water and filtered through carbon. To the filtrate 175 ml. of absolute alcohol were added and the solution allowed to crystallize at room temperature. Crystals were obtained (29 gms.) and were dried in a vacuum oven at 70°. These possessed an optical rotation $[\alpha]_D = -104.5^\circ$ and were considered sufficiently pure (recorded value $[\alpha]_D = -105^\circ$.)

Purification of Xylose

Procedure: Impure Xylose (40 gms.) of rotation 17.6 was dissolved in 35 ml. of water and 35 ml. of 95% alcohol added to the solution. On standing 26.5 gms. of crystals were collected, which after drying in a vacuum oven at 70° for two hours were found to possess a rotation $[\alpha]_D = 19.1^\circ$. This was considered sufficient purity as the recorded value is $[\alpha]_D = 19^\circ$.

Preparation of Hydrochloric acid Solution

Procedure: The method used in making up this solution was to obtain a quantity of solution approximately 12% HCl (3.49 N) by adding the required amount of concentrated acid to a selected

volume of water and adjusting the concentration by titrating samples with standard sodium hydroxide solution (1.018 N). It was considered sufficiently accurate to adjust the acidity so that the volume of base used in titrating differed by less than one milliliter from the calculated volume required to neutralize a 12% hydrochloric acid solution.

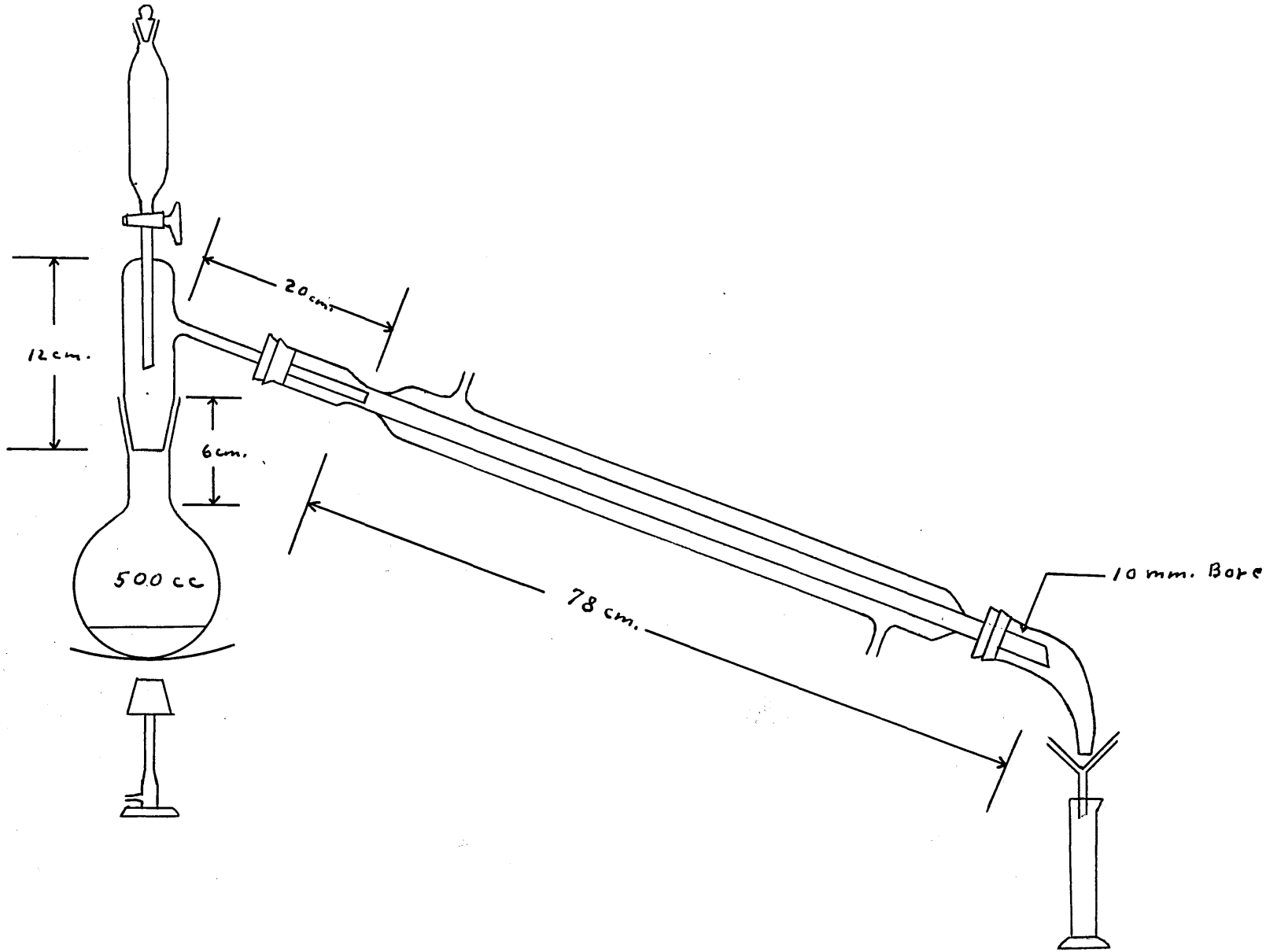
Preparation of Phloroglucinol Solution

Prodedure: Phloroglucinol was first tested for diresorcin by adding to a small amount a few drops of acetic anhydride and heating the mixture to boiling. Concentrated sulfuric acid was then added by drops and the solution examined for a violet coloration. None was observed to be present, so preparation of the solution (which involves a purification) was continued. Phloroglucinol (11gms.) was dissolved in 300 ml. of 12% hydrochloric acid by heating, and more of the same concentration acid added to make the resulting volume 1500 ml. This solution was originally allowed to stand a week before it was used, and always filtered immediately before use.

The Actual Determination Procedure

As the method of pentose determination is empirical the type of apparatus used, and the aquisition of consistent technique in the procedure, are important factors for any degree of accuracy. The apparatus can best be described with a diagram (Fig.4) It consists of a 300 ml. flask with a ground glass joint connected to a glass distillation head with an inserted dropping funnel. Connected with a rubber stopper to the distillation arm is a 78 cm. condenser with an adapter attatched. The distillate

Figure 4



is collected through a small filter paper in a funnal supported by a graduate (50ml.) A bunsen flame protected against drafts with a turret top furnished the heat, while a wire gauze served to protect the flask from superheating. The exact procedure in determinations of known pentoses and of d-lyxose was as follows: The weighed sample of pentose is placed in the flask along with a small amount of paraffin to prevent excessive bumping. To this, 100 ml. of 12% hydrochloric acid is added and distillation maintained at the rate of 30 ml. of distillate in ten minutes (regulated by adjusting burner). On collection of 30 ml. of distillate, the graduated receiver is removed and another substituted. Thirty milliliters more of 12% acid solution is added through the dropping funnel (previously graduated) and the distillates, successively collected in the graduates, are poured into a 500 ml. erlenmeyer flask which is kept stoppered with a rubber stopper. This process is continued until 360 ml. of distillate have been collected; this is then treated with the amount of phloroglucinol solution required for theoretical precipitation (wt. of pentose 115)milliliters plus two or three milliliters extra, the volume is adjusted to 400ml. by adding the required amount of 12% hydrochloric acid, and the solution is allowed to stand over-night. The precipitate formed is collected on asbestos in Gooch crucibles which have been previously dried in an oven at 105°-110° for four hours and weighed. The crucibles plus the precipitate are dried and weighed under the same conditions as before.

B. Results of Determinations of Xylose and Arabinose

The following tables represent data obtained by treating different weighed amounts of xylose and arabinose according to the analytical procedure and recording the amount of phloroglucide precipitate produced. These weights of precipitate were compared with those given by Krober's Tables which contain the amounts of precipitate to be expected from definite amounts of xylose or arabinose.

Grams of Xylose	Grams of Ppt.	Duplicate error in gms.	Kröber's Table Value	Error with Table
0.3000	0.3199			
0.3000	0.3194	0.0005		
0.1000	0.1044			
0.1000	0.1034	0.0010	0.104	0.9%
0.0400	0.0422			
0.0400	0.0418	0.0004	0.038	8.5%

Grams of Arabinose	Grams of Ppt.	Duplicate error in gms.	Kröber's Table Value	Error with Table
0.0500	0.0451			
0.0500	0.0446	0.0005	0.040	11.2%
0.2000	0.1851		0.177	4.6%

Interpretation: It is evident that the results obtained deviate considerably from those recorded in Kröber's Table in spite of the fact that the same procedure and similar apparatus were used in obtaining them. The fact that the duplicate results checked with reasonable accuracy made it seem probable that the technique was not at fault. It remained to obtain some sort of

evidence with the data aquired, to show that the deviation from Kröber's values was due to some constant apparatus error. This was done indirectly by assuming the apparatus error to be a constant one and then considering the equation $A=a+bp$ where "A" represents the weight of the pentose, "a" and "b" are constants, and "p" is the weight of the precipitate formed. (XIII) This represents a linear relationship with "b" as the slope. In a graph where the amount of pentose reacting would be plotted against the amount of phloroglucide precipitate formed this equation would not represent the entire curve, but could be assumed to accurately represent sections of the curve. As this curve would change in slope in a similar manner to the change in slope of the curve shown in figure (2) (the ratio of the furfural formed to the pentose used plotted against the pentose used), the magnitude of the change at different sections could be approximately predicted by examining the curve of figure (2). The data obtained allowed the calculation of two significant values of the slope "b" for two distinct sections of the curve, this was accomplished by solving two sets of simultaneous equations obtained by substituting corresponding values of "A" and "p." With reference to the graph of figure (2) it is obvious, according to the following short table obtained from the data, that the size of the slope is that expected over the two given ranges.

Grams of Pentose		Value of "b"
0.0400	0.1000	0.9694
0.1000	0.3000	0.9272

This evidence was the basis of the conclusion drawn that probably the explanation of the deviation of the weights of precipitate formed with those recorded in Kröber's table was that a standard error of determination existed that was of different value than the one occurring when Kröber's tables were prepared. Since data and time were lacking for a complete standardization of the apparatus, which would involve subjecting numerous different weights of xylose and arabinose to the previously described analytical treatment, it was decided to proceed with the determinations of weights of lyxose in hopes of obtaining enough data, which with the data already obtained on xylose and arabinose, would permit a good comparison of the characteristic yields of furfural attaining the best accuracy possible with the given data and apparatus.

C. Results of Determinations of d-Lyxose

The different weights of lyxose were selected arbitrarily, attempting, as the data was continuously aquired, to cover as adequately as time would permit, a range similar to that covered by the values in Kröber's tables. The results are presented in three forms consisting of a table, equation and a graph (figure 3). The table shows the actual results recorded, while the graph shows the deviation in the yields of furfural produced from identical weights of the three sugars arabinose, xylose, and lyxose. The equation indicates approximately the weight of phloroglucide expected from different amounts of lyxose.

Weight of d-Lyxose in Grams	Weight of Precipitate in Grams
0.0100	0.0080
0.0200	0.0173
0.0200	0.0172
0.0300	0.0264
0.0500	0.0443
0.0700	0.0604
0.1000	0.0915
0.1000	0.0911
0.1500	0.1295
0.2000	0.1749
0.2000	0.1729
0.3000	0.2598

Equation: $A=0.0044+P\ (1.142)$

III RESULTS AND DISCUSSION

A. Interpretation of Results

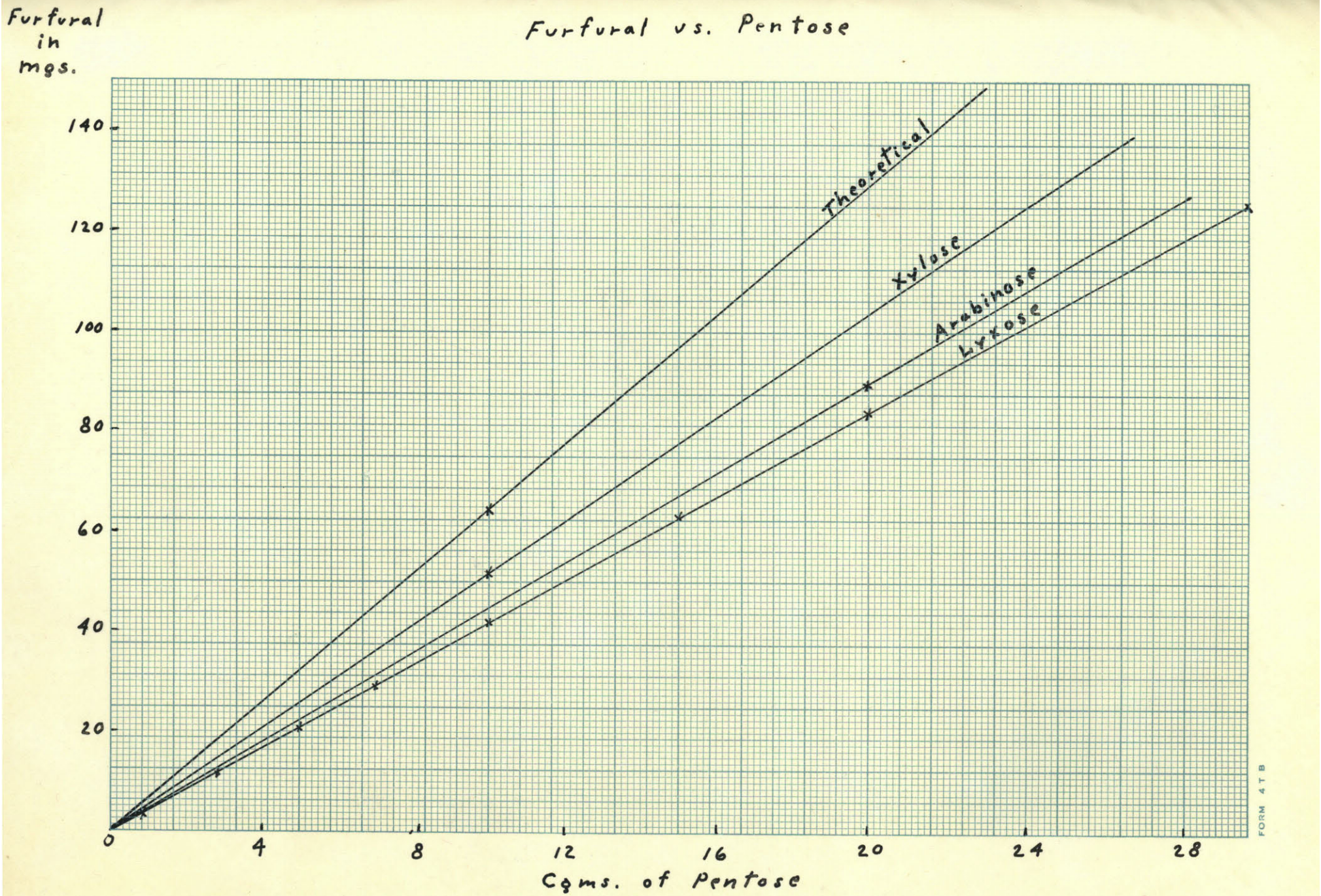
Tabulation of the results obtained in the calculation of the approximate equation throw a little more light on the actual mathematical relationship of the formation of furfural from lyxose. The constants "a" and "b" of the equation $A=a+bp$, discussed on page twenty-one were calculated from the data obtained on lyxose and their values recorded as follows:

A=gms. lyxose	a=horizontal displacement	b=slope
0.01 to 0.02	0.0013	1.086
0.02 to 0.03	0.0013	1.086
0.03 to 0.05	0.0004	1.144
0.05 to 0.07	0.0052	1.243
0.07 to 0.10	0.0114*	0.973
0.10 to 0.15	0.0195*	1.309
0.15 to 0.20	0.0042	1.127
0.20 to 0.30	0.0025	1.164

*These values suggest that the curve probably is slightly convex to the "X" axis instead of the straight line that appears on the graph. More accurate data would be required to present an exact picture, however this seems a reasonable prediction. The approximate equation A=0.0044+p (1.142) was constructed using average values of a and b calculated from the data.

On the graph the amounts of furfural corresponding to the weights of phloroglucide precipitate were calculated by multiplying the weight of the precipitate plus 0.0052 by the chemical factor (0.4700). The figure (0.0052) represents the amount of furfural phloroglucide soluble in 400 ml. of 12% hydrochloric acid under the conditions of the determination. (I) The number (0.4700) is the ratio of the molecular weight of furfural to that of the phloroglucide precipitate. These amounts of furfural are plotted directly against the amounts of lyxose needed to produce them (figure 3). Since corresponding curves of xylose and arabinose when plotted on this scale are shown to appear as practically straight lines (figure 1), their

Figure 3


Furfural vs. Pentose
Furfural in mgs.
140
120
100
80
60
40
20
0
4
8
12
16
20
24
28
Cgms. of Pentose
Theoretical
Xylose
Arabinose
Lyxose
FORM 4 T B

curves were constructed on this graph (figure 3) by plotting one point obtained from experimental data and connecting it to the origin. A line representing the theoretical yield of furfural (64%) has been drawn for further comparison. Although not enough duplicates were made to get a very exact idea of the accuracy, the fact that the points plotted form a fairly straight line is evidence that the accuracy is at least within the scale of the plot. Obviously, the yields of furfural from lyxose are distinctly less than those of either arabinose or xylose. The significance of this result merits a brief discussion of Tollen's method and Kröber's Table (XIV)

B. Defects of Method

It may be stated the method of Tollen's is by far the most widely used method, and the only method accepted by the Association of Official Agricultural Chemists of America. Numerous others have been suggested, as mentioned in the introduction, but so far none have come into extensive use due either to defects or mere lack of evidence in favor of their accuracy. Several defects of the "phloroglucinol method " are indicated below. Many constituents of plants yield interfering substances on analytical treatment. (IV),(XVII) Methyl furfural, hydroxymethyl furfural from hexosans, and formaldehyde from lignin are frequently found to be produced, all of which form insoluble precipitates with phloroglucinol. This difficulty is usually overcome by use of some modification where the precipitates are washed with alcohol which would remove the above "false precipitates. (IV) The fact that the method is empirical

introduces all sorts of difficulties, the time involved being also a decided practical disadvantage.

On considering Kröber's table, more defects are unearthed. The tables deal only with arabinose and xylose and consist of a series of weights of phloroglucide precipitate and the corresponding amounts of xylose, arabinose, xylan, and araban necessary to produce them. Two additional columns are labeled "Pentoses" and "Pentosans", which are constructed by assuming equal amounts of xylose and arabinose (pentoses), or equal amounts of araban and xylan (pentosans) to exist in samples known to contain both constituents. These values are made to correspond with the weights of phloroglucide that would be produced by such mixtures. This error of assumption is undoubtedly a large one in materials of high pentose content. A similar possible error is brought out by the fact that lyxose, since it produces lower yields of furfural than either xylose or arabinose, might cause an appreciable error, if not detected but present in a reasonable amount in material subjected to this method of analysis. At any rate if lyxose is discovered in nature, it would be profitable to carry out more extensive reasearch to provide some method for its accurate determination in plant materials. As there are continual efforts in progress for improvement or reconstruction of the method for pentose determination perhaps future investigators will have better tools to work with. (XV),(XVI). At this particular time, perhaps the next important step in this field would be the procuring of similar data on the pentose ribose which is already known to exist in many plants but in minute quantities.

IV SUMMARY

Data was obtained on the quantitative formation of furfural from d-lyxose employing the standard analytical procedure for pentoses, and by this was shown that lyxose produces lower yields of furfural than either xylose or arabinose.

BIBLIOGRAPHY

I C.A.Browne- Handbook of Sugar Analysis (1912)

II Van Der Haar-Anleitung zum Nachweis zur Trennung und Bestimmung der Monosaccharide und Aldehydsaüre (1920)

III Norman - Biochemistry of Cellulose Polyuronides Lignin etc.

IV Dorèe - The Methods of Cellulose Chemistry (1933)

V Kullgren and Tydèn - Über die Bestimmung von Pentosanen (1929)

VI J.Assoc. Off. Ag. Chem. - Methods of Analysis (1935)

VII Tollens - Abderhalden's Arbeitsmethoden 1909,II,130

VIII Unger and Jäger - Z. Untersuch Lebensm 66, (1933)

IX S. F. Acree- Bur. of Standards Jl. Research Vol.8, (1932) 25 no. 1

X Nelson and Cretcher - J. Amer. Chem. Soc. (1929) 51, 1914

XI R. C. Hockett and C.S. Hudson - J. Amer. Chem. Soc. 56, 1632 (1934)

XII Ruff - Ber., 32,553 (1899); 35, 2360 (1902)

XIII Norris - Biochem. J. (1936), 30, 2146

XIV Tollens and Kröber - J.F. Landwirtsch (1900)

XV E.E.Hughes and Acree - Bur. of Standards Jl. Research Vol. 21, (1938) 327

XVI H.F.Launer and W.K.Wilson - Bur. of Standards Jl. Research Vol.22 (1939) 471

XVII Pervier and Gortner - Ind. Eng. Chem. 15,1167 (1923)

XVIII Mikrochemie 16, (1934) 87