

Formation of Aromatic Compounds from Carbohydrates. X
Reaction of Xylose, Glucose, and Glucuronic Acid in Acidic Solution at 300°C

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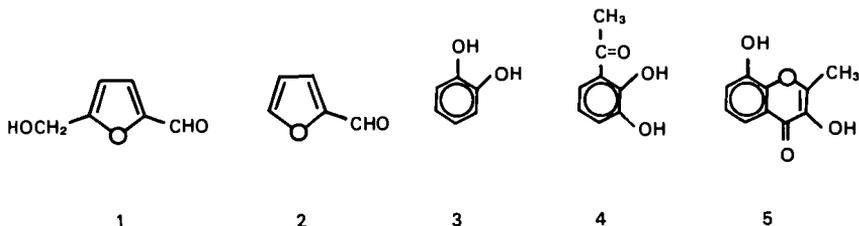
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INTRODUCTION

For several years our respective groups have investigated the formation of aromatic compounds from carbohydrates in aqueous solution at various pH-values under reflux or hydrothermolytic conditions. For instance, previous papers(1-6) in this series concerned the degradation of hexoses, pentoses, erythrose, dihydroxyacetone, and hexuronic acids to phenolic and enolic components. Of particular interest were the isolation and identification of catechols, an acetophenone, and chromones from pentoses and hexuronic acids at pH 4.5 (1,2). The formation of these compounds, as well as reductive acid(7), was found to be more pronounced than that of 2-furaldehyde(2) under acidic conditions. The aromatic precursors of 3 and 4 were also isolated from these reaction mixtures. This is in contrast to the high yields of 2 obtained from pentoses(8) and hexuronic acids(9) at very low pH. Similar products were obtained in lower yield from glucose and fructose under acidic conditions(10). However, the predominant product of these hexoses was 5-hydroxymethyl-2-furaldehyde (1) as would be expected from prior work(11). Surprisingly, similar products are noted at neutral and even alkaline pH with glucose and xylose(12). Previous hydrothermolytic studies of cellulose indicated that certain aromatic products could be obtained when the pH was maintained in the range of 4-11(13). This suggested that aldol condensation, a prime route for the production of aromatics from saccharides, could function under moderately acidic conditions.



The current research was initiated to study the competition between the formation of phenolic compounds (aldol involvement) and that of furans (dehydration and cyclization). Hydrothermolytic (liquefaction) conditions, 5-7.5 minutes at 300°C, were chosen to examine the effect on potential biomass

materials while exposed to mild acid. Xylose and glucuronic acids were previously found to provide higher yields of phenols than glucose. It is also of increasing interest for those involved with the hydrolysis of biomass, including steaming and autohydrolysis under slightly acidic conditions at 170-250°, to obtain substrates for various fermentation processes or as a pretreatment for other uses. It is very likely that the aromatic products, particularly those formed from pentosans and polyuronides, may have an inhibiting effect on fermentation processes. More information, therefore, is needed concerning the formation of aromatic components and their precursors from the high temperature, aqueous processing of biomass.

EXPERIMENTAL

A series of 3.0 mL capacity tubing autoclaves (316 stainless steel) were used. Each tube was 0.6 x 9 cm and sealed with Swagelok™ fittings. The tubes were charged with 0.27 g sodium glucuronate, 0.19 g D-xylose, or 0.22 g D-glucose, respectively. Buffered acid solutions (2.0 mL) were added to the tubes. For instance, sodium acetate-acetic acid buffer was used for the pH 3 to 4 reactions, while a potassium chloride-hydrochloric acid buffer was used for the pH 1.7-1.9 reactions. The void space of each tube was swept with nitrogen prior to insertion into a 300° sand bath. Interior tube temperature as reached 300° within 2.5 minutes, while quenching to below 100° required only 0.1 minute. The solutions after cooling, which in all nine experiments were dark brown, contained minimal or no precipitate. The tube contents were extracted with ethyl acetate, dried, and the solvent was removed. Gas chromatographic analyses were obtained with a Hewlett-Packard 5880A instrument using a DB capillary column.

RESULTS AND DISCUSSION

The yields of the solvent free extracts are presented in Table 1. Column A shows the standard wt.% yields. Column B was formulated to show a loss of

Table 1. Yields of Ethyl Acetate Extracts After Acidic Treatment of Glucose, Xylose, and Glucuronic Acid at 300°

	pH	Time (min.)	A*	B**
Glucose	1.7	5	37	52
Xylose	1.7	5	27	42
	3.6	5	40	62
	3.6	7.5	38	59
Glucuronic Acid	1.9	5	20	41
	3.0	5	22	45
	3.6	5	20	41
	3.6	7.5	31	63
	4.0	5	15	31

*A equals wt.% based on the amount of carbohydrate.

**B equals wt.% based on glucose or xylose minus 3 H₂O, and glucuronic acid minus 3H₂ and CO₂.

three moles of water for glucose and xylose and a loss of one mole of carbon dioxide for glucuronic acid. This represents the conversion of carbohydrates to furan or phenolic components. The standard yields (column A) give mixed results when pH is compared; i.e., xylose shows higher yields at higher pH, while glucuronic acid does not. This may reflect two different mechanisms, however. These solvent extracted yields are rather close to those obtained under basic conditions(13).

There was some change in pH after the acidic hydrothermolysis of glucose, xylose, and glucuronic acid. The aqueous phase of glucose and xylose increased from pH 1.7 to about 2.6 after 5 min at 300°. Those reactions of xylose buffered at pH 3.6 held that acidity level rather well. The pH of the glucuronic acid reactions tended to increase more than those of xylose regardless of buffer; i.e., pH 1.9 to 3.2, 3.0 to 3.4, 3.6 to 3.8, and 4.0 to 5.2. This probably could be partially attributed to the decarboxylation of the glucuronic acid.

Table 2 presents the quantitative results of those components volatile enough for gc analysis. At low pH the furan compounds predominate when both

Table 2. Major Identified Components of Glucose, Xylose, and Glucuronic Acid After Hydrothermolysis at 300° with Various Times and pH

Component	Glucose* pH 1.7 5 min	Xylose pH 1.7 5 min	Xylose pH 3.6 5 min	Xylose pH 3.6 7.5 min	Glucuronic Acid pH 1.9 5 min	Glucuronic Acid pH 3.0 5 min	Glucuronic Acid pH 3.8 5 min	Glucuronic Acid pH 3.8 7.5 min	Glucuronic Acid pH 4.0 5 min
1	19.9	—	—	—	—	—	—	—	—
2	8.4	46.5	6.9	2.9	2.7	0.7	—	—	—
3	—	—	3.5	6.5	3.8	4.2	16.7	4.0	8.5
4	—	—	—	—	0.5	0.5	4.1	0.9	0.6
5	—	0.4	6.3	8.5	2.3	3.3	—	0.7	—

* Values are reported as mole%; oil yields are reported in Table 1; those values not reported are <0.1%.

glucose and xylose are exposed to 300°. This is not unexpected since all pentoses form 2-furaldehyde(2) in high yield when exposed to aqueous acid solution(14). However, the presence of 2 in the glucose reaction mixture is of interest. The major product obtained from hexoses at elevated temperatures and aqueous acid is 5-hydroxymethyl-2-furaldehyde(1) with minor amounts of 2-(hydroxyacetyl)furan(15). The 2-furaldehyde has been detected after acidic

treatment of fructose(16), glucose(15,17), and is a major component after the thermolysis of cellulose in distilled water(13). One plausible explanation for the formation of 2 may involve loss of formaldehyde(18) from glucose with consequent pentose formation. It should be noted that the pyrolysis of 1 does produce a small amount of 2(19). However, the reaction conditions are sufficiently different to suggest a different mechanism for hydrothermolysis.

The xylose results are also notable with the increase of 3 and 5 at pH 3.6 and longer time. In contrast, 2 decreased with increased pH and time. During previous work(1) with xylose in refluxing acid at pH 4.5, 1,2-dihydroxybenzene (3) was not detected. However, 3 has been detected after xylose was exposed to refluxing caustic solution(12). The presence of 3 in basic solutions of xylose was attributed to retro-aldol and re-aldol reactions since both xylose and glucose yielded the same type of products. Unfortunately, this does not explain the presence of 3 in the acidic hydrothermolysis product, but it has been shown that the aldol reaction can occur at pH 4.0(13). Detection of 3,8-dihydroxy-2-methylchromone(5) has been noted previously in xylose solutions at pH 4.5(1,20). Since 5 is a ten-carbon product, it is presumed that at least two moles of xylose were necessary for its composition. Thus, the mole % values of 5 (Table 2) should be doubled to reflect this. Further support for this was recently demonstrated by E. Olsson, N. Olsson, and O. Theander in unpublished work during the preparation of 5 at pH 5 and 100% from 1-¹³C-pentose (prepared by a Kilij synthesis involving erythrose and K¹³CN). The major distribution of the ¹³C-label was at the 2-methyl and C-8a positions.

The results from glucuronic acid do not appear quite as informative as those from xylose. The 2-furaldehyde content decreased with increasing pH; none was observed beyond pH 3.0. Correspondingly, the amount of phenolic components (3 and 4) increased with pH, but reached a maximum at pH 3.6. The decrease of 3 and 4 after 7.5 min at pH 3.6 may be due to instability of those components toward the thermal conditions, however degradation of 3 at pH 4.5 was negligible at 100°(1). The results at pH 4.0 do suggest a contribution from the decreasing acidity. The decrease of 5 with increasing pH is also of interest since it had previously been isolated from glucuronic acid exposed to pH 4.5 and 100°(1,20). The Table 2 values obtained for 3, 4, and 5 from glucuronic acid may also represent only 50% of the mole percentage since each component may require more than one mole of glucuronic acid for its preparation.

Several unidentified components were also observed in the reaction mixtures of hydrothermolized glucuronic acid and xylose. Unfortunately, isolation attempts were not successful for these products. These components (m/e 164 and 162 from glucuronic acid and xylose, respectively) were found in moderate amounts.

It is evident from the results of this research that phenolic products, especially 3, may be obtained by the acidic hydrothermolysis of xylose and glucuronic acid containing materials. The phenolics and 2-furaldehyde could contribute toward the inhibition of fermentation organisms if acidic pretreatment procedures are not carefully controlled.

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