

Formation of Aromatic Compounds from D-Glucuronic Acid and D-Xylose under Slightly Acidic Conditions

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Summary 1,2-Dihydroxybenzene, 2,3-dihydroxytoluene, 2,3-dihydroxybenzoic acid, 2,3-hydroxyacetophenone, 3,8-dihydroxy-2-methylchromone (I), and its precursor 6,7,8,8a-tetrahydro-3,8a-dihydroxy-2-methyl-8-oxobenzopyrone (II) were obtained by reaction of D-glucuronic acid in slightly acidic aqueous solution (the last three products also from D-xylose).

In connection with studies on colour formation produced by degradation of carbohydrates, D-glucuronic acid and D-xylose were treated in an aqueous solution of pH 3.5–4.5 and the low-molecular-weight lipophilic products studied. Except for 3,8-dihydroxy-2-methylchromone (I), isolated in small amounts after heating alginic acid and other polyuronides at 160°,¹ no benzenoid compounds have been reported from acidic degradation of uronic acids or sugars.

From treatment of D-glucuronic acid (pH 3.5, 96°, 48 h) 2-furaldehyde and reductic acid, well known products from acidic treatment, as well as 2-furoic acid, compound (I) (yield 3.5%), and several other phenolic compounds in smaller amounts were isolated pure. The properties of (I) (m.p. 228–230°) and its diacetate were similar to literature values.¹ N.m.r. and mass spectrometric results were in

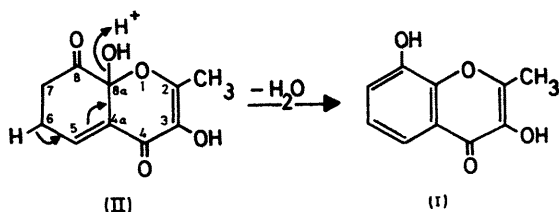
agreement with the structures. Of the other phenolic compounds, four catechols were identified by comparison with authentic samples, namely 1,2-dihydroxybenzene, 2,3-dihydroxytoluene, 2,3-dihydroxybenzoic acid, and 2,3-dihydroxyacetophenone. Two other chromones (C₁₀H₈O₅, with three hydroxy-groups and with m.p. 223–224° and 254–256°, respectively) were isolated and are now being further studied.

The mechanisms involved in the formation of these compounds are complex and obviously include fragmentation and recombination of carbohydrate fragments. A non-aromatic precursor (II) of (I) (C₁₀H₁₀O₅, m.p. 190–192°) was also isolated and identified. Another compound, tentatively identified as 3-acetyl-1-oxocyclohexane-2,3,5-triol (m.p. 149–150°), yielding the 2,3-dihydroxyacetophenone, was isolated in small amounts and is now under investigation. The structure of compound (II) follows from the n.m.r. spectrum (CDCl₃, Me₄Si) of the corresponding diacetate [prepared by treatment of (I) with acetic anhydride–hydrogen chloride]. Compound (II) was transformed into (I) in 50% yield by treatment at pH 4.5 at 96° for 48 h.

Treatment of D-xylose under similar conditions yielded compounds (I) and (II), one of the C₁₀H₈O₅ chromones (m.p. 254–256°), 2,3-dihydroxyacetophenone, and a C₁₀H₈O₄ compound (m.p. 186–191°).

The phenols are readily transformed into coloured products. Most likely, colour reversion of cellulosic material under acidic conditions can occur by such transformations *via* hydrolysis of xylans to uronic acids and pentoses.

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¹ K. Aso, *J. Agric. Chem. Soc. Japan*, 1934, **10**, 1189.

† All solutions were degassed by bubbling nitrogen through them for several hours prior to irradiation.

‡ Satisfactory analyses were obtained for all new compounds.