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CONDENSATION OF AL-SUGARS WITH BARBITURIC ACID

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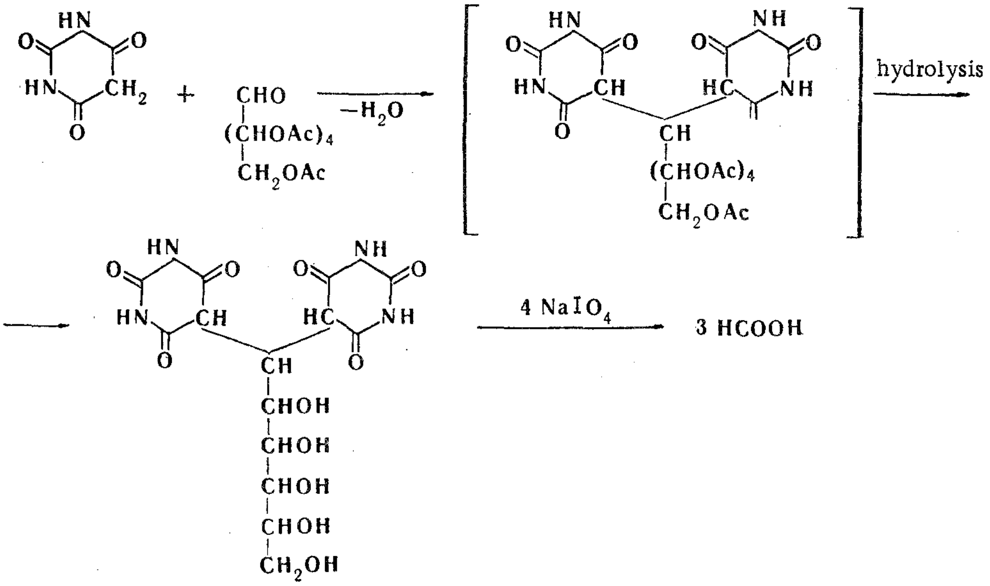
Al-D-glucose and al-D-galactose pentaacetates and al-D-mannose heptaacetate are condensed with barbituric acid in 10% acetic acid to give a bis-product I, while in ethanol, water, and 50% ethanol, a mono-product I is formed.

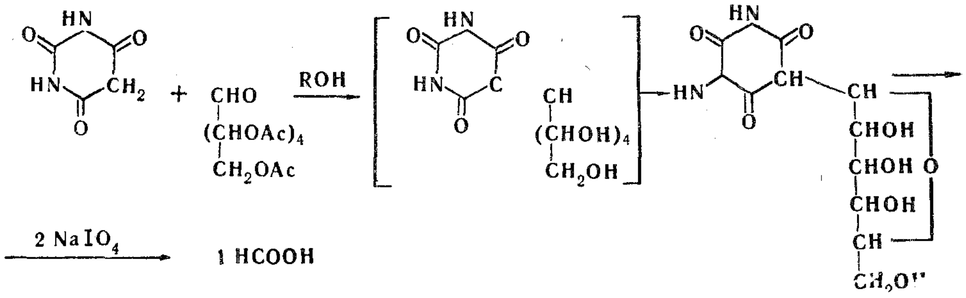
Al-forms of sugars undergo condensations impossible for ordinary monosaccharides, and this explains their enhanced reactivity. Among such reactions is numbered condensation with active methylene compounds [1, 2], barbituric acid being an example of the latter.

Barbituric acid gives mono- and bis-condensation products with aldehydes [3]. Our investigations have shown that barbituric acid can condense with al-forms of the acetates of monosaccharides (D-gucose, D-galactose, D-mannose), to give mono- and bis-products. With a 2:1 (barbituric acid : sugar) reactant ratio and running the reaction in dilute acetic acid, it proved possible to obtain bis products containing deacetylated sugar moieties I, whose structures were demonstrated by elementary analysis and by periodate oxidation of the carbohydrate moiety of the molecule [4].



Running the reaction with equimolecular amounts of the reactants in ethanol (for D-glucose), water (for D-galactose), or 50% aqueous ethanol (for D-mannose) gave mono-products which also had deacetylated sugar moieties (II). In this last case the barbituric acid is not just one of the reactants, but acting as a rather strong acid [5], it deacetylates the carbohydrate part of the molecule.

The monobarbiturates of glucose, galactose, and mannose contain the sugar as an anhydro residue. Such a structure is in accord with the results of periodate oxidation and elementary analysis. Evidently in the reaction process there is anhydro ring closure in the carbohydrate moiety, involving internal addition of the elements of the hydroxyl group at the initially formed double bonds:



The condensation products do not decolorize bromine water, indicating the absence of double bonds in them. Like true C-glucosides, the compounds obtained are not visualized by alkaline silver when paper-chromatographed.

Table 1

Bisbarbituric Acids

Sugar moiety	Charring Temperature, °C	Found, %*			Periodate oxidation		Yield, %
		C	H	N	$NaIO_4$ reacted, mole **	HCOOH formed, mole ***	
D-Glucose	320—330	40.19	3.98	13.28	3.96	3.04	35.2
D-Galactose	280—290	40.14	4.25	13.21	3.96	3.02	57.6
D-Mannose	290—295	40.22	4.20	13.13	3.98	3.02	43

*Calculated for $C_{14}N_{18}N_4O_{11}$: C 41.38; H 4.82; N 9.66%.
**Theory 4 mole.
***Theory 3 mole.

Table 2

Mono-Substituted Barbituric Acids (II)

Sugar moiety	Charring temperature, °C	Found, %*			Periodate oxidation		Yield, %
		C	H	N	$NaIO_4$ reacted, mole **	HCOOH formed, mole***	
D-Glucose	200	41.01	4.52	9.30	1.98	1.08	38.8
D-Galactose	230	41.29	4.72	9.39	1.96	1.06	51.5
D-Mannose	215	41.49	4.44	9.13	1.98	1.08	87.9

*Calculated for $C_{10}H_{14}N_2O_3$: C 41.38; H 4.82; N 9.66%.
**Theory 2 mole.
***Theory 1 mole.

Experimental

(1-Desoxy-1, 1-hexitylidene)bisbarbituric acid. 1.17 g (0.003 mole) al-hexose acetate and 0.77 g (0.006 mole) barbituric acid were dissolved, with heating, in dilute acetic acid (1:10).

The reaction mixture was refluxed for 2 hr, then the AcOH distilled off on a water bath under a water pump vacuum. The residue was treated with warm methanol, the precipitate formed filtered off, and washed with ether. A further quantity of the reaction product was isolated from the methanol solution by adding ether.

The compound was recrystallized from a methanol solution by adding ether. Table 1 gives the results of the syntheses. The reaction products were soluble in water, insoluble in benzene, $CHCl_3$, Me_2CO, AcOEt, dichloroethane. These substances are described for the first time.

5-(1-C-Glycopyranosyl) barbituric acid. 1.3 g (0.003 mole) al-hexose acetate and 0.43 g (0.003 mole) barbituric acid were heated together in 30 ml ethanol (for D-glucose) on a water bath for 8 hr, 30 ml water being used instead of the ethanol for D-galactose, and 30 ml 50% aqueous ethanol for D-mannose. The solvent was then distilled off at 80-90° under a water pump vacuum. The residue was treated with $CHCl_3$, and the precipitate formed filtered off and washed with ether. Solution in methanol followed by addition of ether, led to the isolation of a yellow powder highly soluble in water, insoluble in the usual organic solvents, and which did not decolorize bromine water. The compounds are described for the first time.

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