UDC 547.455 + 547.854 + 542.953 + 543.544

CONDENSATION OF AL-FORMS OF SUGARS WITH THIOBARBITURIC AND IMINO-BARBITURIC ACIDS

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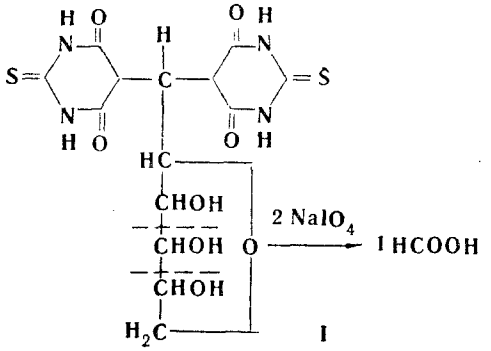
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 5, pp. 773-775, 1966

Fully acetylated al-D-glucose, al-D-galactose, and al-d-mannose condense with thiobarbituric acid in ethanol to give di-products, with deacetylation of the sugar portion, which latter, in the cases of the di-products from glucose and galactose, is a (2, 6) anhydro ring. Condensation of al-D-glucose and al-D galactose with iminobarbituric acid in glacial acetic acid is of the crotonoid type, and gives acetylated monoproducts, while al-D mannose gives a di-product.

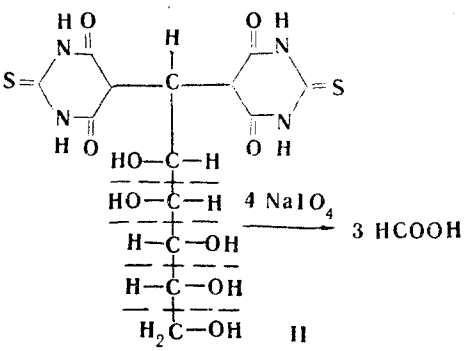
The present authors previously showed [1, 2] that new heterocyclic C-substituted carbohydrates could be synthesized by condensing the fully acetylated al-forms of D-glucose, D-galactose, and D-mannose with heterocyclic compounds containing active methylene groups (4-hydroxycoumarin, barbituric acid). In the present work, the compounds with mobile C–H bonds were thiobarbituric and iminobarbituric acids.

Thiobarbituric acid is more acid than barbituric acid, and hence its methylene hydrogens are more mobile. Unlike what obtains with barbituric acid, its condensation with acetates of al-hexoses gives di-products, but at the same time the thiobarbituric acid acts as a deacetylating agent. The structure of the compounds prepared are proved by elementary analysis and periodate oxidation of the carbohydrate moiety of the molecule . In the glucose and galactose di-products, the sugar is present as a stable pyranose ring (I), in accord with the periodate oxidation and elementary analytical results.

The mannose di-product II contains the sugar in a non-cyclic form.

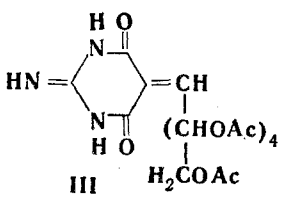


I

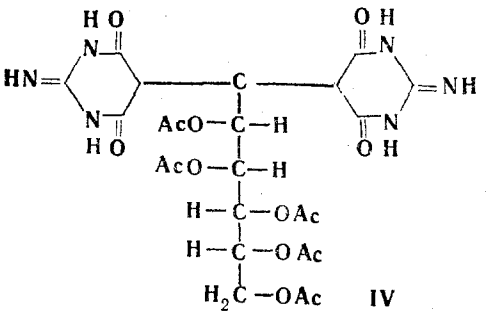


II

Iminobarbituric acid being almost insoluble in ethanol, its condensation with the al-hexose acetates was affected in glacial acetic acid. From the elementary analytical results, and quantitative addition of bromine at the double bond crotonoid condensation between iminobarbituric acid and al-D-glucose or al-D-galactose gives a mono-product III, while al-D-mannose heptaacetate gives a di-product IV.



III



IV

Table 1

Results of the Syntheses

Condensation products	Formula	Found, %				Calculated, %				$NaIO_4$, mole, uptake	Theoretical $NaIO_4$ uptake, mole	HCOOH formed, mole	Theoretical HCOOH, mole	Yield, %
		C	H	N	S	C	H	N	S					
(1-Desoxy-1,1-glucopyranosyl) dithiobarbituric acid	$C_{14}H_{16}N_4O_8S_2$	38.73	3.69	12.60	15.49	38.89	3.70	12.82	14.81	1.92	2	1.08	1	25
(1-Desoxy-1,1-galactopyranosyl) dithiobarbituric acid	$C_{14}H_{16}N_4O_8S_2$	39.00	3.69	12.56	14.95	38.89	3.70	12.82	14.81	1.98	2	1.05	1	30
(1-Desoxy-1,1-mannohexitylidene) dithiobarbituric acid	$C_{14}H_{18}N_4O_9S_2$	37.45	3.77	12.20	14.19	37.33	4.00	12.44	14.22	3.82	4	3.30	3	20

Table 2

Results of the Syntheses

Condensation product	Formula	Found, %			Calculated, %			Bromine uptake, mole	Theoretical bromine uptake, mole	Yield, %
		C	H	N	C	H	N			
5'-(D-Glucosylidene-2,3 4,5,6-penta-O-acetyl) iminobarbituric acid	$C_{20}H_{25}N_3O_{12}$	47.74	4.65	8.20	48.10	5.01	8.42	0.93	1	40
5'-(D-Galactosylidene-2, 3,4,5,6-penta-O-acetyl) iminobarbituric acid	$C_{20}H_{25}N_3O_{12}$	47.95	4.87	8.23	48.10	5.01	8.42	0.96	1	30

Like real C-glycosides, the C-substituted monosaccharides synthesized are not visualized with alkaline silver when paper chromatographed.

Experimental

(1-Desoxy-1,1-hexitylidene)dithiobarbituric acid. 0.39 g (0.001 mole) al-D-glucose acetate or al-D-galactose acetate, or 0.49 g (0.001 mole) al-D-mannose heptaacetate was heated on a water bath for 16 hr with 10 ml EtOH, the solvent removed at 80°–90° under a water-pump vacuum, and the residue recrystallized from AcOH. Addition of ether to the mother liquor gave a further quantity of the compound. The yellow crystals of product did not melt up to 250°, and disolved on heating with MeOH, EtOH, dimethylformamide, and AcOH, were insoluble in acetone, benzene, $CHCl_3$, and dichloroethane. The compounds have not previously been described. The results of the syntheses are set out in Table 1.

5'-(D-glucosylidene-2,3,4,5,6-penta-O-acetyl)iminobarbituric acid. 0.39 g (0.001 mole) al-hexose (D-glucose or D galactose) acetate and 0.14 g (0.001 mole) iminobarbituric acid in 10 ml AcOH were heated for 6 hr on a boiling water bath, the AcOH then distilled off, under a water pump vacuum, and the residue boiled with EtOH. On cooling the solution gave a pale-yellow powder, which was filtered off, and washed with ether. Heat slowly decomposed the products, they were insoluble in most organic solvents. They have not previously been described. The results of the syntheses are given in Table 2.

(D-mannosylidene-1-desoxy-2,3,4,5,6-penta-O-acetyl) diiminobarbituric acid. The above method was applied to 0.49 g al-D-mannose heptaacetate and 0.29 g (0.002 mole) iminobarbituric acid to give a 15% yield of a yellow crystalline product, which decomposed on heating, and was insoluble in most organic solvents. The compound is described for the first time. Found: C 45.77; H 5.04; N 13.20%. Calculated for $C_{24}H_{30}N_6O_{14}$: C 46.00; H 4.79; N 13.45%.

REFERENCES

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2. Yu. A. Zhdanov and G. V. Bogdanova, KhGS [Chemistry of Heterocyclic Compounds], 56, 1966.

19 April 1965

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