A Convenient Method for the Preparation of 3-Deoxyhexosones and 3-Deoxypentosone.

Sir:

The 3-deoxyosones were proved as intermediates in the melanoidin formation of sugars by interaction with amino compounds¹⁾, and a considerable amount of 3-deoxy-glucosone was isolated as its 2,4-dinitrophenylosazone from soy and miso²⁾. Anet³⁾ prepared the two 3-deoxy-D-hexosones by degradation of di-D-fructose- (and di-D-tagatose-) glycine* in dilute aqueous solution at pH 5, and, Machell and Richards⁴⁾ prepared 3-deoxy-D-glucosone by treatment of 3-O-benzyl-D-glucose with 0.05 N sodium hydroxide. The only possible 3-deoxypentosone in its free form, however, remained unknown. In the present communication, the preparation of the two 3-deoxy-D-hexosones and the 3-deoxy-D-pentosone by a simpler method is reported.

D-Xylose was heated with an equimolar amount of *n*-butylamine in methanol with occasional stirring at 60~65°C for twenty minutes, cooled to room temperature and then an equimolar amount of acetic acid was added and warmed at 55°C for seven minutes. Decolorization with active carbon and decationization on a column of Dowex 50-X4 gave a mixture of 3-deoxypentosone, xylose and small amounts of impurities. Separation by chromatography on a cellulose column gave the pure 3-deoxy-D-pentosone (I) as colorless solid, $[\alpha]_D^{20} - 13.4^\circ \rightarrow -17.2^\circ$ (c, 1.86 in water), *Anal.* Found: C, 45.40; H, 6.68. Calcd. for

I: R=H, IIa & IIb: R=CH₂OH.
(Open-chain form)

C₅H₈O₄: C, 45.45; H, 6.10%. D-Glucose was similarly treated except the warming time at 55°C of two hours yielding 3-deoxy-D-glucosone (IIa, 3-deoxy-D-erythrohexosone) as white amorphous powder, $[\alpha]_D^{17} - 2.6^\circ \rightarrow +1.2^\circ$ (c, 6.6 in water), *Anal.* Found: C, 44.29; H, 5.89. Calcd. for C₆H₁₀O₅: C, 44.44; H, 6.22%. In the case of D-galactose, the warming time at 55°C was sixty minutes and 3-deoxy-D-galactosone (IIb, 3-deoxy-D-threohexosone) as white amorphous powder, $[\alpha]_D^{18} + 10^\circ \rightarrow +12.7^\circ$ (c, 5.2 in water), *Anal.* Found: C, 44.77; H, 6.49. Calcd. for C₆H₁₀O₅: C, 44.44; H, 6.22%, was isolated.

Three 3-deoxyosones were extremely hygroscopic, but readily gave crystalline osazones by the reaction with substituted phenylhydrazines (Table I). These 3-deoxyosones showed the same color as parent sugars by aniline hydrogen phthalate, and the color reactions with 2-thiobarbituric acid in dilute phosphoric acid solution were positive. In addition, they revealed the activity in the Strecker degradation with α -amino acid. 3-Deoxypentosone was more unstable showing the stronger reactivity than 3-deoxyhexosones.

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* 1, 1'-(Carboxymethylimino)-bis-[1-deoxy-D-fructose (and -D-tagatose)].

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TABLE I. SUBSTITUTED PHENYLOSAZONES OF 3-DEOXYOSONES

Osone	Substituent	m.p. (°C, dec. uncorr.)	[α] _D		
			degrees	conc. (in dioxane)	temp. (°C)
3-Deoxy-D-glucosone	2, 4-Dinitro-	253~254	+757	0.214	17
	Triacetate of 2, 4-dinitro-	179	+488	0.254	22
	<i>p</i> -Nitro-	251~253	+383	0.188	17
3-Deoxy-D-galactosone	2, 4-Dinitro-	259~260	-613	0.16	17
	Triacetate of 2, 4-dinitro-	203	-349	0.186	21
3-Deoxy-D-pentosone	2, 4-Dinitro-	257~258	+326	0.218	20
	Diacetate of 2, 4-dinitro-	188~189	+427	0.262	22
	<i>p</i> -Nitro-	259~260	+45	0.448	20

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