

Found: C, 66.5; H, 6.1; N, 4.0) of the ketone was reduced to the *dl*-amine, characterized through its *hydrochloride* (m. p. 258–259°; *Anal.* Calcd. for $C_{19}H_{24}NClO_4$: C, 62.4; H, 6.6; Cl, 9.7. Found: C, 62.1; H, 6.6; Cl, 9.6) and *N*-acetyl derivative (m. p. 178–179°; *Anal.* Calcd. for $C_{21}H_{26}NO_5$: C, 67.9; H, 6.8. Found: C, 67.7; H, 6.6)

Colchicol methyl ether [*hydrochloride*, m. p. 258–259°, $[\alpha]^{20}_D - 88.7^\circ$ (*c* 0.76, ethanol); *N*-acetyl derivative, m. p. 201–202°, $[\alpha]^{20}_D - 86.6^\circ$ (*c* 0.67, methanol)] was racemized by heating its *N*-benzylidene derivative [m. p. 145–146°; *Anal.* Calcd. for $C_{26}H_{27}NO_4$: C, 74.8; H, 6.5. Found: C, 75.0; H, 6.3; $[\alpha]^{25}_D + 23.3^\circ$ (*c* 0.73, dioxane)] with methanolic benzyltrimethylammonium hydroxide. The *dl*-colchicol methyl ether then isolated by acid hydrolysis formed a *hydrochloride* (m. p. 258–259°; *Anal.* Calcd. for $C_{19}H_{24}NClO_4 \cdot OCH_3$, 33.9. Found: OCH_3 , 33.4) and *N*-acetyl derivative (m. p. 180–181°) both of which had zero rotation and gave no depression in mixed melting point determinations with the corresponding synthetic compounds. In addition, the ultraviolet and infrared absorption spectra of natural *l*-colchicol methyl ether hydrochloride and *N*-acetyl derivative were identical with those of the synthetic *dl*-counterparts.

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A NEW KETOSE SYNTHESIS

Sir:

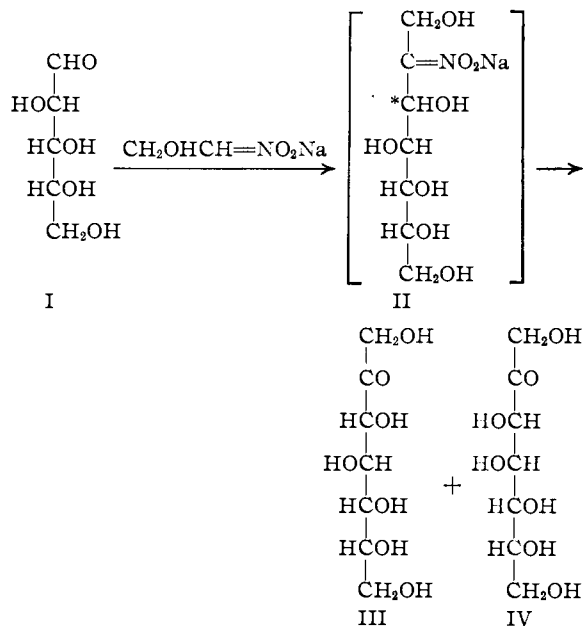
Heretofore, only a single general method has existed for the synthesis of ketose sugars from aldose sugars of lower carbon content. The key reaction of this synthesis is the condensation of diazomethane with a substituted aldonyl chloride to produce a substituted diazodesoxyketose.¹ Hydrolysis of the latter then produces a ketose sugar containing one more carbon atom than the aldose precursor of the substituted aldonyl chloride. The synthesis is generally applicable to the acetylated aldonyl chlorides.² The yields afforded by the individual reactions of this synthesis are satisfactory. However, the number of

(1) Gätzi and Reichstein, *Helv. Chim. Acta*, **21**, 186 (1938).

(2) Wolf from, Waisbrot and Brown, *THIS JOURNAL*, **64**, 2329 (1942).

consecutive reactions involved is relatively large and, consequently, the over-all yield of higher-carbon ketose from aldose is low.

It has now been observed that an aldose sugar may be converted to a mixture of two ketose sugars containing two additional carbon atoms by a sequence of only two reactions: The addition of sodium *aci*-2-nitroethanol to *D*-arabinose (I) produced the amorphous seven-carbon sodium *aci*-nitroalcohols (II). Decomposition of the mixed salts with aqueous sulfuric acid then gave a mixture of *D*-glucoheptulose (III), and *D*-mannoheptulose (IV). From 5 g. of *D*-arabinose



there was obtained 1.6 g. (23%) of the mixed, crystalline heptuloses. Fractional crystallization produced the pure ketose sugars showing the following constants: *D*-glucoheptulose,³ m. p. 170–172°, $[\alpha]^{25}_D 67.4^\circ$, in water, *c* 2; *D*-mannoheptulose,⁴ m. p. 151–152°, $[\alpha]^{25}_D 29.4^\circ$, in water, *c* 2.3.

The method should be generally applicable for the synthesis of higher-carbon ketose sugars from aldose sugars.

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(3) Austin, *ibid.*, **52**, 2106 (1930).

(4) LaForge, *J. Biol. Chem.*, **28**, 511 (1917).