

examined proved similarly inert.²³ Both phenyl triflate and *p*-methoxyphenyl triflate²⁴ were stable to the action of acetic acid for 1 week at 200°; no trifluoromethanesulfonic acid was liberated, and the starting materials were recovered in good yields. Prolonged heating (>1 week) in trifluoroacetic acid at 125° caused complete destruction of the substrates, but less than 1% of the theoretical amount of triflic acid was liberated. Work-up after 4 days under the same conditions gave unreacted starting material as the only substance detectable by glpc. The observed inertness of these aryl triflates provides good evidence that the solvolyses recorded in Table I proceed by alkyl-oxygen and not sulfur-oxygen cleavage.

In summary, use of the triflate leaving group offers the following advantages: (1) systems that are sluggish with ordinary leaving groups can now be studied under less strenuous conditions—conditions which avoid side reactions and permit more sensitive studies (*e.g.*, isotope effects) to be carried out; (2) a number of systems previously found “inert” can now be studied solvolytically.

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(23) Professor A. Streitwieser has also found phenyl triflate to be unreactive in trifluoroethanol (private communication).

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(25) American Chemical Society, Petroleum Research Fund Fellow, 1968–1969.

(26) American Machine and Foundry Fellow, 1967–1969.

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5-Acetamido-3,5-dideoxy-D-galacto-octulosonic Acid, an Eight-Carbon Analog of N-Acetylneuraminic Acid¹

Sir:

We wish to report the synthesis of 5-acetamido-3,5-dideoxy-D-galacto-octulosonic acid (**1**), an eight-carbon analog of *N*-acetylneuraminic acid (NANA) (**2**), and the observation that **1** is a substrate for NANA aldolase.

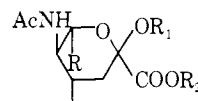
The condensation of 2-acetamido-2-deoxy-D-lyxose² (**3**) with di-*t*-butyl oxaloacetate (**4**) by the general procedure of Kuhn and Baschang³ gave 5-acetamido-3,5-dideoxy-D-galacto-octulosonic acid (**1**). The analog **1**

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(2) R. Kuhn and G. Baschang, *Ann.*, **628**, 193 (1959).

(3) R. Kuhn and G. Baschang, *ibid.*, **659**, 156 (1962).

had the following properties: mp 167–170° dec (microcrystalline powder from methanol-ether), $[\alpha]^{24D} - 53.2^\circ$ (*c* 1.73, water). *Anal.* Found: C, 42.90; H, 6.23; N, 4.88. The pure analog **1** migrated as a single spot when subjected to paper chromatography (in two different solvent systems) or thin layer chromatography.



1, R = $\begin{array}{c} | \\ \text{---} \\ | \\ \text{CH}_2\text{OH} \end{array}$; R₁ = R₂ = H

2, R = $\begin{array}{c} | \\ \text{---} \\ | \\ \text{CH}_2\text{OH} \end{array}$; R₁ = R₂ = H

5, R = $\begin{array}{c} | \\ \text{---} \\ | \\ \text{CH}_2\text{OH} \end{array}$; R₁ = R₂ = CH₃

6, R = $\begin{array}{c} | \\ \text{---} \\ | \\ \text{CH}_2\text{OH} \end{array}$; R₁ = CH₃, R₂ = H

7, R = $\begin{array}{c} | \\ \text{---} \\ | \\ \text{CH}_2\text{OH} \end{array}$; R₁ = CH₃, R₂ = H

8, R = CH₂OH; R₁ = CH₃, R₂ = H

Assignment of structure **1** to the analog was based on the following data: (a) the analog reacted with methanol in the presence of Dowex-50 (H⁺) resin to give a methyl ester, methyl glycoside derivative **5** (compound **5** was assigned the β configuration for the reasons described under e), mp 215° dec, $[\alpha]^{25D} - 64.3^\circ$ (*c* 2.46, methanol) (*Anal.* Found: C, 46.61; H, 6.85; N, 4.42); (b) reaction of the analog with O-phenylenediamine yielded a 2-ketodihydroquinoxaline derivative,⁴ mp 217–219° dec, $[\alpha]^{26D} - 111.9^\circ$ [*c* 0.32, dimethyl sulfoxide-water (1:1)] (*Anal.* Found: C, 54.61; H, 6.17; N, 11.78); (c) the chromophores developed in the direct Ehrlich⁵ and Warren⁶ assays exhibited visible spectra essentially identical with those produced by NANA under similar conditions; (d) the infrared spectrum and periodate consumption were consistent with the assigned structure; and (e) the assignment of the configuration of C-4 and C-5⁷ was based on the fact that the β-methyl glycoside of NANA (**6**) and the methyl glycoside of the eight-carbon analog **7** (obtained by dilute NaOH pretreatment of **4**) were degraded, by periodate treatment, then NaBH₄ reduction, to the same seven-carbon methyl glycoside **8** (previously reported by two groups^{4,8}).

The eight-carbon analog **1**, very interestingly, has proven to be a substrate for the NANA aldolase isolated from *Clostridium perfringens*. The rate of enzymatic decomposition of the analog **1**, in preliminary experiments, was approximately one-fifth that of NANA.

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