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PIPERIDINE DERIVATIVES FROM THE BISULPHITE ADDITION COMPOUNDS OF 5-AMINO-5-DEOXY-D-XYLOSE

D.L. Ingles
Commonwealth Scientific and Industrial Research Organization
Division of Food Preservation, P.O. Box 43, Ryde
New South Wales, Australia

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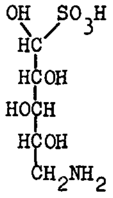
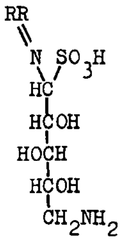
The reactions of the bisulphite addition compound (I) of 5-amino-5-deoxy-D-xylose[1] with amines are of interest since amines might compete with the terminal amino group at C5 in (I) in replacing the hydroxyl group at the C1 position. If the terminal amino group reacted at C1, a piperidine derivative should result.


I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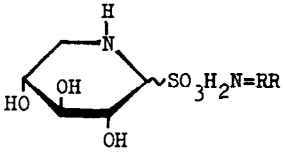
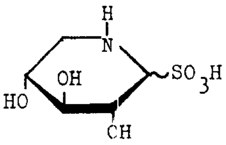
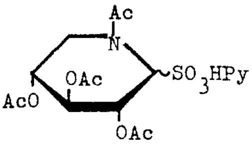

III

RR = $-CH_2CH_2OCH_2CH_2-$

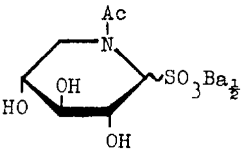
The addition compound (I) did not dissolve in or react with the weak bases aniline or pyridine. With stronger bases such as morpholine or benzylamine a ready exothermic reaction occurred; in the case of morpholine, a new crystalline derivative m.p. 114° $[\alpha]_D^{25}$ -10° (*c*., 1.0 in water) resulted, for which two possible structures (II) and (III) are in accord with the analytical data.



IV



V



VI

Neither the infrared nor the NMR spectrum permitted any distinction between structures (II) and (III). However, treatment with Zeokarb 225 (H^+ form) removed morpholine and gave the crystalline piperidine derivative (IV), m.p. 140° $[\alpha]_D^{25}$ -36° (*c*., 1.0 in water). The corresponding data for the bisulphite addition compound (I) are, m.p. 160°, $[\alpha]_D^{25}$ +9° (*c*., 1.0 in water)[1]. The infrared spectra (KBr) of (I) and (IV) were identical, but analysis confirmed the cyclic structure (IV). This piperidine derivative liberates barium sulphite on treatment with barium hydroxide, as does (I). It may thus be considered to be a bisulphite addition compound of the intramolecular Schiff base form of 5-amino-5-deoxy-D-xylose.

Acetylation of (III) or (IV) with pyridine-acetic anhydride mixture gave the pyridine salt (V), m.p. 166° $[\alpha]_D^{25}$ +30° (*c*., 1.0 in water) which showed $\lambda_{max.}^{KBr}$ 1750 (OAc), 1650

(NAc) 1225 cm^{-1} (SO_3H). This pyridinium salt of 1-acetyl-D-ido(gulo)-3,4,5-tri-acetoxy-2-sulpho-piperidine (V) was very stable and did not eliminate sulphite even with boiling barium hydroxide. Nor did the compound reduce Fehlings' solution. These characteristics contrast sharply with those shown by (III) and other bisulphite addition compounds of sugars[2,3] and amino sugars[1].

Deacetylation of (V) with barium methoxide gave the barium salt (VI) with a consistent infrared spectrum. Oxidation of one mole of (VI) with sodium periodate released 0.9 moles of formic acid, thereby confirming the presence of a six-membered ring containing nitrogen.

It has recently been shown[4,5,6] that 5-acetamido-5-deoxy-D-xylose may exist in both furanose and pyranose ring forms. The piperidine-2-sulphonic acids described in this paper may be considered as sulphonic acid derivatives of the pyranose form of 5-amino-5-deoxy-D-xylose. These piperidine derivatives also provide the first examples of cyclic forms of bisulphite addition compounds of sugars.

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