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PREPARATION AND CONFORMATION OF α-L-ARABINOFURANOSYL-PYRIDINIUM SALTS, AND HYDROLYSIS OF THE 4-BROMOISOQUINOLINIUM COMPOUND

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ABSTRACT

Tri-*O*-benzoyl-α-L-arabinofuranosylpyridinium salts can be made in acceptable yields and high stereochemical purity by the reaction of 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl bromide and the pyridine in the presence of tetrabutylammonium bromide. Analysis of the ^{1}H-n.m.r. signals of the sugar reveals that the benzoylated compounds adopt largely the E_2 conformation whereas the debenzoylated compounds are largely in the $^oT_1$ conformation. The α-L-arabinofuranosyl-4-bromoisoquinolinium ion hydrolyses by both pH-independent and base-catalysed pathways, complicated by the reversible formation of an inert pseudo-base in alkali. The comparatively low rate of the pH-independent reaction is discussed in terms of the acid-lability of furanosides.

INTRODUCTION

Glycopyranosylpyridinium salts have proved very informative about enzymic[1–4] and non-enzymic[5,6] glycoside hydrolysis, by virtue of the absence of any possibility of acidic assistance to the departure of the aglycone, and of the conformational preferences dictated by the reverse anomeric effect of the pyridinium moiety. The preparation of glycofuranosylpyridinium salts and investigation of their hydrolytic behaviour therefore seemed likely to be fruitful. Departure of nicotinamide from the ribofuranosyl ring of NAD^+ is important biologically in the mono-[7] and poly-ADP-ribosylation of proteins[8], and simple NAD^+-glycohydrolases are also known and have been studied mechanistically[9,10]. The C–N cleavage of NAD^+ has been subject to some mechanistic investigations[11,12]; strangely, it is accelerated by anionic buffers, especially phosphate, and, in principle, is complicated by base stacking and the lability of the pyrophosphodiester group. We therefore selected α-L-arabinofuranosylpyridinium salts for investigation, since their spontaneous hydrolysis would not present these problems, yet in all probability[1–4] they would be substrates for α-L-arabinofuranosidases, which are widely distributed.

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