Mass Spectrometric Studies of Some Nucleosides Bearing Triazole Ring

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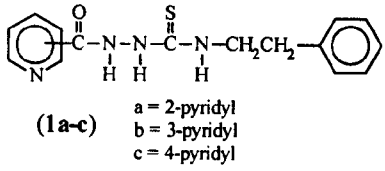
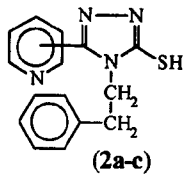
Summary: Electron ionization mass spectra of 2-(2',3',4',6'-tetra-O-acetyl-β-D-galactopyranosyl)-4-(2'-phenylethyl)-5-(pyridyl)-2,5-dihydro-3H-1,2,4-triazol-3-thiones are discussed. The mass fragmentation patterns are reported that are assigned with the help of LREIMS and HREIMS peak matching of molecular ion peaks obtained by EIMS.

Introduction

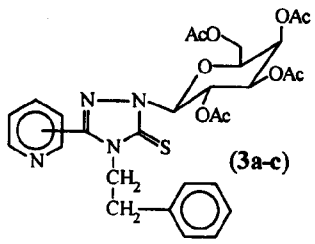
Among the N-substituted azoles, the nucleosides have accumulated special interest both for their biological significance [1-5] and for the particular synthetic methods involved in their preparation. We have reported [6] the synthesis of 2-(2', 3', 4', 6'-tetra-O-acetyl-β-D-galactopyranosyl)-4-(2'-phenylethyl)-5-(pyridyl)-2, 5-dihydro-3H-1, 2, 4-triazol-3-thiones (**3a-c**) and the intermediates (**1a-c** and **2a-c**) involved in the preparation of (**3a-c**). In this article we report EIMS studies of the nucleosides (**3a-c**). The molecular formulae of these compounds have been further confirmed by the HREIMS peak matching of molecular ion peaks exhibited by LREIMS and are listed in table-1



(**1a-c**) a = 2-pyridyl, b = 3-pyridyl, c = 4-pyridyl



(**2a-c**)



(**3a-c**)

Table-1: HREIMS of Molecular Ion Peaks of nucleosides (**3a-c**)

Compd.	Mol. Formulae	$M^+(m/z)$ Calcd.	Found
3a	$C_{29}H_{32}N_4O_9S$	612.1890	612.1880
3b	$C_{29}H_{32}N_4O_9S$	612.1890	612.1895
3c	$C_{29}H_{32}N_4O_9S$	612.1890	612.1885

Results and Discussion

The mass fragmentation patterns of the nucleosides (**3a-c**) are assigned with the help of LREIMS and are depicted in scheme-1.

2-(2',3',4',6'-tetra-O-acetyl-β-D-galactopyranosyl)-4-(2'-phenylethyl)-5-(pyridyl)-2,5-dihydro-3H-1,2,4-triazol-3-thiones (**3a-c**)

The EIMS of (**3a-c**) exhibited molecular ions at *m/z* 612 ($C_{29}H_{32}N_4O_9S$, **3a-c**). Removal of tetraacetylgalactose molecule from the molecular ions yielded radical cations at *m/z* 282 ($C_{15}H_{14}N_4S$ **3aa-ca**) followed by the removal of SH radical yielded cations at *m/z* 249 ($C_{15}H_{13}N_4$ **3ab-cb**). The elimination of cyanopyridine and isothiocyanate molecules from (**3aa-ca**) furnished radical cations at *m/z* 178 ($C_9H_{10}N_2S$, **3ac-cc**) and 119 ($C_6H_5N_3$, **3ad-cd**) respectively. Whereas, the removal of isothiocyanate molecule from (**3aa-ca**) yielded radical cations at *m/z* 223 ($C_{14}H_{13}N_3$, **3am-cm**) followed by the expulsion of substituted pyridine radical gave tropillium cations at *m/z* 105 (C_8H_9, **3an-cn**). Removal of a substituted benzene

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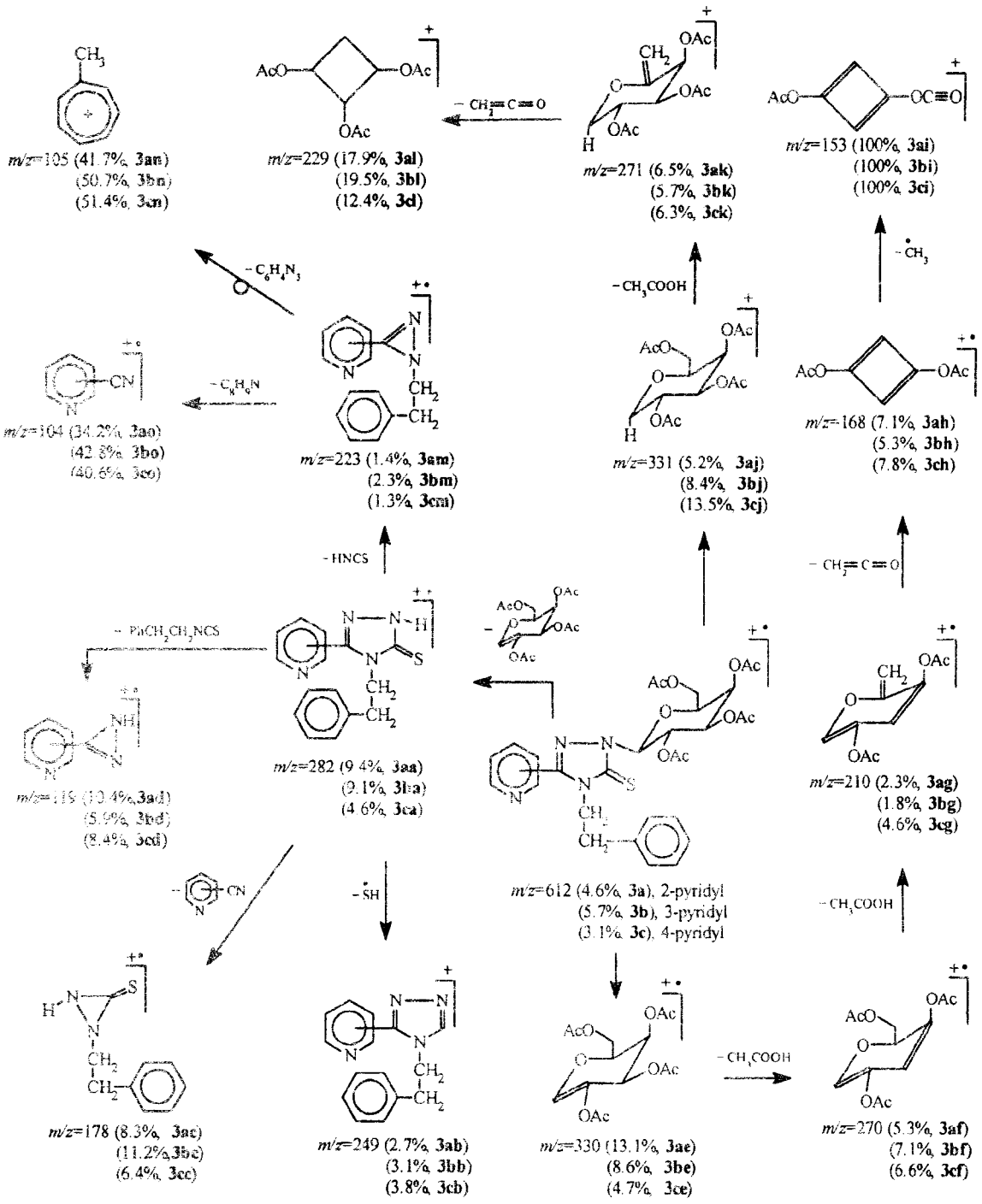

(Scheme, The pathways of the EI-mass fragmentation of the molecular ions of **3a-c**)

molecule from (**3am-cm**) furnished radical cations at *m/z* 104 ($C_6H_4N_2$, **3ao-co**). The elimination of a triazole molecule from molecular ions yielded radical cations at *m/z* 330 ($C_{14}H_{18}O_9$, **3ae-ce**) followed by two successive losses of acetic acid molecules yielded radical cations at *m/z* 270 ($C_{12}H_{14}O_7$, **3af-cf**) and 210 ($C_{10}H_{10}O_5$, **3ag-cg**). Removal of a ketene from (**3ag-cg**) afforded radical cations at *m/z* 168 ($C_8H_8O_4$, **3ah-ch**) followed by the elimination of methyl radical yielded cations at *m/z* 153 ($C_7H_5O_4$, **3ai-ci**). The elimination of a triazole radical from molecular ions afforded tetraacetylgalactose cations at *m/z* 331 ($C_{14}H_{19}O_9$, **3aj-cj**) followed by the loss of acetic acid molecule to afford cations at *m/z* 271 ($C_{12}H_{15}O_7$, **3ak-ck**). Removal of a ketene from (**3ak-ck**) yielded cations at *m/z* 229 ($C_{10}H_{13}O_6$, **3am-cm**) (Scheme).

Experimental

Compounds (**1a-c**, **2a-c** and **3a-c**) were prepared according to the literature procedure [6]. All of these compounds were characterized by IR. MS and ^{1}H-NMR spectral data. The EIMS were recorded on MAT-311 instrument with an accelerating voltage of 3 kV and ionization energy of 70 eV. The temperature of the ion source was maintained at 250°C.

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