

THERMAL BEHAVIOUR OF SOME 4-GLUCOPYRANOSYLAMINO-5-NITROSO-PYRIMIDINE DERIVATIVES

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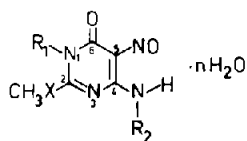
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ABSTRACT

One 4- α -glucopyranosylamino, three 4- β -glucopyranosylamino and two 4- β -xylopyranosylamino 5-nitroso-pyrimidine derivatives have been characterized by elemental analysis, and IR and UV-visible spectroscopies. In the solid state, ketonic tautomeric forms have been established for all of them. The thermal decomposition of the compounds shows three types of processes: (i) dehydration, (ii) solid–solid transitions, (iii) pyrolytic decompositions. Dehydration and solid–solid transition enthalpies have been calculated from DSC curves.

INTRODUCTION

In several recent papers [1–3] the authors report the synthesis and $^1\text{H-NMR}$ spectral characterization of some glucopyranosides and xylopyranosides from some pyrimidine derivatives and their acetyl-derivatives.



Scheme 1.

Compound	<i>n</i>	R ₁	<i>x</i>	R ₂
A	1	H	O	β -Glucopyranosyl
B	–	H	S	β -Xylopyranosyl
C	1	H	S	β -Glucopyranosyl
D	–	CH ₃	S	β -Xylopyranosyl
E	1	CH ₃	S	α -Glucopyranosyl
F	1	CH ₃	S	β -Glucopyranosyl

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In order to use some of these for the synthesis of metal complexes with potential biological importance [4,5], we have considered it necessary to complete their spectral characterization and to carry out the study of their thermal behaviour. In this way, the present paper reports the characterization of glucopyranosides and xylopyranosides of the 5-nitroso-pyrimidine derivatives shown in Scheme 1.

EXPERIMENTAL

All the compounds were synthesized and purified by methods previously reported [1]. All the chemicals used in this work were of analytical reagent grade.

The isolated compounds were characterized by $^1\text{H-NMR}$ spectroscopy using a Hitachi/Perkin-Elmer R-600 FT-NMR spectrometer, $\text{DMSO-}d_6$ as solvent and TMS as internal standard. The microanalyses of C, H and N were performed with a Carlo Erba (Model 1106) microanalyser.

The analysis and yield data for the compounds obtained are given in Table 1.

Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded in KBr pellets, using a Beckman 4250 spectrophotometer.

UV-visible spectra ($750\text{--}200\text{ nm}$) were recorded on a Beckman 25 spectrophotometer, using bidistilled water as solvent. Thermogravimetric analyses were made (in a static pure air atmosphere) with a Mettler TG 50 thermobalance at a heating rate of 10° min^{-1} , whereas the DSC runs were carried out on a Mettler DSC-20 differential scanning calorimeter at a heating rate of 5° min^{-1} . The thermal reactions were obtained with samples varying in weight from 3.02 to 9.58 mg.

RESULTS AND DISCUSSION

Table 2 shows the most significant bands in the infrared spectra of the compounds. These bands are attributed to the potential donor groups present in the molecules.

TABLE 1
Analytical and yield data

Compound	%C	%H	%N	Formula	Yield (%)
A	37.42 (37.71)	4.96 (5.18)	16.28 (16.00)	$\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_8 \cdot \text{H}_2\text{O}$	73
B	37.65 (37.73)	4.47 (4.43)	17.39 (17.60)	$\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_6\text{S}$	90
C	36.11 (36.06)	5.05 (4.95)	15.39 (15.29)	$\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_7\text{S} \cdot \text{H}_2\text{O}$	80
D	39.79 (39.75)	5.02 (4.85)	16.41 (16.86)	$\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_6\text{S}$	85
E	38.00 (37.89)	5.27 (5.30)	15.01 (14.37)	$\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_7\text{S} \cdot \text{H}_2\text{O}$	33
F	37.62 (37.89)	5.19 (5.30)	14.75 (14.37)	$\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_7\text{S} \cdot \text{H}_2\text{O}$	77

The analytical data in parentheses are theoretical values.

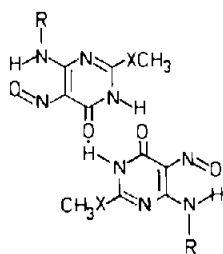
TABLE 2
IR spectral data

Compound	Assignments (cm^{-1})									
	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\delta\text{H}_2\text{O}$	$\nu(\text{C=N})$	$\nu(\text{C=C})$	$\nu(\text{NO})$	$\delta(\text{CH}_3)_{\text{sym}}$	$\nu(\text{C-N})$	$\nu(\text{C-O})$
A	3430 (s)	3330 (s)	1700 (s)	1610 (s)	1585 (s)	1540 (m)	1495 (m)	1345 (m)	1290 (s)	1115 (m) 1080 (s) 1055 (m) 1030 (m)
B	3400 (m)	3250 (w)	1685 (s)	—	1580 (m)	1555 (s)	1480 (m)	1360 (w,br)	1290 (w) 1245 (m)	
C	3460 (s)	3310 (s)	1685 (s)	1620 (w)	1590 (s)	1540 (s)	1480 (m)	1385 (w)	1290 (m) 1265 (m)	
D	3400 (s,br)	3400 (s,br)	1680 (m,br)	—	1580 (s)	1530 (m)	1480 (m)	1345 (m)	1275 (m) 1235 (m)	
E	3420 (s,br)	3200 (m,br)	1675 (s)	1635 (w)	1570 (s,br)	1540 (s,br)	1540 (s,br)	1345 (s)	1270 (m) 1240 (m)	
F	3420 (s,br)	3200 (m,br)	1675 (s)	1635 (w)	1570 (s,br)	1540 (s,br)	1540 (s,br)	1345 (s)	1270 (m) 1240 (m)	

s = strong, m = medium, w = weak, br = broad.

All the compounds, except D, show two sharp bands in the 3500–3200 cm^{-1} range. The band at higher wavenumber can be assigned to a $\nu(\text{OH})$ stretching vibration (due to lattice water and/or OH groups), while the other may be due to a $\nu(\text{NH})$ stretching vibration. In the spectrum of D these two bands overlap, producing one wide, strong band centred at 3400 cm^{-1} .

The IR spectra of A, B and C show several bands, of medium intensities, in the 2500–3000 cm^{-1} range. This fact has been related to the formation, in these derivatives, of dimers by hydrogen bonds, via 6-oxo and $\text{N}_1\text{-H}$ ring groups, according to Scheme 2 [6].



Scheme 2.

Likewise, all the IR spectra present a band (1675–1700 cm^{-1}) assigned to the $\nu(\text{C}=\text{O})$ stretching vibration, which is in agreement with of all these compounds being in the solid phase, in the ketonic tautomeric form as well as in DMSO solutions [1].

UV–visible spectral data are given in Table 3. All the assignments have been done according to the literature data for pyrimidine derivatives [7–9].

TG and DSC plots of the isolated compounds are given in Figs. 1 and 2 respectively. From these two figures, the dehydrations, solid–solid transitions and decomposition temperatures, as well as observed and calculated weight losses and enthalpies, have been calculated. The results obtained are included in Table 4.

The TG and DSC curves show that three types of processes can occur: (i) dehydration, (ii) solid–solid transitions and (iii) pyrolytic decompositions.

Dehydration

These processes appear in TG and DSC plots of A, C, E and F. All the weight losses correspond to the loss of one water molecule which is in agreement with the proposed formulae. On the other hand, the dehydration energies, calculated from the DSC plots, are higher in the cases of A and C (57.8 and 54.0 kJ mol^{-1}) than for E and F (43.5 and 48.0 kJ mol^{-1}). This fact could be related to the existence of a higher number of atoms with potential hydrogen binding capacity in molecules A and C, than in E and F.

Solid–solid transitions

None of the compounds present melting points below their respective temperature decompositions. The DSC curves of B and D show endothermic

effects centred at 162 and 190°C, respectively (ΔH values 2.2 and 6.7 kJ mol⁻¹). Provided that none of the compounds fuse at these temperatures and, likewise, there are no weight losses in the TG curves, these effects can be attributed to solid–solid transitions in which a probable change in crystal structure is accompanied by the absorption of heat [10]. In the IR spectrum of B two bands, centred at 1310 (weak, unassigned) and 1200 cm⁻¹ (strong and sharp, assigned to $\nu(\text{N-H})$ stretching), split in two on heating B at 168°C. This fact could be related to the change in crystalline structure of B.

Figure 2 shows the instability of the solid phase obtained from D at 190°C, after which decomposition begins. Consequently it has not been possible to characterize this solid phase.

TABLE 3
UV–visible data in aqueous solutions

Compound	Concentration (mol l ⁻¹)	λ_{max} (nm)	ξ	Assignments
A	5.14×10^{-5}	201	17.650	$\pi-\pi^*$
		228	16.980	$\pi-\pi^*$
		334	14.050	$n-\pi^*$
B	3.52×10^{-3}	563	58	chromophore
	5.03×10^{-5}	200	26.940	$\pi-\pi^*$
		234	sh	$\pi-\pi^*$
		300	sh	$n-\pi^*$
		352	25.350	$n-\pi^*$
C	3.05×10^{-3}	591	55	chromophore
	4.91×10^{-5}	200	24.540	$\pi-\pi^*$
		236	sh	$\pi-\pi^*$
		299	sh	$n-\pi^*$
		352	24.685	$n-\pi^*$
D	3.28×10^{-3}	585	56	chromophore
	5.72×10^{-5}	217	17.255	$\pi-\pi^*$
		242	sh	$\pi-\pi^*$
		305	sh	$n-\pi^*$
		352	21.905	$n-\pi^*$
E	3.37×10^{-3}	586	59	chromophore
	2.10×10^{-5}	218	28.500	$\pi-\pi^*$
		306	sh	$n-\pi^*$
		350	32.755	$n-\pi^*$
F	8.97×10^{-3}	558	80	chromophore
	5.52×10^{-5}	217	17.990	$\pi-\pi^*$
		238	sh	$\pi-\pi^*$
		299	sh	$n-\pi^*$
		353	23.695	$n-\pi^*$
3.22×10^{-3}	588	56	chromophore	

sh = shoulder.

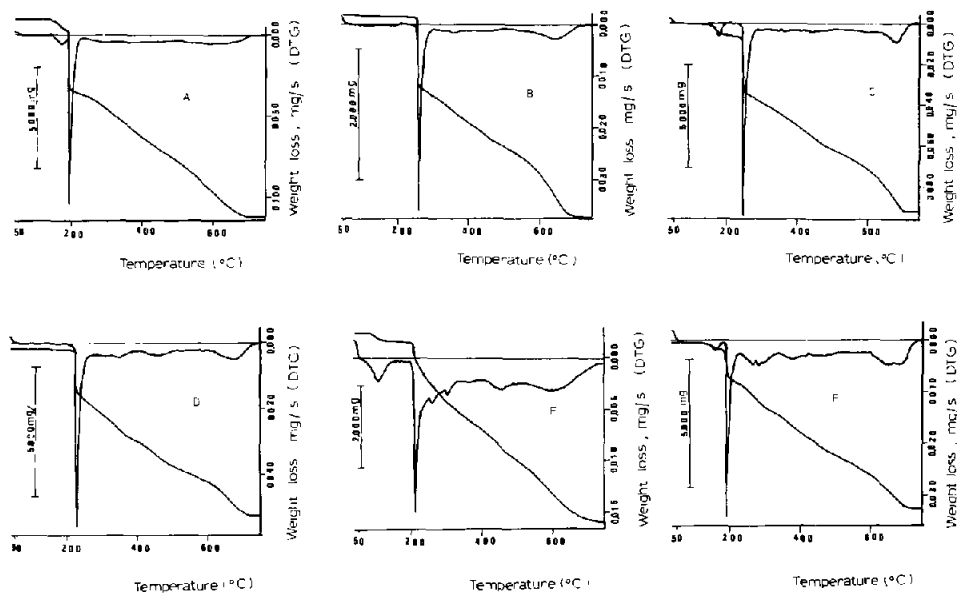


Fig. 1. TG curves.

Pyrolytic decompositions

In all the compounds studied the pyrolytic decompositions start at about 200°C. The DSC curves show a first strong exothermic effect whose energies and temperatures are given in Table 4.

Compounds D, E and F start their pyrolytic decompositions at temperatures similar to those for 4-amino-1,6-dihydro-1-methyl-2-methylthio-5-nitroso-6-oxo-pyrimidine (244°C), from which the above compounds are derived [11]. Furthermore, DSC curves of the pyrimidine derivative and D, E and F are very similar. These data support that the sugar molecules bound to the 4-amino group do not change the probable mechanism of the pyrolytic decomposition of the above pyrimidine derivative. ΔH values for initial exothermic effects in the DSC plots of E and F are similar in accordance with the similarity in their structures.

Pyrolytic decompositions of B and C start at higher temperatures than those for 4-amino-1,6-dihydro-2-methylthio-5-nitroso-6-oxo-pyrimidine (220°C). Likewise, the similarity of DSC curves suggests a similarity in their decomposition mechanism [12]. On the basis of these data, if we assume that some 4-amino-5-nitroso-pyrimidine derivatives start their pyrolytic decomposition by oxidising the 4-amino group [13] it could be concluded that in compounds B and C the N-xylose and N-glucose bonds are stronger than the N-H bond in 4-amino-1,6-dihydro-2-methylthio-5-nitroso-6-oxo-pyrimidine.

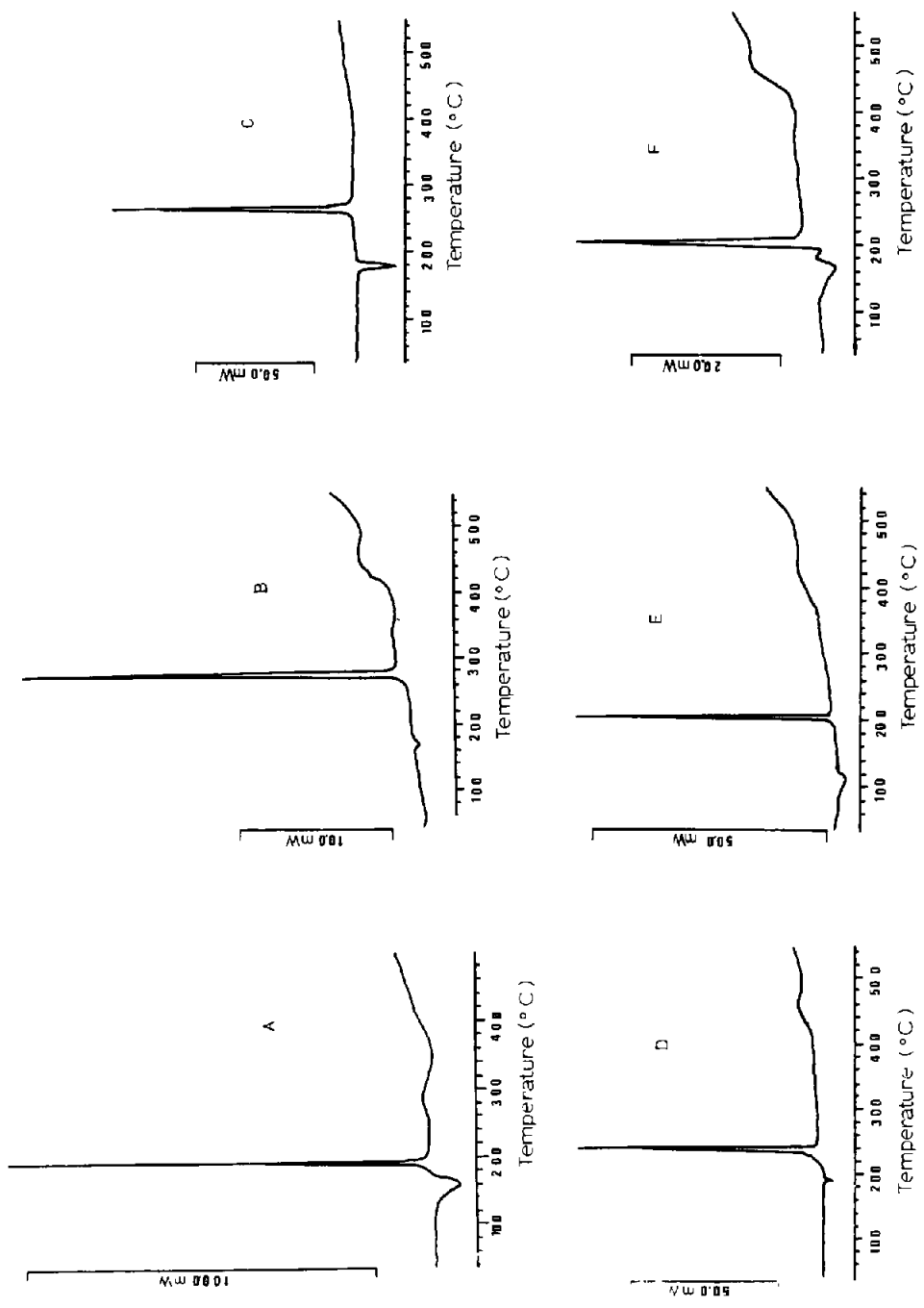


Fig. 2. DSC curves.

TABLE 4
TG and DSC data

Compound	Dehydration		Solid-solid transitions		Other effects	
	T (°C)	Wt. loss (%)	T (°C)	ΔH (kJ mol ⁻¹)	T (°C)	ΔH (kJ mol ⁻¹)
A	157	5.30 (5.14)	-	-	190 (exo) 358 (exo)	- -84.9
B	-	-	162	2.2	273 (exo) 446 (exo)	- -
C	177	5.03 (4.92)	-	-	263 (exo)	-169.2
D	-	-	190	6.7	244 (exo) 458 (exo)	-146.5 -
E	112	5.01 (4.71)	-	-	208 (exo) 420 (exo)	-187.5 -
F	164	4.68 (4.74)	-	-	204 (exo) 427 (exo)	-184.5 -

The analytical data in parentheses are theoretical values.

These lower temperature pyrolytic decompositions correspond to that of compound A (190°C). This fact could be related to the relative low instability of some 5-nitroso-pyrimidine derivatives having methoxy groups as exocyclic substituents [14,15].

The TG curves of all the compounds studied are very similar, showing an abrupt weight loss in the temperature range in which the above-mentioned sharp exothermic effects take place. Then the weight losses continue slowly and uninterrupted. The pyrolytic decompositions finish at about 700°C (Fig. 1), at which time no material remains in the crucible. Since no stable species are formed as intermediates during these pyrolytic processes, it was not possible to propose any hypothesis about the decomposition mechanisms.

A second exothermic effect appears, in all DSC plots, except curve C, at temperatures between 270°C in A and 458°C in D. These values are given in Table 4.

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