Thermochimica Acta, 134 (1988) 67–72
Elsevier Science Publishers B.V., Amsterdam

DTG AND DTA STUDIES ON SUGAR DERIVATIVES

F.J. REY, Mª.C. RAMOS-SANCHEZ, M.L. RODRIGUEZ-MENDEZ, J. MARTIN-GIL and F.J. MARTIN-GIL*
E.T.S.I.I. Universidad de Valladolid, 47011 Valladolid, Spain
* Hospital del Río-Hortega, Valladolid, Spain

ABSTRACT

Many biological compounds which perform essential functions contain saccharides bonded to other types of structures. Sugar derivatives such as aminosugars, sugar alcohols (polyols), nucleosides, nucleotides, etc. (that have recently attracted increased attention, especially in the field of antibiotics) were now subjected to DTG and DTA studies in order to observe the differences with the results obtained on typical sugars.

INTRODUCTION

Interest in the thermal behaviour of sugars carried us to study the DTG and DTA-DSC curves of typical monosaccharides and polysaccharides. Present work on pyrolysis of sugar derivatives is also of great interest in terms of aiding in the understanding of the relationships between chemical structure and thermal activity for carbohydrates and by their medicinal value (aminoglycosides).

EXPERIMENTAL

All the samples were of analytical grade. They were purchased by Merck and the aminoglycoside antibiotics by Hosbon, Upjohn and Antibioticos S.A of Leon. Idoxuridine was supplied by Viñas S.A. of Barcelona and Vidarabine by Parke-Davis. Thermal analysis was carried out on a Perkin-Elmer 3600 and the DTA 1700. Instrument calibration was performed by a standard Indium sample. The material (approximately 5 mg) was wheighed in platinum (TG) or alumina crucibles (ATD). Ignited alumina was used as the reference material. The atmosphere was static air and the heating rate of 10ºC/min.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

RESULTS

We found an excellent agreement between the decomposition phenomena observed for typical sugars and the results now reported (Table 1 and 2). Thus, the first DTG decomposition peak continues being a polymerization marker such as it is evidenced when we compare the DTG curves of amino sugars with those of aminoglycosides or the DTG curves of cardiotonic heterosides with those of di and oligosaccharides. In the same way, the first DTA effects show that the polyols were more stable than sugar analogues and much more stable than sugar acids: The temperature maxima of the peaks for Galactitol and Galactose were 189ºC and 168ºC respectively. The endotherms for Glucose and Gluconic acid having their peaks at 156ºC and 125ºC, respectively (Figs 1a and 1b).

The influence of other structural factors such as the fact that the Ascorbic acid has a γ-lactonic ring unlike the Gluconic acid, also was evidenced by the higher stability of Ascorbic acid

Among the polyols included in this study, Galactitol and Mannitol, showed near identical calorimetric curves; nevertheless, a shoulder at 330ºC of the peak at 316ºC for Galactitol might suggest that their stability is higher than the stability of Mannitol, in agreement with the order of stability of their dehydrogenated analogues, i.e., Galactose > Mannose. When we compare each pair of values, it is obvious that hydrogenation of Galactose and Mannose retarded the onset of decomposition by 30ºC approximately. An other feature is that the cyclitol Inositol is more stable that the polyols to which we have referred above.

As already mentioned in a previous report (1), the specific differences observed in monosaccharides are reflected in the thermal behaviour of polysaccharides: Within the aminoglycosides, Kanamycin, Gentamycin, Klobamycin, Tobramycin and Amikacin were more stable than Ribostamycin, Neomycin and Streptomycin, when judging from the DTG peak temperatures (Fig.2). This in agreement with the relative higher stability of ribofuranosyl versus pyranosyl rings. On the other hand, complex sulfates are more stable than neutral aminoglycoside antibiotics.

Within the sugar nucleosides and nucleotides screened here, the order of stability Vidarabine > Adenosine is in accordance with the stability observed in the corresponding monomers Arabinose and Ribose.

With sugars containing PO_4, I or CN groups, two different types of behaviour could be distinguished: Phosphated sugars AMP and CoA had peak temperatures below Adenosine (similarly occurred with Idoxuridine) whereas the cyanogen glycoside Amygdalin has the same stability than nonsubstituted disaccharides.

TABLE 1

First thermal effects on sugar derivatives (in static air and at rate of 10ºC/min)

Carbohydrates derivatives	Onset TG	effect I		effect II	
		DTA (ΔH)	DTG	DTA endo	DTG
	ºC	ºC cal/g	ºC	ºC	ºC
Polyols					
Galactitol	230	189 (68)	-	-	316 330
Mannitol	240	170 (55)	-	-	315
Inositol	260	228 (64)	-	-	377 411
Other monosaccharide derivatives					
D-Gluconic acid	-	125 (69)	123sh 155	175exo 216 260sh	278
L-Ascorbic acid	190	193 (59)	210 230	220exo 240	-
Esculin 1.5 H_2O (a coumarin glucoside)	210	202 (143)	-	285exo 308	280
Aminosugars:					
D-Galactosamine HCl	166	192 (99)	195	240	-
N-Acetyl-D-Glucosamine	180	216 (100)	209	295 324	-
Aminoglycoside antibiotics					
Tobramycin	235	171 (15) 218 (28) 276 (4)	286	-	-
Amikacin	205	204 (27)	289	-	-
Amikacin SO_4	220	255 (36)	260	300	322
Gentamycin SO_4	220	265	249	-	299
Klobamycin SO_4	240	270 (28)	268	297	307
Kanamycin SO_4	240	262 (25)	261	293	301
Ribostamycin SO_4	205	230 (1)	234	291	272
Neomycin SO_4	205	164 (13) 247 (14)	240	287	294
Streptomycin SO_4	183	228 (2)	220	297	294 330
Lincosamyds					
Lincomycin HCl	180	228 (36)	245	260exo	-
Disaccharide deriv.					
Amygdalin.3 H_2O (a cyanogenic glyc.)	224	221 (26)	-	-	311

TABLE 1 (cont.)

Carbohydrate drivatives	Onset TG ºC	effect I DTA (ΔH) ºC cal/g	DTG ºC	effect II DTA (ΔH) ºC cal/g	DTG ºC
"Sugar nucleosides and nucleotides"					
Vidarabine	272	268 (37)	295	290 (-80)	-
Adenosine	234	239 (50)	-	285 (-97)	285
Thymidine	210	192 (36)	-	250 267 (-53)	
Idoxuridine	186	(188) -	192	192 (-24)	297
AMP	195	208 (8)	214	215 (- 9)	-
CoA	205	205 217 (58)	208 230	(265) -	285
Cardiotonic heterosides					
Digitonin	240	220 (4)	283sh	(280) -	323

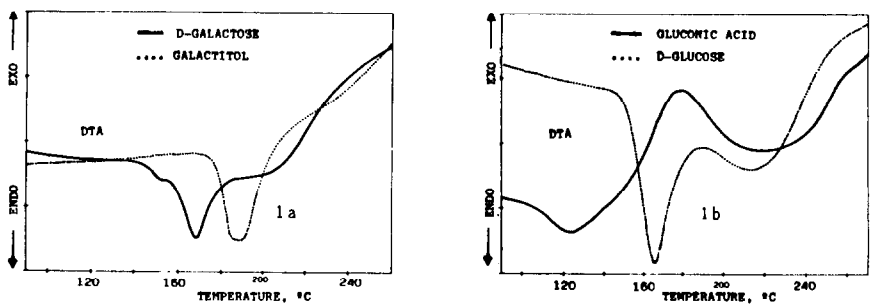

Fig. 1. DTA curves of: 1a) Galactitol and Galactose, 1b) Glucose and Gluconic acid. Heating rate 10ºC min^{-1} in static air.

Finally, and also for characterization purposes the nucleosides and nucleotides Vidarabine, Adenosine, Idoxuridine and AMP (adenosine 5′-monophosphate) showed in their DTA registra succesive endothermic and exothermic peaks in the 200-300ºC region (Fig. 3).

TABLE 2

Last thermal effects on sugar derivatives (in static air and at rate of 10ºC/min)

Carbohydrates derivatives	effect III DTA exo ºC	effect IV DTA exo ºC	combustion ΔH (ΔT) cal/g ºC	DTG ºC
Polyols				
Galactitol	303 338	415	-1663 (220-550)	-
Mannitol	313 341	428	-1221 (230-530)	527
Inositol	346	478	-1606 (260-540)	-
Other monosaccharides derivatives				
D-Gluconic acid	317	430	-1150 (220-490)	408 447
L-Ascorbic acid	360	445	-1715 (245-530)	506
Esculin 1.5 H_2O (a coumarin glucoside)	427 483	558	-1982 (308-600)	520
Aminosugars:				
D-Galactosamine HCl	360	490	-2015 (240-650)	494
N-Acetyl-D-Glucosamine	386	505	-1650 (295-750)	512
Aminoglycoside antibiotics				
Tobramycin	400	479 582	-1710 (400-640)	516
Amikacin	350 380 endo	502 630	-1721 (380-680)	624
Amikacin SO_4	370	493 548	-1574 (305-580)	478 566
Gentamycin SO_4	355	482 560	-1525 (310-650)	529
Klobamycin SO_4	350	516 573 658	-1685 (313-676)	540
Kanamycin SO_4	405	552 625	-1574 (300-650)	580
Ribostamycin SO_4	380 455	510 597 650	-1663 (308-687)	510-580
Neomycin SO_4	365	493 577	-1608 (287-645)	500-530
Streptomycin SO_4	416	530 590	-1528 (300-640)	525 620
Lincosamyds				
Lincomycin HCl	403	483	- 813 (345-655)	500
Disaccharide deriv.				
Amygdalin 3 H_2O	321	443 492	-1400 (250-550)	500

TABLE 2 (cont.)

Carbohydrates derivatives	effect III DTA exo ºC	effect IV DTA exo ºC	combustion ΔH (ΔT) cal/g ºC	DTG ºC
"Sugar nucleosides and nucleotides"				
Vidarabine	380	477 530	-1515 (390-650)	527-560
Adenosine	425	477 532	-1435 (437-635)	520-560
Thymidine	365 386	482	- 462 (307-550)	-
Idoxuridine	385	462 516	-1662 (260-665)	480-530
AMP	378 425	580	-1680 (250-700)	500-620
CoA	376	493	-1603 (265-535)	500-520
Cardiotonic heterosides				
Digitonin	374	442 515	-1895 (280-560)	520-540

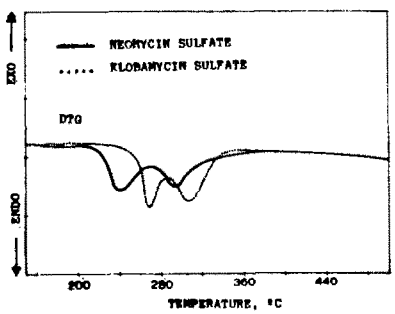

Fig. 2

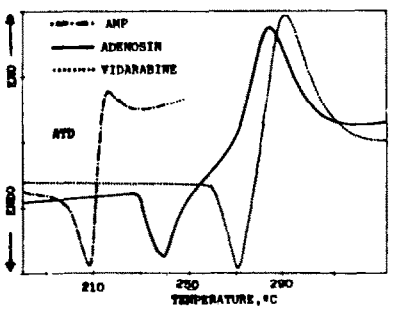

Fig. 3

DTG traces of Neomycin Sulfate and Klobamycin Sulfate (Fig 2) and DTA traces of AMP, Adenosin and Vidarabine in static air, 10ºC min^{-1} (Fig 3).

The reported different phenomena, presented in this communication in a preliminary form, need a precise comparison with the literature concerning carbohydrate derivatives in order to put forward basic contributions in characterizing the thermal behaviour of this very important class of compounds.

REFERENCES

1 Mª. C. Ramos-Sánchez , F.J. Rey, Mª L. Rodrígu -Méndez, F.J. Martín-Gil and J. Martín-Gil, Proc. 9th. ICTA, Jerusalem, 19