Journal of Thermal Analysis, Vol. 31 (1986) 247—251

THERMAL BEHAVIOUR OF SOME 2-BENZYLAMINO-2-DEOXYHEPTONIC ACIDS

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(Received March 20, 1985)

The thermal behaviour of some 2-benzylamino-2-deoxyheptonic acids obtained from 2-benzylamino-2-deoxy-**D**-*glycero*-**L**-*gluco*, 2-benzylamino-2-deoxy-**D**-*glycero*-**D**-*ido* and 2-benzylamino-2-deoxy-**D**-*glycero*-**D**-*talo*heptononitriles (reported) previously has been studied in air (static atmosphere) and N_2 (dynamic atmosphere, flow rate 200 ml/min).

Carbohydrate α-amino acids are interesting not only because they may be regarded as analogues of the sugar moiety of the polyoxins [1], but also because by reaction with nitrous acid, they yield anhydro sugars that are useful intermediates in the synthesis of C-nucleosides.

Experimental

The 2-benzylamino-2-deoxyheptonic acids were obtained by hydrolysis of 2-benzylamino-2-deoxyheptononitriles [2, 3]. The hydrolytic reaction and the identification of these compounds were described in previously [2, 3].

The epimers in C–2 obtained from 2-benzylamino-2-deoxy-D-glycero-L-glucoheptononitrile are denoted *Bn–GA* in the text (Fig. 2a). Those obtained from

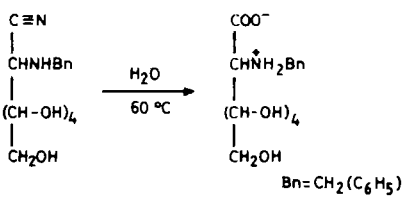

Fig. 1

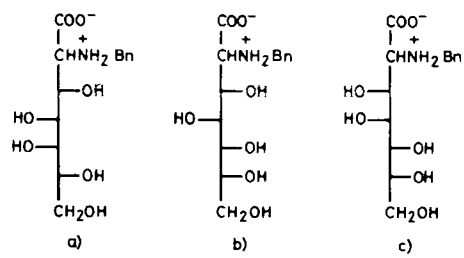

Fig. 2

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2-benzylamino-2-deoxy-D-glycero-D-idoheptononitrile are denoted *Bn–GLU* (Fig. 2b); and those obtained from 2-benzylamino-2-deoxy-D-glycero-D-taloheptononitrile are denoted *Bn–MA* (Fig. 2c).

Thermogravimetric analyses were made in air (static) and N_2 (dynamic, flow rate = 200 ml/min) with a Mettler TG 50 thermobalance, whereas the DSC runs were carried out on a Mettler DSC–20, at a heating rate of 10 deg/min. The thermal reactions were studied with samples varying from 15 to 20 mg in TG, and from 1.5 to 2 mg in DSC.

Results and discussion

The TG and DSC plots of the compounds *Bn–GA*, *Bn GLU* and *Bn MA* are given in Figs 3 (air) and 4 (N_2), the results calculated from which are included in Tables 1 (air) and 2 (N_2).

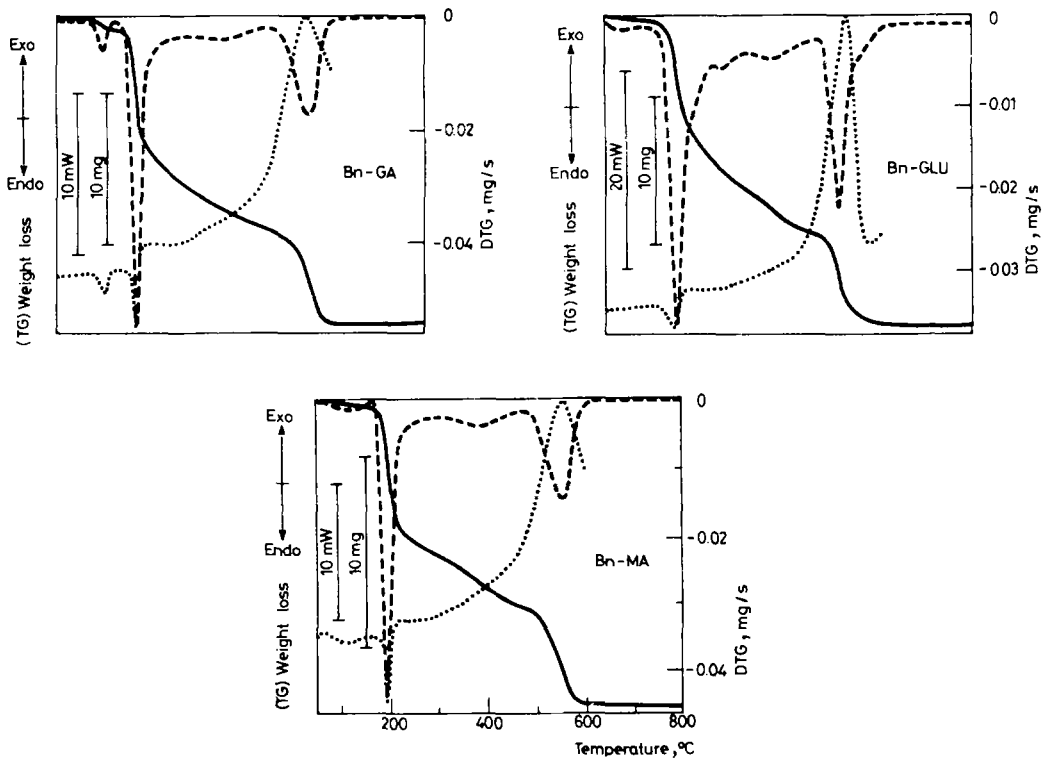

Fig. 3

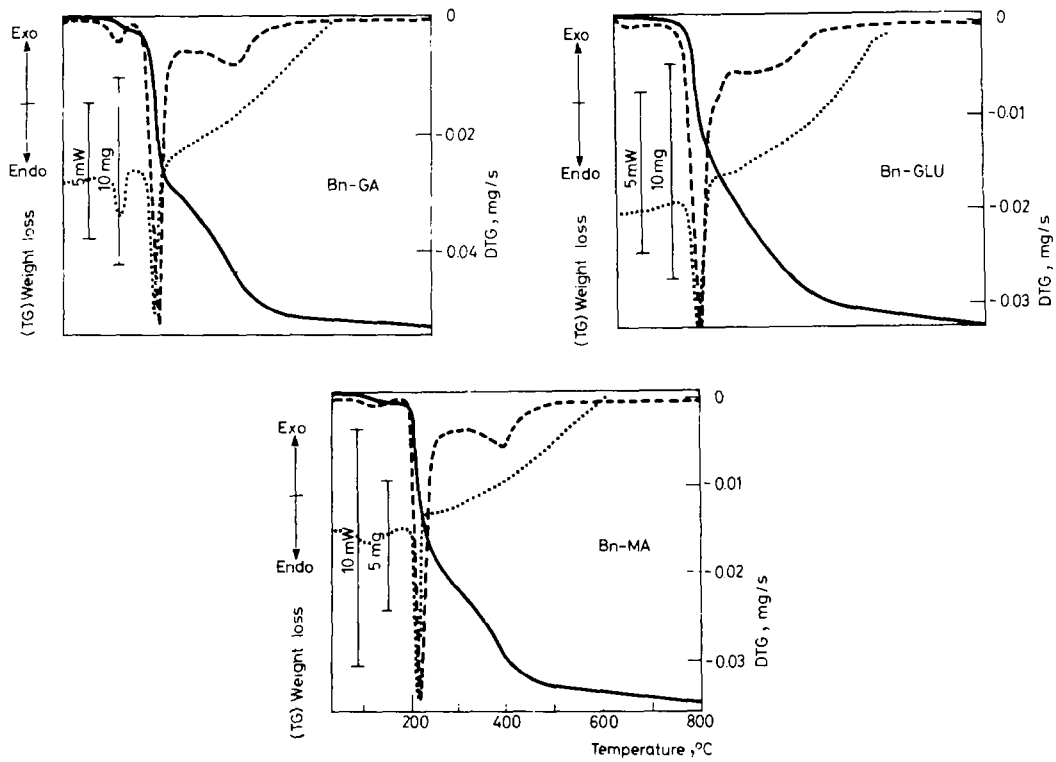

Fig. 4

Table 1 TG and DSC data (air)

Compound	*T*, °C	Effects Wt. loss, %	ΔH (kJ/mol)
Bn-GA	133	5.46 (5.39)	43.04
	202	42.04 (40.48)	65.14
	540	30.58	
Bn-GLU	60	1.55	
	175	44.13 (42.51)	108.06
	530	29.10	
Bn MA	115	3.10 (2.87)	28.54
	190	42.38 (41.98)	60.22
	392	22.94	
	558.	32.51	

Data in parenthesis are theoretical values

Table 2 TG and DSC data (N_2)

Compound	T, °C	Effects Wt. loss, %	ΔH, kJ/mol
Bn–GA	133	5.48 (5.39)	39.83
	201	41.34 (40.48)	70.58
	400	32.51	
Bn–GLU	60	1.16	
	185	45.19 (42.68)	105.07
Bn–MA	115	3.10 (2.87)	29.19
	189	42.71 (41.98)	65.16
	415	28.75	

Data in parenthesis are theoretical values

In the case of *Bn–GA*, a weight loss started at 100° and finished at about 170° (5.46% total weight loss), which corresponds to one water molecule. The expected endothermic behaviour for the dehydration process associated with this weight loss was observed in the same temperature range in the DSC curve. The pyrolytic process of anhydrous *Bn–GA* started at about 180°. At this temperature, a very rapid vigorous decomposition occurred up to about 240–250°. The total weight loss was 42.04% (41.34% in N_2). These values agree well with the theoretical value calculated for the elimination of the —COOH and $-CH_2C_6H_5$ groups (40.48%). In the DSC curves, the endothermic effects associated with the weight losses were observed in the same temperature range; the corresponding enthalpies are given in Tables 1 and 2. After this vigorous effect, a slow decomposition started, which finished at about 500°. From this temperature on, for the *Bn–GA*/air sample, combustion of the carbonaceous residue takes place.

Bn–GLU showed a small weight loss up to about 70–80° (hydration water). The DSC curve shows the anhydrous character of the compound. The pyrolytic reaction of *Bn–GLU* started at 160°. At this temperature, a very rapid decomposition occurred. The total weight losses are shown in the Tables and agree well with the theoretical values for the elimination of —COOH and $-CH_2C_6H_5$. Next, a slow decomposition started, which finished at about 500°. At this temperature, for the *Bn–GLU*/air sample, a new weight loss started due to combustion of the carbonaceous residue. In the DSC curves, the endothermic and exothermic effects associated with the weight losses were observed in the same temperature range as in TG; the corresponding enthalpies are given in Tables 1 and 2.

The TG curves of *Bn–MA* show that the dehydration of amino acid is completed at 190°. The experimental values for the weight losses (Tables 1 and 2) agree very well with the theoretical value for the hemihydrate (2.87%). Pyrolytic decom-

position and combustion (in air) take place analogously as for *Bn-GA* and *Bn-GLU*. The weight losses in the pyrolytic processes, starting at about 215°, are shown in the Tables and agree very well with those calculated for decarboxylation and loss of the benzyl group.

References

1 K. Isono, K. Asahi and S. Suzuki, J. Am. Chem. Soc., 91 (1969) 7490.
2 J. A. Galbis Perez, R. M. Pinto Corraliza, E. Román Galan and M. Gómez Guillen, Ann. Quim., 75 (1979) 387.
3 J. A. Galbis Perez, J. C. Palacios Albarran and E. Román Galan, Carbohydrate Research, 114 (1983) 158.

Zusammenfassung — Das thermische Verhalten einiger aus 2-Benzylamino-2-desoxy-D-glycero-L-gluco-, 2-Benzylamino-2-desoxy-D-glycero-D-ido und 2-Benzylamino-2-desoxy-D-glycero-D-talo-heptononitril (kürzlich beschrieben) erhaltenen 2-Benzylamino-2-desoxy-heptonsäuren wurde in Luft (statische Atmosphäre) und N_2 (dynamische Atmosphäre, Strömungsgeschwindigkeit 200 ml/min) untersucht.

Резюме — В статической атмосфере воздуха и динамической атмосфере азота (скорость потока 200 мл/мин) изучено термическое поведение некоторых 2-бензиламино-2-деоксигептоновых кислот, полученных из нитрилов 2-бензиламино-2-деокси-*Д-глицеро-L-глюконовой*, 2-бензиламино-2-деокси-*Д-глицеро-Д-идоновой* и 2-бензиламино-2-деокси-*Д-глицеро-Д-тало*гептоновой кислот.