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DTG AND DTA STUDIES ON AMINO ACIDS

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ABSTRACT

In this paper, the analysis techniques DTG and DTA were used to study a range of 22 amino acids, the most significant as constituents of proteins. Our research is mainly concerned with the structure—thermal behaviour relationships. In the α-amino acid molecule, the R side chain, which is responsible for specific characteristics of each particular amino acid, influences the thermal effects that occur during their heating.

INTRODUCTION

For many years, research efforts in the field of biological degradation of amino acids were able to establish their derived intermediates and end products, all of them accomodated by unequivocal reaction pathways. In contrast, little attention was paid to the thermal decomposition of the amino acids, being important at present to investigate: i) the stages of their degradation both in general features and in individual details, and ii) the beginning products from the broken down of their molecules. (1-3)

Present work concerning the first task attempted also to correlate the known structural groups in which the amino acids are classified with their respective thermal behaviour.

EXPERIMENTAL

All the α-amino acids were purchased from Merck. Thermal analysis was obtained using a Perkin Elmer 3600 and the DTA 1700. Instrument calibration was performed by a standard Indium sample of known temperature and enthalpy of fusion. The material (approximately 2 mg.) was weighed in platinum (TG) or Al_2O_3 orucibles (DTA). The atmosphere was static air and the heating rate 10ºC/min.

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RESULTS

Thermal behaviour of amino acids is described in Table 1 and 2 and illustrated by the DTA,DTG and TG curves of Ala, Ser and Tyr (Fig.1). Their DTA thermograms show at least a sharp endotherm and some exotherms. The exotherms are due to the sublimation (effect I) and decomposition (effects III and V) of the samples, whereas the endotherm (effect II) corresponds to the melting (and dehydratation or release of hydrochloric acid) phenomena. When occurs, the minor endothermic effect IV is also attributed to decomposition. The TG and DTG thermograms give data in excellent agreement with the DTA features.

Since the most simple amino acid, glycin, shows the same thermal effects (except for sublimation) that exhibit the remaining amino acids, the primary amino function and the carboxyl function bonded to the same carbon atom should be the main responsible of general thermal behaviour. In fact, the dipolar-ion structure for amino acids is enough to account for many of the thermal properties. Thus, the high melting points may be attributed to substantial electrostatic attractions between the oppositely charged groups in the crystal lattice. Nevertheless, the R side chains which exhibit specific characteristics for each particular amino acid influence sufficiently the thermal effects to allow the following conclusions:

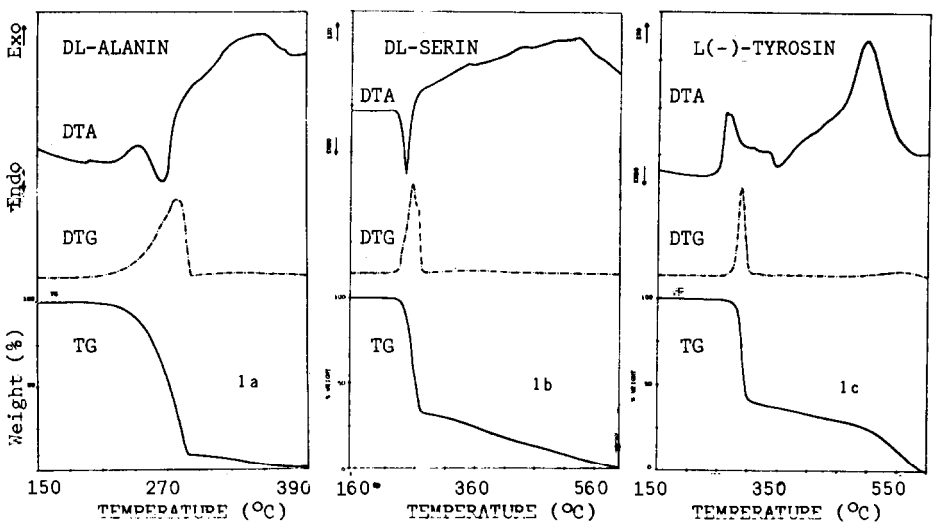

Fig. 1 : DTA, DTG and TG thermograms for Ala (1.a), Ser (1.b) and Tyr (1.c) in air (10ºC/min.).

TABLE I

First characteristic peaks (in ºC) of DTA and DTG heating curves of amino acids.

Amino acid	ONSET TG		ONSET DTA		EFFECT I	DTG I		EFFECT II	
	DTA (exo)							DTA (endo)	
	HCl/ H_2O	Aa	HCl/ H_2O	Aa		HCl/ H_2O	Aa	HCl/ H_2O	Aa
Gly		200		220	-		235 270		263
DL-Ala		205		220	247		279		270
DL-Val		199		193	212		278		267
L-Leu		184		190	211		255		269
L(+)-Ile		186		192	212		260		260
L(-)-Pro		189		209	226		242		231
L(-)-Hypro		230		250	275		295		286
DL-Ser		230		229	-		256		247
DL-Thr		215		198	238		251		247
DL-Met		225		194	240		260		251
L(+)-Cys HCl $.H_2O$	60	138	58 130	165	(224)	70 147	204 236	70 180	235sh 256
L(-)-Cystine		220		223	(224)		257		257
L(+)-Lys HCl		236		258	-	273sh	293	263	285
L(+)-Orn HCl		240		230	-	256sh	280	248	283
L(+)-Arg HCl		238	215	238	-	-	268	224	263
L(+)-Asn		224		225	-		258		237 252
L(+)-Gln		197		201	-		209 255		212 255
L(-)-Phe		247		197	221 239		267 273sh		-
L(-)-Tyr		260		250	275 283		289		-
L-DOPA		268		265	280 297		302		-
L-Trp		240		244	255 268		264		-
L-His HCl	162	250	168	250	-	181	276	173	262

(i) The apolar nature of R in Ala, Val, Leu and Ile results in a sublimation effect previous to the amino acid melting (Fig. 1a) whereas the polar Asn,Gln, Arg, Lys, Orn, Gly and Ser do not sublimate (Fig. 1b).
(ii) The extension of the alkyl chain in aliphatic amino acids has an adverse influence upon the thermal stability. From the DTG I data, the order is: Ala > Val > Ile > Leu; Asn > Gln; except Orn < Lys (for possible molecule cyclation)
(iii) The presence of hydroxilic group in the side chain does not cause sublimation when it is bonded to a primary carbon (Ser) while the sublimation does occur when it is bonded to a secondary carbon (Thr, Hypro). Usually, their effect is stabilizing (DOPA vs. Thr; Tyr vs. Phe; Hypro vs. Pro). (Fig. 2).
(iv) Among the sulphur-containing amino acids, structural differences caused by the presence of a disulphide bridge (in Cystine) instead a thiol (in Cysteine) resulted in a shift of the DTG and DTA peaks of Cystine to higher temperatures. On the other hand, the close similarity of DTA traces of Cysteine and Serine evidences the lability of the Cysteine -SH group regarding oxydation when heated (Fig. 3).

$$\text{Cys-SH} \xrightarrow[\Delta]{O_2} \text{Ser}$$

(v) When R is an aromatic group the first exothermic process has an specific double effect very useful for characterization purposes. Also, their peak temperatures are higher than those of remaining amino acids. (Fig. 1c).

Nevertheless, in all cases the exothermic effects that follow melting and/or sublimation features are more suitable for differentiation purposes. With this idea, we present their temperatures above 400ºC (Table 2).

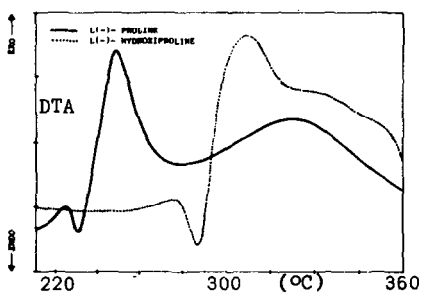

Fig.2 Thermogram for Pro and Hypro

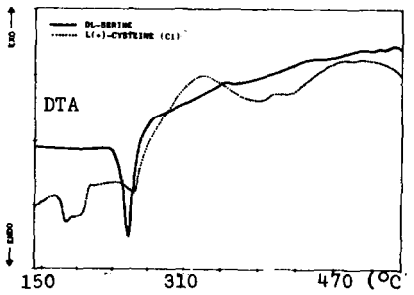

Fig. 3 Thermogram for Ser and Cys.

TABLE II
Last characteristic peaks (in ºC) of DTA and DTG heating curves of Amino acids.

Amino acid	EFFECT III DTA (exo)	DTG II	EFFECT IV DTA (endo)	EFFECT V DTA (exo)	DTG III
Gly	290sh 340	(370)	356	450sh 484	582
DL-Ala	290sh 360	(350)	388	465 492	-
DL-Val	295sh 360	-	375	399 460	-
L-Leu	298 365sh	(310)	390	435-480	-
L(+)-Ile	280 334	-	387	417-430	-
L(-)-Pro	249 330	-	420-423	481	-
L(-)-Hypro	310 350sh	358	384	516	-
DL-Ser	256sh 356	-	364	448 534	-
DL-Thr	254sh 335	-	365	454 502	-
DL-Met	236sh 336	-	395-405	495	-
L(-)-Cys HCl.H_2O	300sh 334	-	392	480-515	-
L(-)-Cystine	300 348	-	380-390	490	-
L(+)-Lys HCl	310sh 334	340	-	430sh 475	445 515
L(+)-Arg HCl	284sh 310	335 357 372	-	488 555sh	576
L(+)-Orn HCl	309	-	-	497 565sh	527
L(-)-Asn	315	-	340	382 430 561	414 601
L(-)-Gln	301	-	319	350-370 520	523
L(-)-Phe	360	355	401	419sh 487	590
L(-)-Tyr	322	-	361	415sh 504	560
L-DOPA	-	340	-	430 563sh	490
L-Trp	-	340	409	546	566
L-His HCl	300sh 333	-	-	565	596

Addendum

Relative to the elucidation of the thermal products from the amino acids decomposition, this is a difficult and time-consuming task. The characterization of Taurine, Histamine and Serine as thermal decarboxylation/oxidation products from Cystine, Hystidine and Cysteine, respectively, has been initiated. Other amino acids metabolites have been reported in the literature from biological degradation reactions, however this has only value as a stimulus since they resulted due to the participation of enzymes in such reactions.

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