

It has been demonstrated that, in X-irradiated aqueous solutions of histidine³ and probably tyrosine⁴, decarboxylation occurs to a very low amount. This is possible, because in aromatic amino-acids there are a number of sites to be attacked by the free radicals produced from the water. Our results with rather small *G*-value indicate that 5-HTP (an aromatic amino-acid too) behaves similarly.

It has been noted⁵ that 5-HT in aqueous solution undergoes many changes in its structure under the influence of different oxidizing agents. Taking into account the low conversion-rate of 5-HTP to 5-HT, one should consider the possibility of transformations of 5-HT molecules when under the influence of X-irradiation. It seems to us likely that the low amount of 5-HT formed could be partly explained by the action of the various oxidizing species produced by the X-rays.

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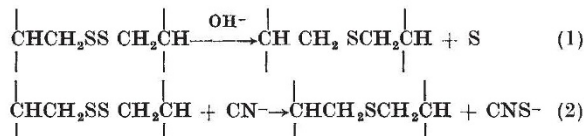
³ Flemming, K., *Arch. Exp. Path. Pharmacol.*, **239**, 425 (1960).

⁴ Rowbottom, J., *J. Biol. Chem.*, **212**, 877 (1955).

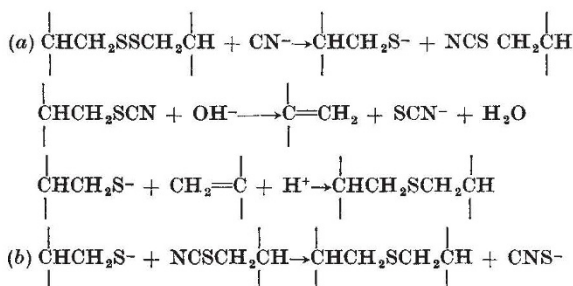
⁵ Eriksen, N., *J. Biol. Chem.*, **235**, 1662 (1960).

Lanthionine Formation in Keratin

REACTION of wool keratin with solutions of alkalis or potassium cyanide leads to the elimination of one of the sulphur atoms of the dithio bond of the cystine residues with the formation of a thioether (lanthionine) linkage:

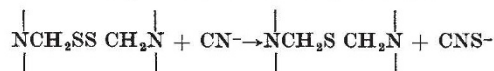


It is considered that the reaction with cyanide ions, which overall may be represented by equation (2), can follow two possible courses:



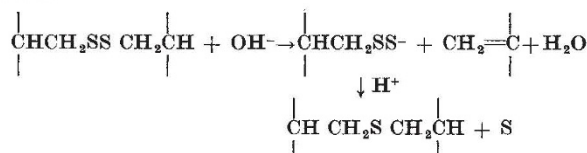
The β -elimination reaction (a) was first proposed by Swan¹, who later suggested the possibility of lanthionine formation by SCN^- displacement² without removal of β -hydrogen atoms. This was confirmed by Earland and Raven³, who studied the reaction of N-mercaptomethylpolyhexamethyleneadipamide disulphide with cyanide ions, and showed that a thio-

ether bond is formed under conditions identical to those which produce lanthionine in wool:



Since β -elimination is impossible, it must be concluded that a reaction such as (b) is very probably an important route for lanthionine formation in wool.

On the other hand, in the alkaline reaction, Swan⁴ has shown the importance of a β -elimination mechanism:



since α' -dimethylcystine is degraded only extremely slowly under these conditions, compared with free cystine.

The reaction of N-mercaptomethylpolyhexamethyleneadipamide with alkalis has now been examined, as it is probably a better model for wool⁵ than Swan's compounds, in that the reaction, as with wool, is heterogeneous, giving the ruptured disulphide residues a greater chance to re-unite in a lanthionine linkage.

2.00 gm. of disulphide (sulphur, 4.20 per cent) were boiled under reflux for 5 hr. with 400 ml. of the solution of alkali. After reaction, the solid product was collected, washed with water and dried *in vacuo*. The results obtained are given in Table 1. The analytical methods used have been described previously³.

Table 1

Solution	pH	Wt. loss (per cent)	Sulphur in product (per cent)	Disulphide sulphur (per cent)	NH ₂ m.equiv. 100 gm.
0.10 M Na ₂ HPO ₄	—	—	4.20	4.07	1.5
0.05 M Na ₂ B ₄ O ₇	8.0	1.0	3.99	4.26	1.5
0.10 M Na ₂ CO ₃	9.2	0	4.14	4.27	1.6
0.10 M Na ₂ CO ₃ *	10.5	2.5	3.70	3.94	2.3
0.10 M Na ₂ CO ₃ *	10.5	11.0	3.39	3.28	2.7
0.10 M NaOH	12.0	35.0	2.23	1.90	4.7

* Boiled for 10 hr.

It is shown that a lanthionine type of reaction does not occur when the β CH group is replaced by nitrogen, which must be regarded as strong supporting evidence for the β -elimination mechanism, and against mechanisms which involve formation by direct attack on the α -carbon atom⁶.

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