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Scission of the *N*-Terminal Residue from a Protein after Transamination

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The *N*-terminal residue of a protein can be transaminated with glyoxylate and copper to an α-oxo acyl residue, which can then be cleaved from the rest of the protein (Dixon & Moret, 1965). Bifunctional nucleophiles such as *o*-phenylenediamine have been used for the scission of transaminated *Pseudomonas* cytochrome, and yield of des-Glu[1]-protein estimated by chromatography on CM-cellulose.

Dixon & Moret never obtained yields greater than 65%, but they transaminated the cytochrome using pyridine as catalyst. We have now shown, by chromatography in a system where transaminated cytochrome emerges greatly retarded, that this method gives about 35% of unknown, less retarded, side products. Using acetate buffer without pyridine (Dixon, 1967*a*,*b*), side products are only about 8%, and if the transaminated cytochrome is purified chromatographically and used as starting material, up to 90% scission can be obtained with *o*-phenylenediamine.

The diamine presumably forms a Schiff base with the α-oxo group before reaction. To see whether isomerization about this double bond might be rate-limiting, we tried reduction with borohydride but yields were not improved. *NN'*-Dimethyl-*o*-phenylenediamine, which could not form a Schiff base, was no faster than *o*-phenylenediamine when tested on cytochrome, although it gave much better results with a model compound, pyruvoylglycine.

Substituent groups on the benzene ring of the diamine have variable effects. 4-Nitro- and 4,5-dichloro-*o*-phenylenediamine are inactive, but 3-chloro-*o*-phenylenediamine gives some yield, and 4-chloro- or 4-methyl-*o*-phenylenediamine differs little from *o*-phenylenediamine. A carboxyl group at position 4 might decrease the activity of the amino groups both for the desired reaction and for side reactions. In fact, 3,4-diaminobenzoic acid reacted more slowly than *o*-phenylenediamine but gave marginally higher yields after 48hr. The half lives were 6·0 and 1·6hr. respectively. When the carboxyl group was methylated, yields were much lower.

The best yields (95%) of des-Glu[1]-cytochrome were obtained by incubating transaminated cytochrome (about 0·1mM) at 37° *in vacuo* in 2M-sodium acetate, 2N-acetic acid, and 40mM-diamine. At 3°, about 60% scission was obtained in 3 days.

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Effects of Silver Ions on Deoxyribonucleic Acid–Polycyclic Hydrocarbon Complexes

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Addition of ions such as Na^+ or Mg^{2+} (which bind primarily to DNA phosphate groups) to native or denatured DNA in water, respectively decreases or increases its solubilizing activity towards polycyclic hydrocarbons but causes no appreciable shift in spectrum of the bound form (Boyland & Green, 1964; Boyland, Green & Liu, 1964).

In contrast, addition to benzo[*a*]pyrene in DNA solution in water of increasing ratios (R_F) of added silver nitrate/DNA phosphate caused further long wavelength shifts in the hydrocarbon absorption spectrum up to 8–9mμ at $R_F \geq 1$ and about 5mμ at $R_F = 0{\cdot}5$; in addition to the 10mμ shift observed after reaction with DNA alone. Addition of excess cyanide or thiosulphate to complex the Ag^+ ions resulted in immediate reappearance of the spectrum corresponding to the original DNA-bound hydrocarbon. Ag^+ ions bind mainly to the bases of DNA (Jensen & Davidson, 1966; Daune, Dekker & Schachman, 1966).

Similar shifts were observed in 30% (v/v) ethanol/water solution of DNA, where the hydrocarbon absorption peaks corresponded to those of the free form only, if either Ag^+ ions or DNA were omitted i.e. the shift in maxima (reversed by cyanide) on addition of Ag^+ ions was 15mμ at R_F 0·5.

Ag^+-induced spectral shifts, reversible by cyanide, were also observed for pyrene, perylene and 7,12-dimethylbenz[*a*]anthracene in aqueous DNA solutions.

No spectral shift was seen when Ag^+ ions (0·1M) were added to pyrene in water or to benzopyrene

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