It is evident that this degradation involves the unusual step of a direct cleavage of a saturated carbon chain. It is envisaged as arising from the separation of the anion X^- from (X) ($X = OH, Cl$ or $OCOMe$) with consequent electronic re-arrangement in the cation, the electron displacement a , assisted by b , entailing breaking of the bond between carbon atoms 2 and 3. At the same time the anion becomes attached to the electrophilic carbon atom 3, presumably to give (XI) or decomposition products thereof. The hypothetical intermediate (XI) ($R = Ph, X = OCOMe$) from (III) will react further with acetic anhydride to give cinnamic acid by a mechanism similar to that involved in the Perkin reaction.

This reaction, which might be regarded as an anionotropic degradation, is reminiscent of the anionotropic re-arrangement of allyl esters²; in the latter reaction, however, the electron shift consequent upon the separation of the anion can be accommodated, without cleavage of the carbon-carbon bond, since the cation is already unsaturated.

Further work is in progress to determine the generality of this reaction.

D. W. ADAMSON

Chemical Division,
Wellcome Research Laboratories,
Beckenham, Kent.
March 18.

¹ Adamson, *J. Chem. Soc.*, S 144 (1949).

² Burton and Ingold, *J. Chem. Soc.*, 904 (1928).

A Synthesis of *iso*-Pelletierine and Methyl *iso*-Pelletierine

ACCORDING to Robinson's¹ theory of the biogenesis of alkaloids, the piperidine (that is, coniine) group of alkaloids is derived from *iso*-pelletierine (I) and methyl *iso*-pelletierine (II), which are formed by the condensation of δ -amino- and ξ -methylamino-valeraldehydes respectively with acetoacetic acid or acetone dicarboxylic acid.

We have now prepared both δ -amino- and ξ -methylamino-valeraldehyde diethylacetals and have

found that after mild acid hydrolysis to the corresponding free aldehydes the alkaloids (I) and (II) can be synthesized by condensation with acetoacetic acid in dilute aqueous solution at room temperature. The yield of (II) at pH 7 was more than 70 per cent, but at this pH (I) was formed in traces only. However, at pH 11 a yield of about 50 per cent of (I) was obtained. In each case the identity of the alkaloid was established by its boiling point and by the melting points and analyses of several of its derivatives.

While this work was in progress there came to our notice a report by E. Herzog² of a lecture delivered by C. Schöpf. Although the report contains several obvious misstatements or misprints, it does state that Schöpf has synthesized (I) from Δ -1-piperidine³ and acetoacetic acid at pH 11, but no mention is made of (II).

Full details of our work will be published elsewhere in due course.

E. ANET
G. K. HUGHES
E. RITCHIE

Department of Organic Chemistry,
Chemistry School,
University of Sydney.
July 27.

¹ Robinson, R., *J. Chem. Soc.*, 111, 876 (1917).

² Herzog, E., *Chimia*, 2, 206 (1948).

³ Schöpf, C., *et al.*, *Ann.*, 559, 1 (1948).

Identification of the End-Amino Groups of Wool by Means of their 2 : 4-Dinitrophenyl Derivatives

THE amino-acids with free α -amino groups in wool have been identified using Dr. F. Sanger's technique¹. Considerable use was made of buffered, as well as unbuffered, silica gel columns, using Sanger's original solvents. The gel was buffered at pH 6.0 with 0.5 ml. buffer solution (9.36 gm. $NaH_2PO_4 \cdot 2H_2O$ + 14.32 gm. $Na_2HPO_4 \cdot 12H_2O$ per 100 ml. solution) per gm. silica. This was used in conjunction with (a) ether, (b) 1 per cent butanol-chloroform, (c) 30 per cent butanol-chloroform, (d) 5 per cent propanol-cyclohexane, (e) 33 per cent ether-ligroin as solvents. The ether was freed from peroxides by shaking with an acid solution of ferrous ammonium sulphate, followed by several changes of distilled water, and stored in a dark bottle. In agreement with other workers^{2,3}, leucine could not be separated from valine on unbuffered columns, but this was easily achieved by using 0.5 ml. solution (7.16 gm. $Na_2HPO_4 \cdot 12H_2O$ + 7.60 gm. $Na_3PO_4 \cdot 12H_2O$ per 100 ml. solution) per gm. silica with ether as solvent. The acids were identified as (a) valine, (b) alanine, (c) glycine, (d) threonine, (e) serine, (f) glutamic acid, (g) aspartic acid.

For quantitative determination of these 2 : 4-dinitrophenyl amino-acids, which is now being carried out, it is found most convenient to run the ether-soluble fraction on a 2-gm. silica gel column buffered at pH 6.0 with ether as solvent. This achieves individual separation of the glycine, threonine, serine, glutamic and aspartic derivatives in one operation, the valine and alanine moving as a fast band together with the decomposition products containing 2 : 4-dinitroaniline and 2 : 4-dinitrophenol. This mixture is run with chloroform on a column buffered at pH 7.2 with 0.5 ml. buffer solution (14.32 gm.