

The anionic behaviour could be explained simply by assuming that sulfuric acid is added to the conjugated system and conveys an acidic character to the carotenoids. However, such a reaction should not involve the change of colour from yellow to blue, nor would it be easy to reconcile this view with the reversibility of the reaction by simple addition of water.

Nothing was known until now about the existence of an electrochemistry of carotenoids. Our experiments revealed not only its existence but also its rather complicated nature. We wish to extend these investigations to a larger number of well defined carotenoids in acids of different strength in different solvents, and we should be glad if specialists in carotenoid chemistry would join in this investigation. We hope to be able to investigate also the magnetic behaviour of the yellow, green and blue solutions.

I wish to express my gratitude to Prof. P. TUZSON for having made me acquainted with carotenoid chromatography and for his valuable advice concerning purification and identification of carotenoids. I am also greatly indebted to Prof. P. KARRER for his valuable and helpful correspondence.

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#### Zusammenfassung

Carotinoide und Carotinoid-Epoxyde bilden mit verschiedenen Säuren und Salzen intensiv blau gefärbte Produkte, deren Natur unbekannt ist. Das elektrolytische Verhalten dieser Stoffe wird untersucht, und es wird festgestellt, dass die Wanderungsrichtung in hohem Mass davon abhängt, ob die Behandlung der Carotinoide mit Säuren in wässriger oder in wasserfreier alkoholischer Lösung vorgenommen wurde.

### The Identity of Vincamajoridine and Akuammine

Akuammine,  $C_{22}H_{26}O_4N_2$ , the main alkaloid in the seeds of *Picralima Klaineana*<sup>1</sup> and *P. nitida*<sup>2</sup> was recognized as a 5-hydroxy-N-methylindoline as a result of a study of its reactions and of its U.V. and I.R. spectra<sup>3</sup>.

Independently, vincamajoridine, recently isolated from *Vinca major* L., was similarly characterized as a 5-hydroxy-N-methylindoline of the formula  $C_{22}H_{26}O_4N_2$ <sup>3</sup>.

The descriptions of the two substances left little doubt in our minds that they were identical and a direct comparison has established that this is indeed the case. The specimen of vincamajoridine, separated chromatographically, was slightly more pure than that of akuammine. Both specimens crystallized from ethanol in short, slender, microscopic needles of identical appearance.

Heated together in capillaries in the same bath vincamajoridine had (uncorr.) m.p. 258–260° (decomp.), and akuammine had m.p. 255° (decomp.); a mixture had m.p. 255–256° (decomp.). The m.p. varied with the rate of heating but a mixture of the two specimens never melted lower than did the akuammine.

<sup>1</sup> T. A. HENRY and T. M. SHARP, J. Chem. Soc. 1927, 1950. – T. A. HENRY, J. Chem. Soc. 1932, 2759.

<sup>2</sup> M. F. MILLSON, R. ROBINSON, and A. F. THOMAS, Exper. 9, 89 (1953).

<sup>3</sup> M. M. JANOT and J. LE MEN, C. r. Acad. Sci. 240, 909 (1955).

The colour reaction with ferric chloride was exhibited identically by the two specimens in respect of colour, intensity, and duration. Vincamajoridine has  $[\alpha]_D^{20} -104^\circ \pm 4^\circ$  (pyridine)<sup>1</sup>; we now find that akuammine has  $[\alpha]_D^{20} -105.3^\circ$  (c, 1.31 in pyridine).

The U.V. absorptions of akuammine<sup>2</sup> and vincamajoridine<sup>1</sup> are the same within experimental error and the complete correspondence of the I.R. spectra is quite remarkable. The curve has already been recorded<sup>1</sup>. Incidentally this agreement in spectra of specimens isolated from different plants, by two groups of workers, and taken on different instruments, shows that even apparently insignificant details are characteristic and signalize real properties of the molecule.

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#### Résumé

Les auteurs démontrent que la vincamajoridine  $C_{22}H_{26}O_4N_2$ ; F. 258;  $(\alpha)_D^{20} -104 \pm 4^\circ$  (py) récemment extraite de la Grande Pervenche (*Vinca major* L.) est identique à l'akuammine antérieurement découverte dans les graines d'une autre Apocynacée *Picralima nitida* (STAPP) T. et H. DURAND.

<sup>1</sup> M. M. JANOT and J. LE MEN, C. r. Acad. Sci. 240, 909 (1955).

<sup>2</sup> M. RAYMOND-HAMET, C. r. Acad. Sci. 230, 1183 (1950).

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### Oriented Crystallization of Inorganic Salts in Collagen

In an attempt to study in detail the reported "addition compounds" of collagen with alkali<sup>1</sup>, the authors observed some interesting phenomena which are reported here. All the experiments described below were performed with kangaroo tail tendon.

A fibre of collagen about 1 mm diameter was kept under tension in 0.25 N sodium hydroxide for about 15 h and was then dried. An x-ray photograph of this specimen is reproduced in Figure 1. In addition to the collagen pattern, the figure exhibits a number of spots on definite layer lines, suggestive of the existence of well crystallized material all oriented parallel to the fibre axis. The spots (excluding those due to collagen) could be indexed on the basis of an orthorhombic unit cell with  $a = 5.25$  Å,  $b$  (fibre axis) = 6.45 Å,  $c = 10.7$  Å. On repeating the experiment a second pattern was obtained, which again corresponded to a well crystallized material, oriented with one of its axes along the fibre, but whose unit cell was monoclinic with  $a = 20.4$  Å,  $b$  (fibre axis) = 3.5 Å,  $c = 10.3$  Å,  $\beta = 106^\circ$ . The positions of the spots closest to the direct beam in the first pattern agreed with those reported earlier<sup>1</sup>, but those in the second pattern were quite different. The sharpness of the reflections and also the fact that they could be observed right up to  $\Theta = 90^\circ$ , indicated that they cannot be ascribed to an

<sup>1</sup> G. L. CLARK and A. SCHAAD, Radiology 27, 339 (1936).