

ALKALOIDS OF THE *Papaveraceae*. XLVII.\*

## IDENTITY OF BOCCONINE WITH CHELIRUBINE

J. SLAVÍK and F. ŠANTAVÝ

*Institute of Medical Chemistry, Purkyně University, Brno, and**Institute of Medical Chemistry, Palacký University, Olomouc*

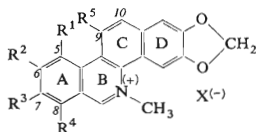
Received September 29th, 1971

The identity of bocconine with chelirubine was confirmed by direct comparison of these two substances. The assignment of the structures *Ia* and *Ib*, respectively, to chelirubine was discussed on the basis of ultraviolet spectral data.

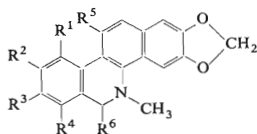
Onda and coworkers<sup>1</sup> isolated, besides saguinarine and chelerythrine, a presumably new alkaloid from the roots of the plant species *Bocconia cordata* WILLD. (Synonymum: *Macleaya cordata* (WILLD.) R. BR.) (yield 0.004%) which they called bocconine. For the quaternary cation of this benzophenanthridine base<sup>2</sup>, they deduced structure *Ia* (X = anion) from the NMR spectrum. Contrary to the structures of the so far known alkaloids of this type, structure *Ia* is characterized by an unusually substituted ring A. The properties of bocconine<sup>1,2</sup> are strikingly similar to those of chelirubine<sup>3,4</sup> (*Ib*) which was isolated from *Chelidonium majus* L.<sup>5</sup> and, later on, from many other plants of the family *Papaveraceae*. This alkaloid was also isolated from the root of *Macleaya cordata*<sup>6</sup> (yield 0.002%). At the same time, its identity with the "base B", which was isolated from the same plant by Tani and Takao<sup>7</sup>, could be established. The assumed identity of bocconine with chelirubine was confirmed by direct comparison of the melting and the mixed melting points, the IR and UV spectra, and the  $R_F$ -values of pseudoethanolates ("ethoxy-bocconine"<sup>1,2</sup>) (*Iia*), pseudocyanides (*Iib*), and chlorides (*Ia*, and *Ib*, respectively, X = Cl) which were prepared from the samples of these two substances. Consequently, the designation "bocconine" is synonymous with the older designation chelirubine which possesses priority. The discrepancy between the structures<sup>2,4</sup> *Ia* and *Ib* results from the different interpretation of the NMR spectrum, though it can by no means suffice for this structural elucidation. However, the determination of the position of the substituents of the ring A might be possible by a comparison of the ultraviolet spectra of the salts of the above-mentioned compounds with those of the quaternary benzophenanthridine alkaloids of the sanguinarine<sup>8</sup> (*Ic*) and the nitidine<sup>8,9</sup> (*Id*) type and with those of isoquinoline derivatives<sup>8,10</sup> substituted in vari-

\* Part XLVI: This Journal 36, 2385 (1971).

ous positions by methoxyl or methylenedioxy groups. The ultraviolet spectra of these model compounds show unambiguously that the longest wavelength of substances with an oxygen electron donating substituent in *para*-position ( $C_{(6)}$ ) to the  $C=N$  bond of the heterocyclic ring undergoes a hypsochromic and hyperchromic shift.



- Ia*,  $R^1 + R^2 = OCH_2O$ ,  $R^3 = R^5 = H$ ,  $R^4 = OCH_3$   
*Ib*,  $R^1 = R^2 = H$ ,  $R^3 + R^4 = OCH_2O$ ,  $R^5 = OCH_3$   
*Ic*,  $R^1 = R^2 = R^5 = H$ ,  $R^3 + R^4 = OCH_2O$   
*Id*,  $R^1 = R^4 = R^5 = H$ ,  $R^2 = R^3 = OCH_3$



- II*,  $R^1 + R^2 = OCH_2O$ ,  $R^3 = R^5 = H$ ,  $R^4 = OCH_3$   
 or  $R^1 = R^2 = H$ ,  $R^3 + R^4 = OCH_2O$ ,  $R^5 = OCH_3$ ,  
*a*,  $R^6 = OC_2H_5$ ; *b*  $R^6 = CN$

On the contrary, substitution by three electron donating oxygen substituents<sup>8,11</sup> at  $C_{(7)}-C_{(8)}$  results in a bathochromic and hypochromic shift of this band. However, the longest wavelength band of the chloride of chelirubine and of its derivatives (in a mixture of ethanol and 0.1M-HCl 6 : 1) appears at 510 nm ( $\log \epsilon$  3.75), whereas that of sanguinarine at 474 nm ( $\log \epsilon$  3.72), and of nitidine at 368 nm ( $\log \epsilon$  3.99). From that follows that the cation of chelirubine cannot have structure *Ia* or any other structure proposed by Onda and coworkers<sup>2</sup> for bocconine. Likewise, the methoxyl group cannot be attached to the nucleus D because this nucleus with its oxygen substituents forms an inseparable moiety of the benzophenanthridine system, thus taking part in the ultimate formation of the ultraviolet spectrum. Hence, the only possible location of the methoxyl group of alkaloids of the chelirubine type is at  $C_{(9)}$  or  $C_{(10)}$  in the ring C. The biogenetic viewpoint and the NMR spectrum<sup>4</sup> favour the location of the methoxyl group at  $C_{(9)}$ , which is consistent with the proposed<sup>4</sup> structure *Ib* for chelirubine.

## EXPERIMENTAL

The melting points (uncorrected) were determined in capillaries. The UV spectra were measured in ethanol on a Unicam Spectrophotometer Model SP 700, the IR spectra on an Infracscan, Hilger and Watts apparatus.

**Material:** For purposes of comparison, chelirubine was used which was isolated from *Sanguinaria canadensis*<sup>3</sup> and an authentic sample of bocconine which was designated<sup>1,2</sup> "ethoxybocconine".

**Chelirubine-ps-ethanolate:** Prisms of m.p. 224–225°C (ethanol)<sup>3</sup>, on admixture with authentic "ethoxybocconine" (m.p. 224–226°C)<sup>1,2</sup>, the m.p. was undepressed. The ultraviolet spectrum of "ethoxybocconine" (in ethanol)  $\lambda_{\max}$  (log  $\epsilon$ ) 227 nm (4.52), 281 nm (4.46), 339 nm (4.25), 353 nm (4.20);  $\lambda_{\min}$  253 nm (4.13), 313 nm (3.95), 349 nm (4.20) is identical with the spectrum of chelirubine-ps-ethanolate. The infrared spectra (in chloroform) of these two substances are identical.

**Chelirubine chloride:** From "ethoxybocconine" a chloride was prepared<sup>3</sup> which gave purple needles of m.p. 282°C (diluted hydrochloric acid). On admixture with authentic chloride of chelirubine (m.p. 282°C), the m.p. was undepressed. The ultraviolet spectrum of the chloride of bocconine (ethanol + 0.1M-HCl 6 : 1)  $\lambda_{\max}$  (log  $\epsilon$ ) 236 nm (4.45), 285 nm (4.51), 355 nm (4.36), 510 nm (3.77);  $\lambda_{\min}$  257 nm (4.12), 307 nm (3.86), 442 nm (3.42) is identical with that of the chloride of chelirubine recorded in the same solvent system. The infrared spectra (in KBr) of the two samples under investigation are identical. The  $R_F$ -values (Whatman No 1, butanol-acetic acid-water 10 : 1 : 3) of these two samples are identical (0.65; in ultraviolet light a fluorescent purple spot).

**Chelirubine-ps-cyanide:** ps-Cyanide was prepared<sup>3</sup> from the chloride of bocconine, prisms of m.p. 273–274°C (chloroform-ethanol), mixed m.p. with ps-cyanide of chelirubine<sup>3</sup> (m.p. 273–274°C) undepressed. The ultraviolet spectrum of ps-cyanide of bocconine (ethanol),  $\lambda_{\max}$  (log  $\epsilon$ ) 230 nm (4.12), 279 nm (4.04), 343 nm (3.87), 356 nm (3.86);  $\lambda_{\min}$  254 nm (3.80), 312 nm (3.42), 351 nm (3.83) is identical with that of chelirubine-ps-cyanide. Likewise, the infrared spectra of these two samples (in KBr) are identical.

*The authors wish to thank Prof. M. Onda, Kitasato University, Tokyo, Japan, for the supply of the authentic sample of ethoxybocconine, and Mrs D. Walterová, Chemical Institute, Olomouc, for the measurements of the UV and IR spectra.*

## REFERENCES

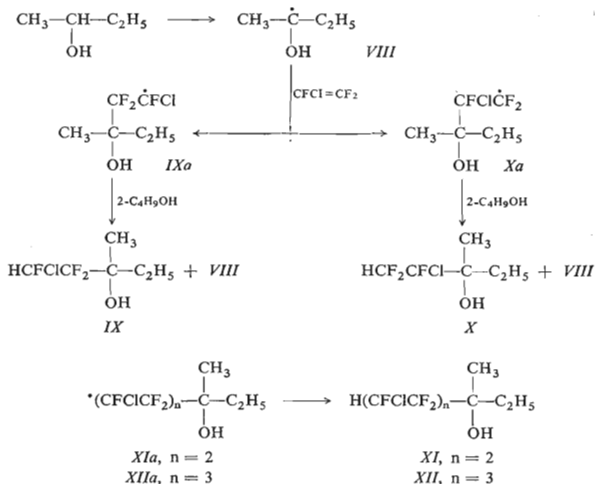
1. Onda M., Takiguchi K., Hirakura M., Fukushima H., Okagawa M., Naoi F.: *Nippon Nogei-kagaku Kaishi* 39, 168 (1965); *Chem. Abstr.* 63, 18964 (1965).
2. Onda M., Abe K., Yonezawa K., Esumi N., Suzuki T.: *Chem. Pharm. Bull. (Tokyo)* 18, 1435 (1970).
3. Slavík J., Slavíková L.: *This Journal* 25, 1667 (1960).
4. Slavík J., Dolejš L., Hanuš V., Cross A. D.: *This Journal* 33, 1619 (1968).
5. Slavík J., Slavíková L.: *Chem. listy* 48, 1382 (1954); *This Journal* 20, 21 (1955).
6. Slavík J., Slavíková L., Appelt J.: *This Journal* 30, 887 (1965).
7. Tani C., Takao N.: *Yakugaku Zasshi* 82, 755 (1962).
8. Hruban L., Šantavý F., Hegerová S.: *This Journal* 35, 3420 (1970).
9. Šimánek V., Preininger V., Hegerová S., Šantavý F.: *This Journal* 37, 2446 (1972).
10. Bossi A., Teitel S.: *Helv. Chim. Acta* 53, 1779 (1970).
11. Šantavý F., Walterová D., Hruban L.: *This Journal* 37, 1825 (1972).

Translated by I. Bartošová.

CHEMISTRY OF ORGANIC FLUORINE COMPOUNDS. XIII.  
 RADICALIC ADDITION OF 2-PROPANOL AND 2-BUTANOL TO  
 TRIFLUOROCHLOROETHYLENE

F. LIŠKA, M. NĚMEC and V. DĚDEK

This Journal 37, 2091 (1972). The following Scheme 2 was omitted:



SCHEME 2

ALKALOIDS OF THE *Papaveraceae*. XLVII.  
 IDENTITY OF BOCCONINE WITH CHELIRUBINE

J. SLAVÍK and F. ŠANTAVÝ

This Journal 37, 2805, 2806 (1972). p. 2805, 2nd paragraph should read: On the contrary, substitution by two electron ... P. 2806, reference 9. should read: This Journal 37, 2746 (1972).