

ALKALOIDS OF *ALSTONIA PLUMOSA**

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Abstract—Nineteen indole alkaloids have been isolated from the root and stem barks of *Alstonia plumosa*, from New Caledonia. Twelve of them were known compounds: fluorocarpamine, pleiocarpamine, 11-methoxy compactinervine (alstovine), cabucraline, cathafole, caberine, quaternoxine, caberoline, quaternoline (raucubaine), deacetylidesformo akuammiline (strictamine), pleiocraline and pleiocorine. Among the seven novel alkaloids, there are four monomers: 3,4-seco 3,14-dehydrocabucraline, cabucraline *N*(4)-oxide, cabucraline 10-carboxaldehyde, 2,7-dihydroxypleiocarpamine and three dimers: plumocraline, desoxy-cabufiline and nordesoxycabufiline.

INTRODUCTION

As a continuation of our chemotaxonomic work on the New Caledonian *Alstonia*, we herein describe our results on the alkaloid content of *Alstonia plumosa* Labill. var. *communis* Boiteau forma *glabra* Boiteau[1]. Plant material was collected in the Mandjelia Forest and was identified by T. Sevenet (Sevenet-Pusset voucher No. 1619). The present study was limited to the barks of the roots and of the stem; the alkaloid content of the leaves was low and its examination was not pursued.

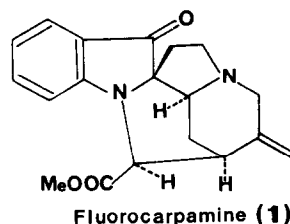
RESULTS AND DISCUSSION

The root bark was extracted in the usual fashion[2] to yield 16.9 g/kg of crude alkaloid mixture (AM), which was separated by medium pressure liquid chromatography. Seven alkaloids were separated; they are in order of increasing polarity (Whatman plate, C_6H_6 - Et_2O - $MeOH$, 6:4:1): fluorocarpamine, 1 (1.5% of AM), pleiocarpamine, 2 (20% of AM), cabucraline, 3 (4.5% of AM), 11-methoxy compactinervine, 4 (also known as alstovine, 1% of AM)[3], cabucraline *N*(4)-oxide, 5 (0.5% of AM), 3, 4-seco 3, 14-dehydrocabucraline, 6 (0.5% of AM) and plumocraline, 7 (3.3% of AM).

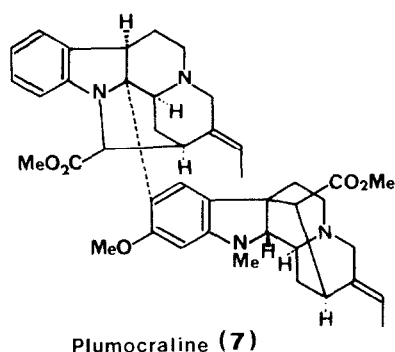
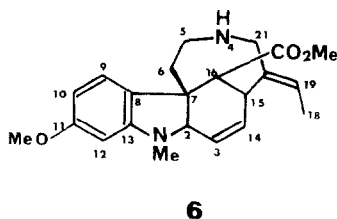
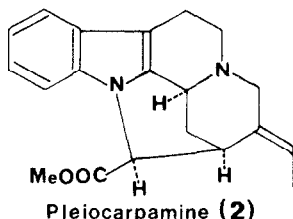
Alkaloids 2–4 were identified by comparison with authentic samples available from previous studies of *Alstonia*. Fluorocarpamine (1) was identified by comparison of its physical and spectral properties with literature data[4, 5]. Among these it is worth noting its fluorescence on TLC and its UV spectrum (maxima at 237, 258 and 410 nm). Compound 5 dis-

played spectral properties (UV, MS, IR) similar to those of cabucraline 3; slight differences are found in the NMR spectra in the δ 4–4.5 region, which corresponds to the H–C–N protons of the molecule. The hypothesis of 5 being the *N*-oxide of 3 stemmed from their behaviour on TLC (different mobilities but identical colors with spray reagents); this was verified by the conversion of 3 to 5 (MCPBA) and by the reverse transformation (Ph_3P , $HOAc$). Compound 6 was also very similar to 3. A major difference was found in the 400 MHz 1H NMR spectrum of 6 which showed extra signals at δ 6.23 and 5.76 for two olefinic protons. All other elements of 3 were also found in this NMR spectrum except the H-14; the structure 3,4-seco 3,14-dehydrocabucraline was therefore proposed for 6. Paucity of material precluded all chemical investigations on 6. Compound 7, the most polar alkaloid isolated from the bark of the roots is the novel plumocraline (7); arguments leading to its structural determination have been the object of a preliminary note[6]. A complete description of 7 is given in the Experimental.

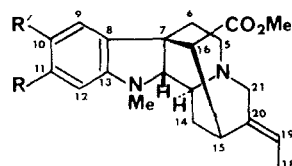
In the same fashion the aerial bark was extracted to give a 8.6 g/kg yield of a very complex alkaloid mixture. Seventeen alkaloids were separated from this



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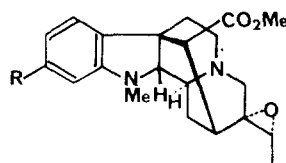
(12) are known alkaloids from *A. vitiensis* [3] and *A. quaternata* [9]. The 10-methoxy substituted analogs 3, 9 and 11 were originally discovered in several species of *Cabucala* from Madagascar [10]. Alkaloid 12 has also been found by Kutney *et al.* in *Rauwolfia salicifolia* and given the name raucubaine, the structure of which was confirmed by X-ray crystallography [7]. Alkaloids 11 and 12 can be prepared in excellent yield by heating or by acid treatment of 9 and 10 and it is questionable whether they are natural or not. Strictamine (14) [11], deacetyldeformo akuammiline, was obtained 90% pure and its physical properties were close to those of the natural product and of those of a sample made from akuammiline. It was contaminated by a compound showing a M^+ at m/z 352 and fragments in the mass spectrum 30 atomic mass units above those of strictamine. The coexistence of the related cathafoline (8) and cabucraline (3) in *A. plumosa* allows us to propose a 10-methoxy strictamine structure for the impurity; this point awaits further isolation of pure material to be confirmed.



Cabucraline (3) $R = OMe$, $R' = H$

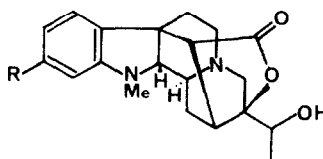
Cathafoline (8) $R = R' = H$

13 $R = OMe$, $R' = CHO$



Caberine (9) $R = OMe$

Quaternoxine (10) $R = H$



Caberoline (11) $R = OMe$

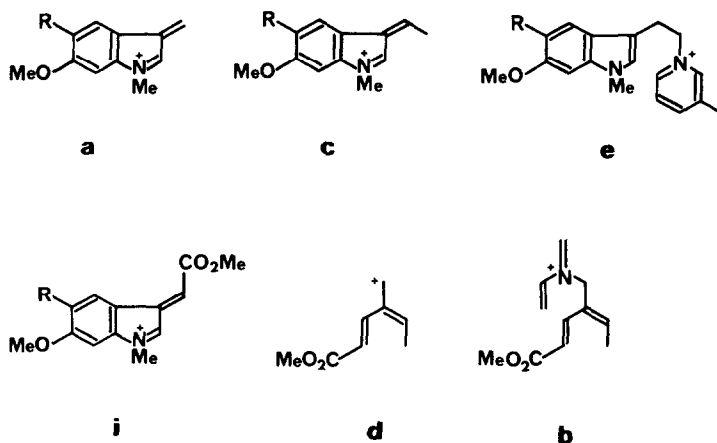
Quaternoline (12) $R = H$

mixture by medium pressure liquid chromatography followed by prep. TLC. Due to the complexity of the mixtures, all the liquid chromatography fractions were not investigated and the figures given correspond to approximate yields. The isolated alkaloids are: fluorocarpamine, 1 (2% of AM), pleiocarpamine, 2 (30% of AM), cabucraline, 3 (15% of AM), 11-methoxy compactinervine, 4 (5% of AM), cabucraline *N*(4)-oxide, 5 (*ca* 2% of AM), cathafoline, 8 (5% of AM), caberine, 9 (*ca* 2% of AM), quaternoxine, 10 (*ca* 2% of AM), caberoline, 11 (2% of AM), quaternoline, 12 (also known as raucubaine) [7] (2% of AM), (10-carboxaldehyde) cabucraline, 13 (3% of AM), strictamine, 14 (deacetyldeformo akuammiline) (1% of AM), 2, 7-dihydroxypleiocarpamine, 15 (*ca* 2% of AM), pleiocorine, 16 (*ca* 2% of AM), pleiocraline, 17 (*ca* 2% of AM), desoxycabufiline, 18 (7% of AM) and nordesoxycabufiline, 19 (3% of AM).

All the alkaloids of the rootbark except 6 and 7 were also isolated from the stembark. As both extractions were conducted in the same manner, it must be noted that 7 is of natural origin and not an artifact as could be supposed from its facile preparation from 2 and 3 [6].

Among the other alkaloids the three pairs 3–8, 9 and 10, and 11 and 12 differ only by a methoxy substituent on the aromatic ring; their separation was tedious and was only achieved by multiple migration TLC. Alkaloid 8, previously known as alkaloid-X from *Catharanthus longifolius* [8] has also been found in *A. quaternata*. Quaternoxine (10) and quaternoline

The novel alkaloid 13 is characterized by an UV spectrum with maxima at 215, 258, 303 and 354 nm, unchanged in acidic or basic media. Its mass spectrum was reminiscent of that of 3 but the M^+ and ions a, c, e and i were 28 atomic mass units greater than those of 3. Ions b and d pertaining to the terpenic part of the molecule were common to 3 and 13. The extra substituent could be detected in the ¹H NMR spec-



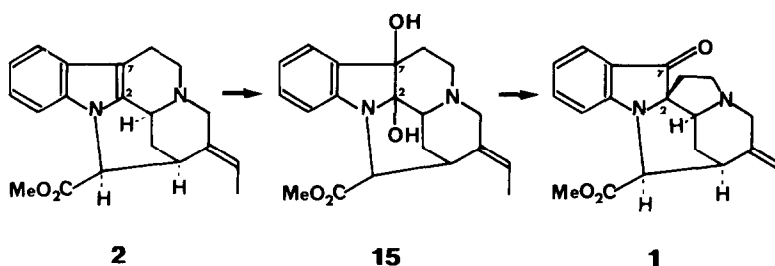
trum of **13**, which showed two singlets for the aromatic protons at δ 6.05 and 7.34 and a sharp singlet at 10.1. This signal was attributed to an aldehyde to account for its chemical shift; it also explains the 28 supplementary mass units and the UV and IR vibrations at 1660 and 1605 cm^{-1} . This aldehyde was placed on C-10 to account for the appearance of the ^1H NMR spectrum; a reversal of the aromatic substituents was ruled out because it could not explain the shifts of H-9 from δ 6.8–7.3 and of H-12 from δ 6.2–6.05.

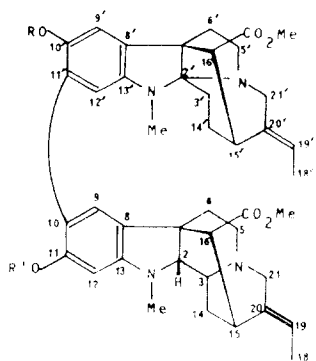
The presence of an extraneous carbon atom in compound **13**, whose biogenesis probably involves tryptophan as in most indole alkaloids, may be an artifact of extraction. The same problem is encountered in vindolicine from *C. longifolius* [12] and in the dimeric indole alkaloids from *Melodinus celastroides* [13]. The nucleophilicity of the C-10 of cabucraline is a well established fact as demonstrated by the formation of plumocraline (**7**). The electrophile may be here an activated form of chloroform, reacting in a Vilsmeier–Haack-like reaction to give after hydrolysis an aldehyde. Although chloroform was not used during the extraction process, it has been used for the liquid chromatography; the complexity of the alkaloid mixture before chromatography did not allow us to check for the presence of **13** before purification.

The electron-impact mass spectrum of alkaloid **15** and of fluorocarpamine (**1**) are superimposable (ions

at m/z 338, 279, 265, 231, 193, 172, 160 and 121). The UV spectrum of **15**, however, is that of a dihydroindole (215, 250 and 293 nm); the IR spectrum shows hydroxyl vibrations at 3500 cm^{-1} and a double carbonyl absorption at 1760–1740 cm^{-1} as in pleiocarpamine. The ^1H NMR spectrum of **15** shows a four-spin system for the aromatic protons, with one of them being shielded at δ 6.15 (dd ; $J = 8, 2$ Hz); an ethylidene side chain is characterized by a quartet at δ 5.4 and a three-proton doublet at δ 1.6. The methyl of a CO_2Me group is located at δ 3.65 while the signal of H-16 appears as a doublet at δ 4.3 ($J = 4$ Hz). In an attempt to correlate the novel alkaloid **15** with known compounds, **15** was treated with sodium methoxide in dry methanol. A single faster running spot was observed after 5 hr reflux and the newly-formed compound was identical to fluorocarpamine (**1**) (TLC, UV, IR); it is a similar reaction to that which takes place in the inlet chamber of the mass spectrometer. These data best fit a 2, 7-dihydroxypleiocarpamine structure for **15**. It is similar to 'C-alkaloid Y', a curare alkaloid described in 1958 [14]. Compound **15** is formed by oxidation of pleiocarpamine (**2**) and might be the link between **2** and fluorocarpamine (**1**). Precedents for the C-ring contraction are found in hydroxy indolenine chemistry [15].

The isomeric pleiocorine (**16**) and pleiocraline (**17**) were identified by comparison with authentic samples from *A. deplanchei* [16, 17] and *A. odonthophora* [18].



Desoxycabufiline (18) $R = R' = \text{Me}$ Nordesoxycabufiline (19) $R = \text{Me}, R' = \text{H}$
or
 $R = \text{H}, R' = \text{Me}$

The novel desoxycabufiline (18) and nordesoxycabufiline (19) are related to cabufiline (20) isolated from *Cabucala caudata*. The elucidation of their structure was the object of a preliminary communication [19].

Extraction of the leaves of *A. plumosa* gave a low yield of a complicated alkaloid mixture (< 2 g/kg). Cabucraline (3) was the only alkaloid isolated from this mixture.

Conclusion

The alkaloids of *A. plumosa* belong to the corynane type, the most primitive one, and among these the picraline type (7–16 bond) is preponderant; it is worth noting the absence of monomeric ϕ -N-C-N alkaloids while this chromophore is present in three dimers.

According to Monachino [20], the *Alstonia* of New Caledonia belong to the *Dissuraspermum* section (= *Dissuraspermum orientale*, Pichon) which is different from the *Monuraspermum* section (Monach.) (= *Dissuraspermum occidentales*, Pichon). Botanical differences are the ciliation degree of the seeds and the number of leaves inserted at the same node. Chemical differences between the two sections are the presence (*Monuraspermum*) or absence (*Dissuraspermum*) of macroline type alkaloids; as for the other New Caledonia *Alstoniae*, *A. plumosa* is no exception to this rule. This feature and other chemotaxonomic considerations will be part of a forthcoming survey of the *Alstonia* alkaloids.

EXPERIMENTAL

General. Mps are uncorr. NMR were measured in CDCl_3 solns at 60 and 270 MHz or at 400 MHz on a prototype at the Institut d'Electronique Fondamentale (Orsay). Chemical shifts are given in δ -values with TMS as int. standard; coupling constants are given in Hz (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Medium pressure liquid chromatography expts were run at 10 bar. Colour reactions (CR) were obtained by spraying plates with a soln of $\text{Ce}_{\text{IV}}(\text{NH}_4)_2\text{SO}_4$. Material was collected in the Mandjelia Forest (18 Nov. 1978).

Extraction and isolation of alkaloids. The ground root bark (530 g) was extracted in the usual fashion [2] to yield 9 g crude alkaloid mixture (16.9 g/kg). The AM was fractionated on 1 kg Merck Si gel H-60 (elution pressure: 10 bar). Pleiocarpamine was eluted in fractions 50–80 (25 ml tubes); 1.8 g with CHCl_3 -MeOH (19:1). After 180 fractions, the solvent was changed to CHCl_3 -MeOH (9:1); cabucraline was in fractions 180–300 (400 mg) and 11-methoxycompactinervine (80 mg) in fractions 221–300; they were purified by prep. TLC. Fluorocarpamine (130 mg) was in fractions 371–400; cabucraline *N*(4)-oxide in fractions 410–440 (40 mg). Plumocraline (300 mg) and 3,4-seco 3,14-dehydrocabucraline (40 mg) were in fractions 640–700 eluted with CHCl_3 -MeOH (3:1) (change of solvent after fraction 500).

In the same manner, the ground stem bark yielded 8.8 g/kg of crude AM. The mixture (16 g) was chromatographed on 1 kg Si gel; 28 ml fractions were collected. Solvents were: CHCl_3 -MeOH (19:1) fractions 1–240; (9:1) fractions 241–450; (4:1) fractions 451–644; (7:3) fractions 645–720; (1:1) fractions 721–854. Pleiocarpamine and fluorocarpamine were in fractions 132–233; caberoline and raucubaine in fractions 167–188; cathafoline and cabucraline in fractions 264–388; alstovine in fractions 256–300; desoxycabufiline in fractions 365–427; nordesoxycabufiline in fractions 389–570; and pleiocorine and pleiocraline in fractions 645–802.

Description of new alkaloids. *Cabucraline N*(4)-oxide (5). $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4$ (CR: red), $[\alpha]_D = -37^\circ$ (CHCl_3 ; c 0.37); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 215, 248, 295; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3400, 1740, 1620, 1490, 1460, 1210; MS m/z (rel. int.): 368, 338, 295, 279, 232, 194, 188, 187, 174, 167 (100%), 139 (no M^+); ^1H NMR: δ 6.8 (d , $J = 8$ Hz, 1H), 6.2 (m , 2H), 5.55 (q , $J = 7$ Hz, 1H), 3.8 (s , 3H), 3.75 (s , 3H), 2.8 (s , 3H), 1.6 (d , $J = 7$ Hz, 3H). 3, 4-Seco 3, 14-dehydrocabucraline (6). $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$ (CR: pink), $[\alpha]_D = -21^\circ$ (CHCl_3 ; c 1.0); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 215, 245, 296; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3400, 1740, 1620, 1590, 1490, 1260, 1210, 1150, 1070, 1060; MS m/z (rel. int.): 382, 368 (M^+), 232, 208, 200, 194, 188, 187, 174 (100%), 122, 108; ^1H NMR (400 MHz) δ : 6.9 (d , $J = 8$ Hz, 1H), 6.4 (dd , $J = 8$ and 2 Hz, 1H), 6.35 (d , $J = 2$ Hz, 1H), 6.23 (d , $J = 7$ Hz, 1H), 5.76 (d , $J = 7$ Hz, 1H), 5.7 (q , $J = 7$ Hz, 1H), 3.8 (s , 3H), 3.75 (s , 3H), 2.8 (s , 3H), 1.6 (d , $J = 7$ Hz, 3H). *Plumocraline* (7). $\text{C}_{42}\text{H}_{50}\text{N}_4\text{O}_5$ (CR: orange), $[\alpha]_D = +20^\circ$ (CHCl_3 ; c 1.0); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 258 (4.3), 300 (3.9); IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1760, 1740, 1610, 1480, 1460, 1300, 1190; MS m/z (rel. int.): 690 (M^+ , 100%), 631, 617, 496, 446, 382, 368, 345, 323, 270, 194, 143, 139; ^1H NMR (270 MHz) δ : 7.0 (m , 2H), 6.6 (t , $J = 8$ Hz, 1H), 6.43 (s , 1H), 6.18 (s , 1H), 6.12 (d , $J = 8$ Hz, 1H), 5.4 (m , 2H), 4.9 (d , $J = 5$ Hz, 1H), 4.35 (d , $J = 10$ Hz, 1H), 4.1 ($br s$, 1H), 3.85 (s , 3H), 3.82 (s , 3H), 3.7 (s , 3H), 2.6 (s , 3H), 1.55 (d , $J = 7$ Hz, 3H), 1.52 (d , $J = 7$ Hz, 3H). ^{13}C NMR, see ref. [6]. (10-Carboxaldehyde) cabucraline (13). $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4$ (CR: pink), $[\alpha]_D = -33^\circ$ (CHCl_3 ; c 0.5); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 215 (4.19), 258 (3.91), 303 (3.63), 354 (3.97); IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1740, 1660, 1605; MS m/z : 396, 337, 323, 260, 216, 215, 202, 194 (100%), 139, 121; ^1H NMR (400 MHz) δ : 10.1 (s , 1H), 7.34 (s , 1H), 6.05 (s , 1H), 5.35 (q , $J = 7$ Hz, 1H), 4.05 (d , $J = 4$ Hz, 1H), 3.85 (s , 3H), 3.76 (s , 3H), 2.78 (s , 3H), 1.43 (dd , $J = 7$ Hz and 2 Hz, 3H). 2, 7-Dihydroxypleiocarpamine (15). $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$ (CR: yellow), mp 152–158° (Me_2CO), $[\alpha]_D = +66^\circ$ (MeOH ; c 0.5); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 213 (4.2), 250 (4.09), 293 (3.47); IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3500, 1755, 1735, 1610; MS m/z : 338, 321, 281, 279, 265, 231, 193, 172, 160, 121 (100%); ^1H NMR (60 MHz) δ : 7.40–6.80 (m , 3H), 6.15 (dd , $J = 8$ Hz and 2 Hz, 1H), 5.40 (dq , $J = 2$ and 7 Hz, 1H), 4.3 (d , $J = 3$ Hz, 1H), 4.20 (m , 1H), 3.7 (s , 3H), 1.60 (dd , $J = 2$ and 7 Hz, 3H). *Desoxycabufiline* (18). $\text{C}_{24}\text{H}_{30}\text{N}_4\text{O}_3$ (CR: blue-green), $[\alpha]_D = -114^\circ$ (MeOH ; c 0.9); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log

ϵ): 217 (4.59), 255 (4.17), 309 (4.02), 332 (3.99); $\lambda_{\text{max}}^{\text{MeOH}+\text{HCl}}$ nm: 220, 247, 315; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1745, 1735, 1610; MS m/z (rel. int.): 734 (80, M^+), 719, 675, 598, 567, 554, 540, 382, 368 (40), 354, 338, 295(35), 232(30), 194(80), 188, 187, 174, 170(100); ^1H NMR (400 MHz) δ : 7.05 (s, 1H), 6.9 (s, 1H), 6.3 (s, 1H), 6.15 (s, 1H), 5.4 (q, $J = 7$ Hz, 2H), 4.25 (d, $J = 4$ Hz, 1H), 3.8 (s, 3H), 3.75 (s, 3H), 3.7 (s, 3H), 3.65 (s, 3H), 2.75 (s, 3H), 2.6 (s, 3H), 1.7 (d, $J = 7$ Hz, 3H), 1.5 (d, $J = 7$ Hz, 3H); ^{13}C NMR, see ref. [19]. **Nordesoxycabufiline (19)**. $\text{C}_{43}\text{H}_{52}\text{N}_4\text{O}_6$ (CR: blue), $[\alpha]_{\text{D}} = -100^\circ$ (pyridine; c 0.46); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 218(4.38), 253(3.97), 315(3.87), 332(3.86); $\lambda_{\text{max}}^{\text{MeOH}+\text{HCl}}$ nm: 217, 245, 325; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3300, 1740, 1620, 1470, 1450, 1220, 1190, 1105, 1060; MS m/z (rel. int.): 720 (M^+), 100, 705, 661, 584, 540, 530, 526, 395, 338, 279, 194; ^1H NMR (60 MHz) δ : 7.05 (s, 1H), 6.9 (s, 1H), 6.25 (s, 1H), 6.05 (s, 1H), 5.4 (q, $J = 7$ Hz, 2H), 4.1 (d, $J = 5$ Hz, 1H), 3.8 (s, 3H), 3.7 (s, 6H), 2.7 (s, 3H), 2.55 (s, 3H), 1.6 (d, $J = 7$ Hz, 3H), 1.5 (d, $J = 7$ Hz, 3H).

Oxidation of cabucraline (3 \rightarrow 5). Cabucraline (10 mg) was dissolved in 1 ml CH_2Cl_2 to which 8 mg *m*-chloroperbenzoic acid was added. After 15 min the soln was stirred with 1 ml 2 N NaOH and usual treatment of the organic layer yielded 7 mg cabucraline *N*-oxide identical to **5** (TLC, UV, IR, MS).

Conversion of caberine to caberoline (9 \rightarrow 11). A soln of **9** (31 mg) in a mixture of CHCl_3 (0.5 ml) and $\text{CF}_3\text{CO}_2\text{H}$ (0.5 ml) was stirred at room temp. for 24 hr. It was then evaporated and neutralized to yield 29 mg of a pure compound identical to **11** (TLC, UV, IR, MS, NMR).

Transformation of 2, 7-dihydroxypleiocarpamine to fluorocarpamine. (15 \rightarrow 1). Starting material (5 mg) was dissolved in 2 ml MeOH containing 100 mg NaOMe; after 5 hr at room temp. it was diluted with 10 ml CHCl_3 , washed with 1 N HCl satd NaCl soln then evaporated. Work-up yielded 3 mg of a compound identical to **1** (TLC, UV, IR).

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