ISOLATION AND STRUCTURAL ELUCIDATION OF THE MAJOR COMPONENT FROM *PLEIOCARPIDIA SP.* : " 3-α-19-S-DIHYDROCADAMBINE "

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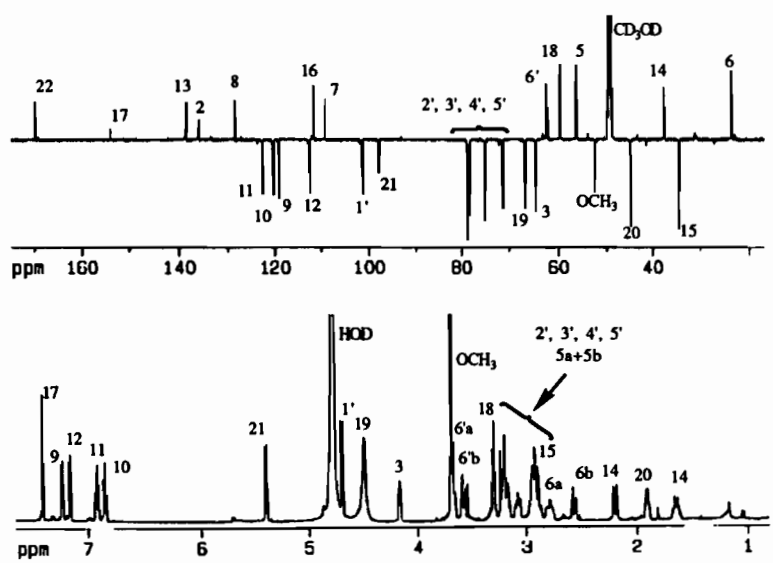
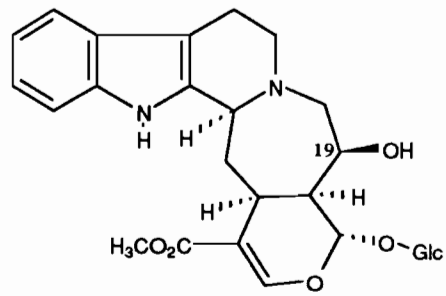
Résumé *: des expériences RMN de corrélations hétéronucléaires ^{1}H-^{13}C en mode inverse et dipolaires (ROESY), et une comparaison avec les données de la littérature pour la dihydrocadambine et dérivés, nous permettent de proposer une structure 3α-H pour l'alcaloïde indolique glucosidique isolé des fruits de* Pleiocarpidia nova sp. *(Rubiacées) récolté en Malaisie.*

Abstract *: heteronuclear reverse ^{1}H-^{13}C correlation spectroscopy and ROESY NMR experiments along with comparison with literature data for dihydrocadambine derivatives, allow us to propose a 3α-H isomer structure to the heterosidic indole alkaloid isolated from the fruits of* Pleiocarpidia nova sp. *(Rubiaceae) collected in Malaysia.*

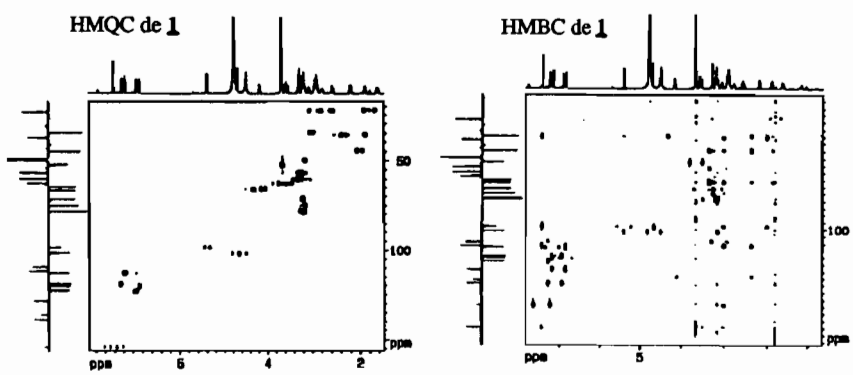
This *Pleiocarpidia* is a small tree owning orange berries with 5 multi-seeded carpels. The crude ethanolic extract of these fruits (100 mg; 0.6 g/kg) is separated by multiple preparative TLC ($CHCl_3$-CH_3OH 15% and $CHCl_3$-Acetone-CH_3OH, 45/45/20 v/v). The major component **1** (30% of totum) is a pale yellow amorphous compound (mp = 186-8°C) at R_F = 0.55 ($CHCl_3$-CH_3OH ; 65-35) on silica gel with a greenish-yellow spot on spraying with Ce IV^+ sulfate.





1 = 3-α-dihydrocadambine

A complete set of physical and spectroscopic data is then collected from **1** : $[\alpha]_D$ = -98° (c = 0.2; CH_3OH); UV : λ_{max} nm (MeOH) (log ε) = 223 (4.54) ; 280 (3.80) ; IR ν cm^{-1} = 3347, 1693, 1637; MS (FAB^+) = 547 ($M+H^{+\cdot}$) and mainly NMR whose some of them are presented : COSY ^1H-^1H allows signal proton assignment to the genin moiety. Reverse heteronuclear direct (^1J) and long range (^2J and ^3J) experiments (HMQC, HMBC) fully confirm these attributions along with those for all ^{13}C ones.



Comparison with "gathered data" from the literature (2) shows very much similarity between our compound 1 and 3-α-dihydrocadambine depicted above.

ROESY correlation experiment confirm the absolute configuration of C-19 as (S) for which coupling constants are not obvious arguments for that purpose.

This compound possess a strong hypotensive effect on injection into rats (3).

References

1. Groupe d'Etude des Substances Naturelles à Intérêt Thérapeutique - Laboratoires de Pharmacognosie et de Mycologie et Biologie Végétale ("Jeune équipe" DRED - 1991-1994).
2a. Brown R. T. and Fraser S. B., *Tetrahedron Lett.*, 1957-1959 (1974)
2b. Dimitrienko G. I., Murray D. G. and McLean S., *Tetrahedron Lett.*, 1961-1964 (1974)
2c. Brown R. T., Fraser S. B. and Banerji J.,*Tetrahedron Lett.*, 3335-3338 (1974)
2d. Brown R. T. and Chapple C. L., *Tetrahedron Lett.*, 2723-2724 (1976)
2e. McLean S., Dimitrienko G. I. and Szakolcai A., *Can. J. Chem.* **54**, 1262-1277 (1976)
2f. Saunders G. N., Hamilton R. G. and McLean S., *Tetrahedron Lett.* **23**, 2359-2360 (1982)
2g. Hamilton R. G., Saunders G. N. and McLean S., *Can. J. Chem.* **61**, 284-287 (1983)
3. Endo K., Oshima Y., Kikuchi H., Koshihara Y. and Hikino H., *Planta Med.* **49**, 188-190 (1983)

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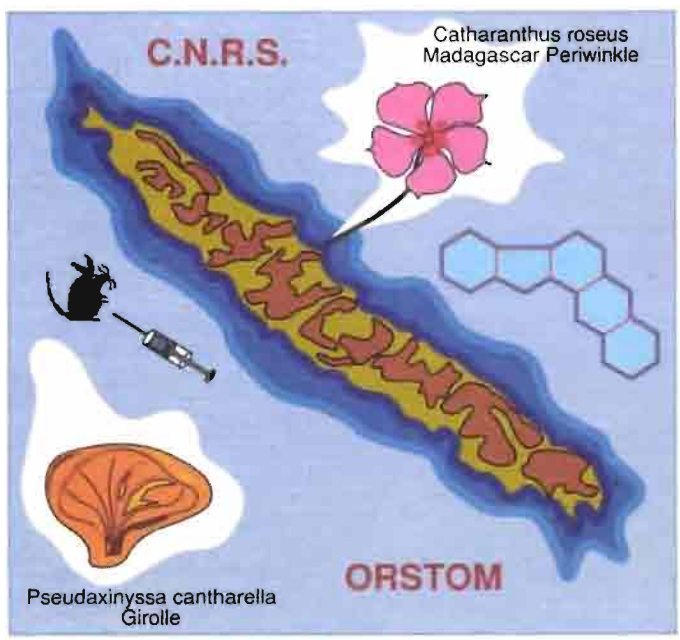

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