NEW INDOLE ALKALOIDS FROM TWO MALAYSIAN KOPSI A,
K. LARUTENSIS AND K. LAPIDILECTA (APOCYNACEAE)

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Résumé: six alcaloïdes ont été isolés de Kopsia larutensis King & Gamble, dont deux, l’eburnaminol 1 et la larutensine 2 sont nouveaux. Ces deux alcaloïdes sont de type eburnane, le second possédant un cycle oxygéné supplémentaire. Trois alcaloïdes ont été isolés de Kopsia lapidilecta van der Slees en, dont deux, la lapidilectine A 4 et la lapidilectine B 5, peuvent être considérés comme constituant une classe nouvelle d’alcaloïdes indoliques. La structure de tous les alcaloïdes nouveaux a été élucidée par les méthodes spectrales, essentiellement RMN 2D pour 4 et 5.

Abstract: Kopsia larutensis King & Gamble afforded six alkaloids, two of which were new: eburnaminol 1 and larutensine 2. Both possess the eburnane skeleton and the latter has an additional ether linkage between C-16 and C-18. Kopsia lapidilecta van der Sleesen gave three alkaloids in which two of them lapidilectine A 4 and lapidilectine B 5 were found to be a novel class of indolic alkaloids. Structural elucidation of the new alkaloids was done by extensive spectral studies.

Plants of the genus Kopsia are known to have alkaloids possessing new and interesting indole skeletons. The most recent indole skeleton discovered was that of kopsijasminilam. In addition, some of the alkaloids found in this genus have interesting biological activities such as rhazinilam.

For the above reasons, the Centre National de la Recherche Scientifique (CNRS) of France and University Malaya of Malaysia have undertaken the study of two Kopsia species collected in the Malaysian forests.

Kopsia larutensis King & Gamble (Batu Gajah forest collection) has been extracted to afford six alkaloids, two of which are new: eburnaminol 1 and larutensine 2. The spectral data indicated that both have the eburnane skeleton and the latter has an additional ether linkage between C-16 and C-18.
Kopsia lapidilecta van der Sleesen (Mersing forest collection) gave three alkaloids: venalstonine 3, lapidilectine A 4, lapidilectine B 5. The latter two alkaloids were found to be a novel class of Kopsia alkaloids. Structural elucidation of these alkaloids were done by extensive 2D NMR spectral studies.

The presence of the five membered ring olefin in the new alkaloids (4 and 5) was proven by the coupling constant values $J = 6$ Hz between H-14 and H-15 and $J = 1$ Hz between H-14 and H-3, whereas in the case of venalstonine and other similar alkaloids, the values are 10 - 12 Hz for the former and 1 Hz for the latter. In 4, the presence of both ester groups was assured by the appearance of two peaks in the $^{13}$C NMR corresponding to two carbonyl esters at $\delta$173-174 and a strong and broad IR absorption at about 1730 cm$^{-1}$. The urethane carbonyl exhibited a peak at $\delta$154 and a strong carbonyl absorption at 1695 cm$^{-1}$. The $^{13}$C - $^1$H long range correlations supported further the proposed structure of 4 as illustrated in Scheme 1. 4 could be related to kopsijasminilam 6, an alkaloid previously isolated from Kopsia jasminiflora.
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