



IDENTIFICATION OF MONOTERPENE INDOLE ALKALOIDS FROM *Palicourea minutiflora* BY ESI-MS/MS

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INTRODUCTION

Palicourea minutiflora (Müll. Arg.) C. M. Taylor, is a native plant of the Atlantic Forest areas, mainly found in northeastern region of Brazil. The major metabolites described for this plant are alkaloids, iridoids, flavonoids and terpenoids.

MATERIAL AND METHODS

The hydromethanolic fraction (HF) obtained by partition liquid/liquid of crude methanolic extract was investigated using ESI-MS/MS experiments. The analyses allowed to elucidate the structures of three monoterpene indole alkaloids. The chemical structure of compounds **1-3** were assigned by MS/MS experiments through the analysis of fragmentation of the precursor ion and comparing our MS data with literature.

RESULTS

Alkaloid **1** and their isomeric epoxide derivative **2** were isolated as a brown amorphous powder in mixture. The molecular formula were assigned in the protonated form at m/z 499 $[M+H-C_{26}H_{31}N_2O_8]^+$ and m/z 515 $[M+H-C_{26}H_{30}N_2O_9]^+$, based on its the positive ionization mode ESI-MS/MS, respectively. The presence of epoxide moiety was suggested by a gain of oxygen atom (16 Da) to raise main ions at m/z 515. Compound **1** showed the base peak at m/z 337 $[M+H-C_6H_{10}O_5]^+$ and the fragment at m/z 319 $[M+H-C_6H_{12}O_6]^+$ was attributed the neutral loss could of a glucose residue (180 Da), and in alkaloid **2** this loss was observed by the fragment at m/z 335 $[M+H-$

$C_6H_{12}O_6]^+$. The fragment at m/z 267 and m/z 283 occurs mechanistically for both alkaloids by a retro-Diels-Alder reaction of the product ion at m/z 337 $[M+H-C_6H_{10}O_5]^+$ and m/z 353 $[M+H-C_6H_{10}O_5]^+$, respectively, corresponding a neutral loss of (*E*)-1-3-butadienol (70 Da). Comparing our MS data with literature, the compounds **1** and **2** were assumed to be vincosamide and strictosamide epoxide, respectively. The alkaloid **3** identified as ophiorine, showed two major fragment ions in the ESI-MS/MS spectrum of m/z 513 $[M+H-C_{26}H_{29}N_2O_9]^+$, of m/z 469 and m/z 351, attributed from a neutral loss of CO₂ and a neutral loss could of a glucose residue. Additionally, the fragment m/z 333 formed from the dehydration of the cation $[C_{20}H_{19}N_2O_4]^+$ of m/z 307, and the presence of the ion of m/z 263 $[M+H-C_6H_{10}O_5]^+$, we suggest that it comes from the fragmentation by neutral loss of the precursor cation through hydrogen displacement rearrangement and consecutive loss of a neutral CO₂ molecule.

CONCLUSIONS

The alkaloids strictosamide epoxide and ophiorine are reported for the first time in the genus *Palicourea*, contributing for the chemotaxonomic of Rubiaceae family.

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