

NMR of limonoids from roots of *Raputia Praetermissa* (Rutaceae)

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Abstract: *Raputia praetermissa* is a rain forest tree found only in the Adolpho Ducke Forest Reserve¹, Amazonas, Brazil. As part of a continuing study of the chemistry of the Rutaceae, we have examined the roots of this previously uninvestigated species. Ground roots were extracted with hexane, dichloromethane, and finally with methanol. Dichloromethane extract concentrate was purified by repeated column chromatography on silica gel, sephadex LH-20, and then by HPLC to give furoquinoline, indol alkaloids, and two new limonoids. The new natural products were identified by ¹H, ¹³C NMR, DEPT, HMBC, HSQC, and COSY analyses. They are as follows: raputialactone and 1-deacetoxy-1,2-dihydrokiadalactone.

Raputia praetermissa is a rain forest tree found only in the Adolpho Ducke Forest Reserve¹, Amazonas, Brazil. As part of a continuing study of the chemistry of the Rutaceae, we have examined the roots of this previously uninvestigated species.

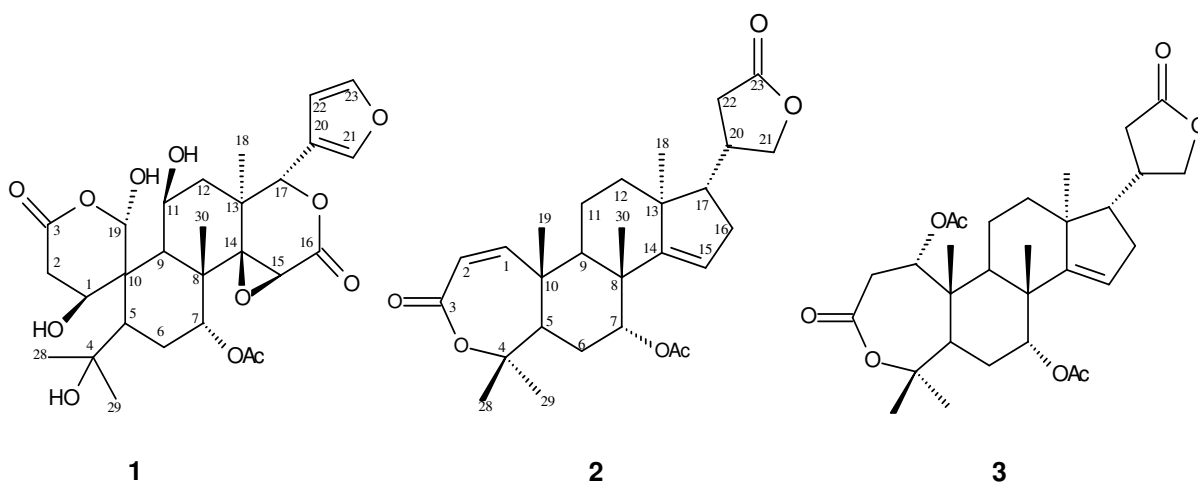
Ground roots were extracted with hexane, then dichloromethane and finally with methanol. The concentrated dichloromethane extract was purified by repeated column chromatography on silica gel, sephadex LH-20, and then by HPLC to give furoquinoline and indol alkaloids and two new limonoids.

Limonoid **1** was identified on the basis of the following data: the ¹H NMR spectrum indicated the presence of four non-coupled methyl groups (δ 1.10, δ 1.17, δ 1.26, δ 1.48), three downfield shifted signals attributed to a β -substituted furan ring (δ 7.44, δ 7.43, δ 6.31), and six signals characteristic of protons attached to a carbon adjacent to an oxygen atom (δ 6.13 s, δ 5.76 s, δ 4.67 br s, δ 4.64 m, δ 3.64 s). From the HMBC experiments, it was observed that the correlations between ¹H signal at δ 5.76 (δ_C 77.5) and the ¹³C signals at

δ 141.3, assigned to C-21 (δ_H 7.44), determined the position of the furan ring at C-17 and indicated the presence of a 16,17-lactone ring (δ_C 166.8, δ_C 77.5). A 14 β ,15 β -epoxide must be attached to this lactone ring due to the observed correlations between the ¹H signal at δ 3.64 (br s) with ¹³C signal at δ 166.8 (C-16), and H-17 (δ 5.76) with ¹³C signal at δ 69.5 attributed to C-14. The methyl proton at δ 1.17 showed long-range correlation with the C-17 signal (δ_C 77.5), allowing the assignment of this signal to Me-18. In the same way, the unsubstituted C-12 emerged from the correlation between the H₃-18 signal and the ¹³C signal at δ 31.6 (³J, C-12), which was coupled to the ¹H signal at δ 4.64 (td, J = 7.9 and 4.6 Hz) and thus placing the secondary hydroxyl substituent at C-11 (δ_C 73.9). Orientation of the hydroxyl followed by coupling between H-11 and H-9 (δ_H 2.94, d, J = 4.6 Hz) requires H-11 to be in the equatorial position. Moreover, the existence of correlations between the two methyl signals at δ 1.10 (δ_C 22.3) and δ 1.26 (δ_C 28.3) with the ¹³C signal at δ 79.5, assigned to Me-28, Me-

29, and C-4, respectively, indicated the presence of an A-seco limonoid, requiring a hydroxyl attached at C-4. A carbonyl resonance at δ 167.8 and a singlet at δ 6.13

(δ_C 102.8) were also observed in the ^{13}C NMR spectrum and suggested the presence of a 3-19 lactone ring, since it was the only location left in the nucleus.



This implies that limonoid **1** has only four methyl groups. A hydroxyl group must also be attached at C-19 due to the deshielded resonance observed for H-19 (δ 6.13, δ_C 102.8). The oxymethine proton at δ 4.12 (br t, $J = 1.5$ Hz) can be attributed to H-1, as it showed cross-peaks with C-3 (δ 167.8) and C-19 (δ 102.8). The coupling constant between H-1 and 2H-2 is characteristic of 1 β -hydroxyl. The EI-Mass spectrum showed an ion at m/z 563, confirming the molecular formula ($\text{C}_{28}\text{H}_{36}\text{O}_{12}$). The structure of the new limonoid was therefore named as 1 β ,4,11 β ,19 α - tetrahydroxy - 14 β ,15 β -epoxy-3,4-*seco*-3,19-lactone-gedunin, and the stereochemistry suggested for **1** was supported by g-NOESY experiments.

Limonoid **2** exhibited spectra data similar to that of kiadalactone (**3**) isolated from

*Phellodendron amurense*² and *Raulinoa echinata*³. The ^1H NMR spectrum, instead of signals for an acetoxy group at C-1, showed signals of a ring-A 1-en-3-lactone (δ 6.45, d, $J = 12.3$ Hz, H-1; δ 5.89, d, $J = 12.3$ Hz, H-2). Thus, limonoid **2** was found to be 1-deacetoxy-1,2-dehydrokiadalactone.

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