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

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**Abstract:** *Raputia praetermisa* is a rain forest tree found only in the Adolpho Ducke Forest Reserve\(^1\), 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 \(^1\)H, \(^{13}\)C NMR, DEPT, HMBC, HSQC, and COSY analyses. They are as follows: raputialactone and 1-deacetoxy-1,2-dihydrokiadalactone.

*Raputia praetermisa* is a rain forest tree found only in the Adolpho Ducke Forest Reserve\(^1\), 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 \(^1\)H NMR spectrum indicated the presence of four non-coupled methyl groups (\(\delta 1.10, \delta 1.17, \delta 1.26, \delta 1.48\)), three downfield shifted signals attributed to a \(\beta\)–substituted furan ring (\(\delta 7.44, \delta 7.43, \delta 6.31\)), and six signals characteristic of protons attached to a carbon adjacent to an oxygen atom (\(\delta 6.13\) s, \(\delta 5.76\) s, \(\delta 4.67\) br s, \(\delta 4.64\) m, \(\delta 3.64\) s). From the HMBC experiments, it was observed that the correlations between \(^1\)H signal at \(\delta 5.76\) (\(\delta C 77.5\)) and the \(^{13}\)C signals at \(\delta 141.3\), assigned to C-21 (\(\delta H 7.44\)), determined the position of the furan ring at C-17 and indicated the presence of a 16,17-lactone ring (\(\delta C 166.8, \delta C 77.5\)). A 14\(\beta\),15\(\beta\)-epoxide must be attached to this lactone ring due to the observed correlations between the \(^1\)H signal at \(\delta 3.64\) (br s) with \(^{13}\)C signal at \(\delta 166.8\) (C-16), and H-17 (\(\delta 5.76\)) with \(^{13}\)C signal at \(\delta 69.5\) attributed to C-14. The methyl proton at \(\delta 1.17\) showed long-range correlation with the C-17 signal (\(\delta C 77.5\)), allowing the assignment of this signal to Me-18. In the same way, the unsubstituted C-12 emerged from the correlation between the H-18 signal and the \(^{13}\)C signal at \(\delta 31.6\) (\(^3\)J, C-12), which was coupled to the \(^1\)H signal at \(\delta 4.64\) (td, \(J = 7.9\) and 4.6 Hz) and thus placing the secondary hydroxyl substituent at C-11 (\(\delta C 73.9\)). Orientation of the hydroxyl followed by coupling between H-11 and H-9 (\(\delta H 2.94, d, J = 4.6\) Hz) requires H-11 to be in the equatorial position. Moreover, the existence of correlations between the two methyl signals at \(\delta 1.10\) (\(\delta C 22.3\)) and \(\delta 1.26\) (\(\delta C 28.3\)) with the \(^{13}\)C signal at \(\delta 79.5\), 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 \( \delta 167.8 \) and a singlet at \( \delta 6.13 \) (\( \delta_C 102.8 \)) were also observed in the \( ^{13} \text{C} \) 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 (\( \delta 6.13, \delta_C 102.8 \)). The oxymethine proton at \( \delta 4.12 \) (br t, \( J = 1.5 \) Hz) can be attributed to H-1, as it showed cross-peaks with C-3 (\( \delta 167.8 \)) and C-19 (\( \delta 102.8 \)). The coupling constant between H-1 and 2H-2 is characteristic of 1\( \beta \)-hydroxyl. The EI-Mass spectrum showed an ion at \( m/z \) 563, confirming the molecular formula \( (C_{28}H_{36}O_{12}) \). The structure of the new limonoid was therefore named as 1\( \beta \),4,11\( \beta \),19\( \alpha \)-tetrahydroxy - 14\( \beta \),15\( \beta \)-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 \( ^1 \text{H} \) NMR spectrum, instead of signals for an acetoxyl group at C-1, showed signals of a ring-A 1-en-3-lactone (\( \delta 6.45, \text{d, } J = 12.3 \) Hz, H-1; \( \delta 5.89, \text{d, } J = 12.3 \) Hz, H-2).

Thus, limonoid 2 was found to be 1-deacetoxy-1,2-dehydrokiadalactone.

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**References**

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