# LACTONIC AMINES FROM GARNIERIA SPATHULAEFOLIA

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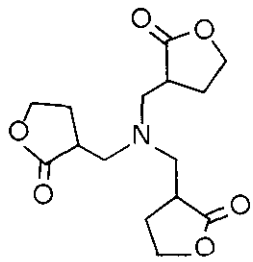
Abstract - An investigation of Garnieria spathulaefolia led to the isolation and characterization of two nitrogen-containing α-methylene-γ-butyrolactone derivatives.

## INTRODUCTION

The genus Garnieria (Proteaceae) consists of the single species G. spathulaefolia Brongn. et Gris, which is endemic to New Caledonia.[1,2] We have investigated the leaves of the plant and isolated two lactonic amines 1 and 2, which are described in the present paper.



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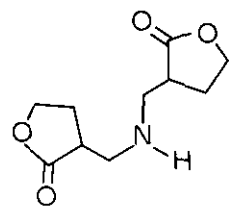

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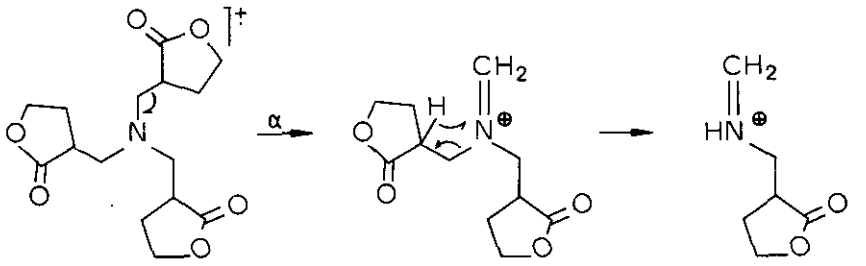
## RESULTS AND DISCUSSION

The main compound 1 was isolated as white crystals. Its structure was deduced from IR, NMR and MS data.

In the EI mass spectrum of 1 the $M^+$ peak at m/z 311 was hardly detectable but the CI spectrum showed the $(M+1)^+$ peak at m/z 312 indicating the molecular formula $C_{15}H_{21}NO_6$. The most prominent peaks in the EI spectrum were at m/z 226 and 128 due to α-cleavage and even-electron ion rearrangement, respectively (Fig. 1):

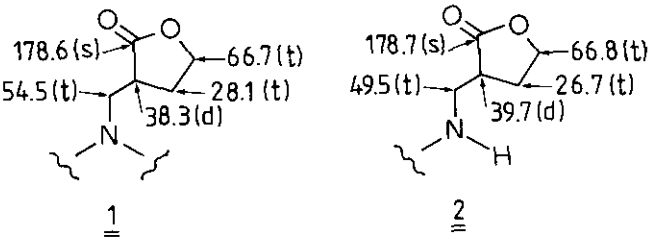



1 m/z 226 m/z 128

Figure 1.

The IR spectrum of 1 showed a strong broad band at 1750 $cm^{-1}$ suggesting the presence of at least one γ-lactone ring. In the $^1H$ NMR spectrum the only distinct signal was a six proton multiplet centred at δ 4.27 due to three $-CH_2-O-$ groups. The rest of the spectrum (δ 3.5-1.5) was not interpreted with certainty because of overlapping of signals.

The $^{13}C$ NMR spectrum was indicative of a highly symmetric molecule: only five signals were detected and all were in good agreement with the proposed structure 1 (Fig. 2). The signals at δ 54.5 and 38.3 are slightly broadened.




1 2

Figure 2.

Along with the tertiary amine 1 a small amount of the secondary amine 2 was isolated.

As in compound 1, the molecular peak (m/z 213, $C_{10}H_{15}NO_4$) in the EI mass spectrum of compound 2 was hardly detectable and was confirmed by the CI mass spectrum (m/z 214, $(M+1)^+$). The IR spectrum (3340, 1630 $cm^{-1}$, secondary amine; 1750 $cm^{-1}$, γ-lactone) and the $^1H$ NMR spectrum (δ 4.29, 4H, m) of 2 resembled those of 1. The difference in the chemical shifts ($^{13}C$ NMR spectra, Fig. 2) of the carbon atoms adjacent to nitrogen in compounds 2 (secondary amine) and 1 (tertiary amine) are in good agreement, as could be expected.

A few years ago Bick et al.[3] isolated from another proteaceous plant Bellendena montana R.Br. a lactonic compound called B2, the structure of which was not elucidated. The reported data strongly suggest that our compound 1 is identical with that compound.

Both 1 and 2 are artefacts formed in the course of the extraction procedure in a reaction between ammonia and a suitable lactonic precursor in the plant (cf. α-methylene-γ-butyrolactones, e.g. tulipalin A[4,5]). When the extraction procedure was executed using aqueous sodium bicarbonate solution instead of ammonia, no traces of 1 or 2 were detected.

## EXPERIMENTAL

Plant material collection and identification. The plant material used (voucher sample; Pusset 219) was collected in January 1981 on Mont Kaala (at alt. 550 m) in northern New Caledonia.

Isolation of products. Dried powdered leaves (5.2 kg) were moistened with 20% $NH_4OH$ and then exhaustively percolated with $CH_2Cl_2$. After normal work-up a mixture of crude basic compounds was obtained. Column chromatography (silica gel, $CH_2Cl_2$/MeOH/EtOAc, 97.5:1.5:1) followed by preparative TLC (alumina, $CH_2Cl_2$/MeOH, 90:10) permitted the isolation of two products 1 (290 mg) and 2 (10 mg).

Compound 1. mp. 184-6°C (MeOH) (dec.), IR $\nu_{max}^{KBr}$ $cm^{-1}$; 2950, 2850, 1750 (C=O), 1460, 1380; $^1H$ NMR (60 MHz, $CDCl_3$) and $^{13}C$ NMR (15.04 MHz, $CDCl_3$): see text. EIMS (probe) 70 eV, m/z (rel.int.): 311 $M^+$ (<1), 226 (65), 212 (5), 128 (100). CIMS (isobutane, probe), m/z (rel.int.): 312 $(M+1)^+$ (100), 226 (25), 214 (90), 128 (25), 116 (65).

Compound 2. colourless oil (partly crystallized on standing). IR $\nu_{max}$ $cm^{-1}$: 3340 (NH), 2930, 1750 (C=O), 1630, 1460, 1380; $^1H$ NMR (60 MHz, $CDCl_3$) and $^{13}C$ NMR (15.04 MHz, $CDCl_3$): see text. EIMS (probe) 70 eV, m/z (rel.int.): 213 $(M^+)$ (<1), 128 (100). CIMS (isobutane, probe), m/z (rel.int.): 214 $(M+1)^+$ (100), 117 (20), 99 (10).

## REFERENCES


1. A. Lemée, Dictionnaire Descriptif et Synonymique des Genres de Plantes Phanérogames, Tome III, Imprimerie Commerciale et Administrative, Brest, 1931, pp. 199-200.
2. A. Guillaumin, Flore Analytique et Synoptique de la Nouvelle Calédonie, Phanérogames, Office de la Recherche Scientifique Coloniale, Paris, 1948, p. 101.
3. I.R.C. Bick, J.W. Gillard and H.-M. Leow, Aust. J. Chem. 1979, 32, 1827.
4. U.W. Brongersma-Oosterhoff, Recl. Trav. Chim. Pays-Bas, 1967, 86, 705.
5. B.H.H. Bergman, J.C.M. Beijersbergen, J.C. Overeem and A. Kaars Sijpesteijn, Recl. Trav. Chim. Pays-Bas, 1967, 86, 709.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