LACTONIC AMINES FROM GARNIERIA SPATHULAEFOLIA

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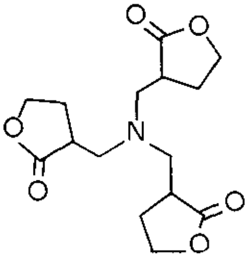
Abstract - An investigation of Garnieria spathulaefolia led to the isolation and characterization of two nitrogen-containing α-methylene-γ-butyrolactone derivatives.

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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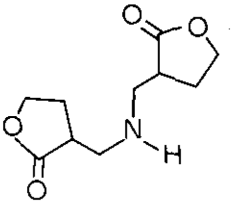

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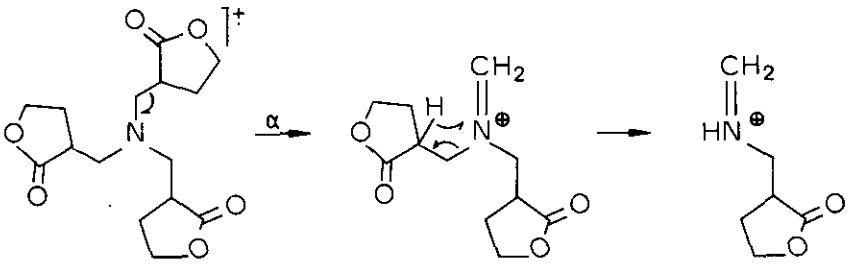
RESULTS AND DISCUSSION

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):

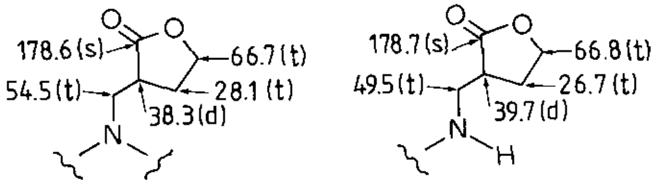


1 m/z 226 m/z 128

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 ν_{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 ν_{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).

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