Phytochemistry, Vol 22, No 1, p 293, 1983
Printed in Great Britain

0031-9422/83/010293-01$03 00/0

SHORT REPORTS

β-STACHYDRINE, A NOVEL BETAINE FROM *GRIFFITHSIA FLOSCULOSA*

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(*Received* 29 *March* 1982)

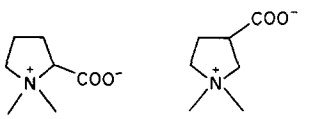
Key Word Index—*Griffithsia flosculosa*, Ceramiaceae, betaines, β-stachydrine

Abstract—From the marine red alga, *Griffithsia flosculosa*, a novel quaternary ammonium compound, β-stachydrine, has been isolated

On TLC examination of a methanolic extract of *Griffithsia flosculosa* (Ceramiaceae), a strongly Dragendorff-positive compound was detected which was different from those recorded previously for marine algae [1, 2] After purification of the extract by passage through a column of cation exchange resin, the compound was isolated by prep TLC and converted to its hydrochloride, mp (uncorr) 236–238° (dec), $[\alpha]_D^{23}$ − 5 5° (MeOH *c* 0 27) Both elemental analysis and mass measurement (M^+, *m/z* 144) established the molecular formula of the base as $C_7H_{14}O_2N$ The field desorption mass spectrum showed pronounced peaks at *m/z* 287 and 430, in addition to the one at *m/z* 144, and closely matched the spectrum of stachydrine (2-carboxylato-*N*,*N*-dimethylpyrrolidinium) (1) The ions at *m/z* 287 and 430 have been reported to be due to dimer and trimer formation [3] As the isolated compound can be separated readily from stachydrine by TLC [1], it was considered probable that the unknown substance is β-stachydrine (3-carboxylato-*N*,*N*-dimethylpyrrolidinium) (2) This was synthesized from β-proline, using the method of Patchett and Witkop [4], and was found to be identical to the isolated compound (mp, mmp, TLC, NMR and IR)

The ^{1}H NMR spectrum (270 MHz, D_2O) of β-stachydrine shows resonances at δ 2 35 (1H, *m*, $W_{1/2}$ ≃ 21 5 Hz, H-4), 2 49 (1H, *m*, $W_{1/2}$ ≃ 27 5 Hz, H-4^1), 3 10 (3H, *s*, Me), 3 14 (3H, *s*, Me^1), 3 33 (1H, *m*, $W_{1/2}$ ≃ 21 5 Hz, H-3), 3 53 (2H, *t*, *J* ≃ 7 5 Hz, H_2-5) and 3 68 (2H, *d*, *J* ≃ 9 Hz, H_2-2) These assignments were confirmed by NMR decoupling experiments, irradiation of the H-4 and H-4^1 signals simplified the triplet at δ 3 53 identifying this as arising from the 5-protons

Compared with the ^{1}H NMR spectrum of β-stachydrine, that of its hydrochloride shows only very small lowfield shifts of the 4-protons (0 09 and 0 08 ppm)



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and of the 2-protons (0 07 ppm), but a marked deshielding (0 2 ppm) of H-3, confirming the assignments of the multiplet to the proton α to the carboxyl group

EXPERIMENTAL

G flosculosa (Ellis) Batt was collected from Southsea, Hampshire, in October 1980 and from Kimmeridge, Dorset, in June 1981 The plant material was identified by Dr W F Farnham, Department of Biological Sciences, Portsmouth Polytechnic The methods of extraction of fresh algae, purification of the extracts, TLC examination and isolation of the Dragendorff-positive components by prep TLC have been described previously [1]

Acknowledgements—We thank Mr C Turner for the NMR spectra and Professor Yoshio Okamoto, Department of Chemistry, Osaka University, for the gift of a sample of (*R*)-β-proline We are grateful to Dr R J Pryce, Shell Biosciences Laboratory, Sittingbourne Research Centre for the MS

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