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α-ALANINEBETAINE FROM *CLADOPHORA* SPECIES

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Key Word Index—*Cladophora prolifera; C. crispula; C. rupestris;* Cladophoraceae; betaines; α-alaninebetaine.

Abstract—From the marine green algae, *Cladophora prolifera, C. crispula* and *C. rupestris*, the quaternary ammonium compound, α-alaninebetaine, has been isolated.

INTRODUCTION

The quaternary ammonium compounds, known as betaines and their sulphonio analogues, have been shown to be widespread in marine algae [1]. Moreover, either the presence or absence of certain of these compounds within a genus appears to be taxonomically significant [2]. As part of a programme of study of Venezuelan algae, the betaines and tertiary sulphonium compounds present in the collected species are being determined. In this communication we record the isolation of α-alaninebetaine (2-trimethylammonium propionic acid) from *Cladophora* species. This is the first record of this compound from a plant source.

RESULTS AND DISCUSSION

On two-way TLC examination of an extract of *Cladophora prolifera*, purified by passage through a column of cation exchange resin, two Dragendorff-positive spots were detected. The major component, which had a slightly lower R_f value than the minor one, produced a purplish-blue colour with Dragendorff's reagent. The two compounds were isolated separately by prep. TLC. The minor component proved to be glycinebetaine from TLC and ^{1}H NMR spectroscopic evidence. The ^{1}H NMR spectrum of the major compound resembled closely that of α-alanine. At pH 6, a doublet at δ 1.58 (3H, J = 7.2 Hz; Me) and a quartet at δ3.86 (1H, J = 7.2 Hz; CH) were observed in addition to a large singlet (9H; $\overset{+}{\mathrm{N}}$-Me) at δ 3.18. This evidence indicated that the isolated compound was α-alaninebetaine. This identification was consistent with the FAB mass spectrum, which showed a $(M+1)^+$ peak at m/z 132 (calculated for α-alaninebetaine 132) [3]. α-Alaninebetaine was synthesized from α-alanine and the synthetic and isolated compounds were found to be identical (TLC, ^{1}H NMR, MS).

In the ^{1}H NMR spectrum of α-alaninebetaine the chemical shifts of both the methyl and methine groups are significantly different with changes in pH of the solution. At pH 1.5 and 8 the values for Me are δ1.64 and 1.58, respectively, and for the CH, 4.08 and 3.86.

α-Alaninebetaine was isolated also from extracts of both *C. crispula* and *C. rupestris*. In both these species, however, glycinebetaine was the major Dragendorff-positive compound detected. This latter substance has been reported previously for *C. rupestris*, as well as for other *Cladophora* species [1].

EXPERIMENTAL

Cladophora prolifera (Roth) Kütz and *C. crispula* Vickers were collected from Punta Brava, Morrocoy and near San Juan de los Cayos, respectively, both in Falcon State, Venezuela, in October 1986, and *C. rupestris* (L.) Kütz. from Kimmeridge, Dorset, U.K. in May 1986. The plant material was identified by Dr R.L. Fletcher, School of Biological Sciences, Portsmouth Polytechnic.

After collection, the algae were immersed in ethanol until processed further. The method of extraction, purification of the extracts, two-way TLC examination and isolation of the Dragendorff-positive components by prep. TLC have been described previously [4,5].

^{1}H NMR spectra were obtained in D_2O using a Brüker WH-270 spectrometer and FAB MS were recorded using a Jeol DX303 spectrometer coupled to a DA5000 data system. The samples were applied in glycerol, and xenon was used as the bombardment gas.

α-Alaninebetaine was synthesised by the addition of methyl iodide to a solution of α-alanine in potassium carbonate [6].

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