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Phytochemistry, Vol. 20, No. 7, pp. 1750–1751, 1981.
Printed in Great Britain.

0031-9422/81/071750-02 $02.00/0
Pergamon Press Ltd.

A BROMOPHENOL IN THE RED ALGA *HALOPITYS INCURVUS*

GUILLAUME DE NANTEUIL and PIERRE MASTAGLI

Ecole Supérieure de Chimie Organique et Minérale, 12, rue Cassette, 75006 Paris, France

(*Revised received* 27 *November* 1980)

Key Word Index—*Halopitys incurvus*; Rhodomclaceae; bromophenol; 2,6-dibromo-3,5-dihydroxyphenylacetic acid.

Abstract—A new dibromophenol has been isolated from the acidified ethanolic extracts of the red alga *Halopitys incurvus*, and is shown to be 2,6-dibromo-3,5-dihydroxyphenylacetic acid, probably derived from a disulfate dipotassium salt.

INTRODUCTION

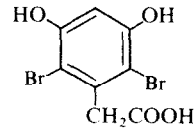
The existence of brominated phenolic compounds in the extracts of *Halopitys incurvus* (Hud.) Batt. has been known since Augier and Mastagli [1] described a sulfonic acid, dipotassium salt. Later Chantraine [2] and Glombitza [3, 4] isolated various phenolic acids and benzyl alcohols, identified after various extraction procedures.

RESULTS AND DISCUSSION

After acid hydrolysis, the aqueous EtOH extracts of *Halopitys incurvus* (5 kg dry alga) yielded 2.5 g of a compound which gave a positive ferric chloride test. A bromine analysis [5] showed the presence of two atoms per molecule (found: Br, 49.02. $C_8H_6Br_2O_4$ requires: Br, 49.08%). IR, ^{1}H NMR, ^{13}C NMR broad band and off resonance decoupling spectra showed the presence of single aromatic hydrogen and a phenylacetic group. Moreover, the broad band spectrum presented only four peaks for the aromatic ring, which implied a structure similar to 4,6-dibromoresorcinol.

To determine the phenylacetic group, we synthesized the 4,6-dibromoresorcinol [6]; comparison of its ^{1}H NMR spectrum with that of the algal compound showed that the phenylacetic group is most probably situated between the two bromine atoms. Hence the new compound has structure **1**.

When the aq. EtOH extracts were saturated with absolute alcohol, several mg of a very hygroscopic product crystallized, giving a purple colour with 2% aqueous $FeCl_3$ and decomposing at a temperature higher than 250°. The IR spectrum showed the presence of a phenylacetic group. Analysis also gave two bromine atoms per molecule (found: Br, 27.12. $C_8H_3Br_2O_{10}S_2K_2Na$ requires: Br, 27.39%). The lability of the product permitted only a qualitative determination of sulfate, potassium and lesser amounts of sodium. We therefore assume that this compound is the disulfate dipotassium salt of the diphenol **1**, present as the sodium salt [1, 7, 8]. During extraction, approximately 2 g needles of (2-glyceric acid sodium salt) α-D-mannopyranoside [9] crystallized and were identified by their IR, ^{1}H and ^{13}C NMR spectra; they decomposed at above 250°.



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EXPERIMENTAL

Halopitys incurvus was collected in September at low tide in the Rade de Brest (Brittany). Immediately after harvest, the alga was extracted with cold EtOH (35 l) for 2 weeks, then concd to give 3 l. of a dark brown soln.

Hydrolysed compound. This soln was hydrolysed with dil. HCl (10%) and heated on a steam bath for 15 min. After cooling and filtration, the resulting soln was extracted with EtOAc, and the yellow organic extract was washed with water, then dried. The residue after evapn was chromatographed on a column of 100 g Si gel (Merck 70–230 mesh), using $CHCl_3$–MeOH (9:1) as eluant.

Further evapn afforded 2.5 g red leaflets: R_f 0.28; mp 191°; IR (vaseline) cm^{-1}: 1705, 3000; ^1H NMR (Me_2CO-d_6): δ 3.90 (2 H, *s*), 6.85 (1 H, *s*), 8.35 (3 H, *br s*); ^{13}C NMR (DMSO-d_6): δ 32.7 (*t*), 128.6 (*d*), 140.0 (*s*), 166.3 (*s*), 167.1 (*s*), 170.7 (*s*).

4,6-*Dibromoresorcinol.* ^1H NMR (Me_2CO-d_6): δ 6.80 (1 H, *s*), 7.60 (1 H, *s*), 8.65 (2 *H*, *br s*).

Natural compound. A portion of the 3 l. conc. aq. EtOH soln was first saturated with EtOH, which cleared it of pigments and NaCl and afforded the mannoside. After treatment with a soln of 50% basic lead acetate and bubbling with H_2S, the residue (20 ml) was passed through a cationic exchange resin (20 g of Amberlite IRC 50, treated with $AgNO_3$), which eliminated more NaCl. Concn then saturation with EtOH gave, after several days at −18°, colourless needles. The presence of sulfate was determined with $BaCl_2$ [10], Na^+ and K^+ detected with flame spectrometer. IR (KBr disk) cm^{-1}: 1560, 1610, 1685, 2980.

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