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A BROMO COMPOUND IN *HALOPITYS INCURVUS* (HUDS.) BATTERS

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HALOPITYS INCURVUS
RHODOMÉLACÉE
BROMO-3 DIHYDROXY-4-5
BENZALDEHYDE

RÉSUMÉ. – Les auteurs décrivent un composé phénolique bromé, isolé de *Halopitys incurvus* (Rhodomélacée). La formule élucidée de ce composé est bromo-3 dihydroxy-4-5 benzaldehyde.

HALOPITYS INCURVUS
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3-BROMO-4,5-
DIHYDROXYBENZALDEHYDE

ABSTRACT. – The autors describe a bromo compound extracted from *Halopitys incurvus* (Huds.) Batters (Rhodomelacea). The isolated compound was identified as 3-bromo-4,5-dihydroxybenzaldehyde.

Introduction

Many authors have drawn attention to the bromo compounds from the alga *Halopitys incurvus*. Firstly, Augier and Mastagli (1956) isolated a bromo compound from this alga and partially characterized it as $C_6(SO_3K)_2$ $Br(OH)_2$ COOH. In 1973 Chantraine *et al.* found 3,5-dibromo-4-hydroxyphenylacetic acid and 3,5 dibromo-4-hydroxyphenylpyruvic acid in the same alga. Finally, 3-bromo-4-hydroxybenzyl alcohol was extracted by Glombitza *et al.* (1974) also from *H. incurvus*. Here we described the isolation and characterization of 3-bromo-4,5-dihydroxybenzaldehyde from the same source.

Material and Methods

The algae were collected from Izmir (Aegean Sea) in May through September 1977-78 and dried and milled to a coarse powder. Then it was extracted with 80% ethanol for 3 h under a reflux condenser. The extract was filtered and concentrated in a rotary vacuum evaporator. The residue was shaken three times with 0.1 N hydrochloric acid and then filtered. The filtrate was extracted two times with ethyl acetate. The organic phase was distilled. Acetone was added to the residue and filtered. Then petroleum ether was added to the filtrate and dark coloured drops were formed. The upper phase was decanted and then again filtered. The filtrate was distilled. The residue was crystallized from diethyl ether.

Results

Fine needles from diethyl ether, m.p.218°. It gives positive test with $FeCl_3$, Na_2 $Mo0_4$ and Folin-Ciocalteau reagents on t.l.c.

Identification of this compound

UV (MeOH) : λ max. = 214, 235 (sh), 285, 315 (sh) and 354 (sh) nm.

IR (KBr) : $\bar{\upsilon}$ max. = 3440 (O-H), 3000 (O-H), 1645 (C = O), 1570 (Ar-H), 1430, 1400, 1352, 1300, 1250, 1180, 989, 856 and 685 cm^{-1}.

^{1}H-NMR (DMSO-d_6, TMS int.) : δ = 7.29 (d, J : 2, H-6); 7.59 (d, J : 2 Hz, H-2); 9.56 (s, CHO) and 9.5-10.7 ppm (broad peak, OH).

MS (EI 70 eV, 300 A, 4 KV, 200°, DI 100°, 5.10^{-7} T): m/e = 218 (85), 217 (100), 216 (88), 215 (96), 189 (16), 187 (16), 161 (6), 137 (8), 108 (12), 107 (18), 79 (20), 63 (16), 62 (17), 53 (24), 52 (19), 51 (44) and 50 (30% rel. int.).

One proton of the aromatic aldehyde group and two of the aromatic ring are distinguished in NMR spectrum by n-coupling (J : 2 Hz). Two 2 M^+ peaks at m/e 218/216 and two 2 $M^+ - 1$ peaks at 217/215 are present in mass spectrum; this means that the molecule contains an isotopic bromine.

In IR spectrum, the presence of C=O band at 1645 cm^{-1} proves the aromatic aldehyde function. In IR and NMR spectra, at least two OH groups may be detected.

Anal. Calculated for $C_7H_5O_3Br$: C, 38.74%, H, 2.32%, Br, 36.82%. Found: C, 39.05%, H, 2.75%, Br, 34.01%.

According to these data this compound is 3-bromo-4,5-dihydroxybenzaldehyde. It was synthesized from 3,4-dihydroxybenzaldehyde and bromine in acetic acid (Pschorr, 1912) and the spectroscopic characteristics of this synthetic product is identical with natural product.

Antibacterial activity

The bromo compound obtained was tested for antibacterial activity by disc diffusion technique using *Pseudomonas aeruginosa, Staphylococcus aureus* and *Escherichia coli.* It inhibited the growth of *Pseudomonas aeruginosa* in a concentration of 0.054 μg/ml and *Staphylococcus aureus* and *Escherichia coli* in 0.027 μg/ml concentration.

Discussion

The occurrence of 3-bromo-4,5 dihydroxybenzaldehyde in *Halopitys incurvus* is biologically interesting because it was found in other genera of Rhodomelaceae. In fact, Saito and Ando (1955) found the bromo compound in *Polysiphonia morrowii* and the same compound was found by Glombitza *et al.* (1974) in the other two species of the same genera *Polysiphonia,* i.e. *P. lanosa* and *P. elongata.* The antibiotic activity of 3-bromo-4,5-dihydroxybenzaldehyde suggests that it may play a role in the survival of these algae under adverse living conditions.

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