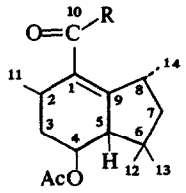
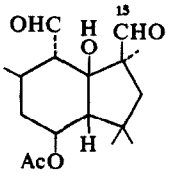
was confirmed by heating botrydial with alumina which gave a low yield of norbotryal acetate through dehydration and subsequent deformylation of the vinylogous β-dialdehyde. The β-orientation of the hydrogen at C-8 was suggested by the long-range 'W' coupling (2 Hz) between the C-5 and C-8 protons which was established by decoupling experiments. This interrelationship raised



1 R = H
3 R = OMe



2

the possibility that norbotryal acetate was an artefact of the purification procedure. However it may be detected TLC and by GLC of a crude EtOAc broth extract. This does not of course preclude its formation by non-enzymatic means from botrydial or a C-15 carboxylic acid, in the culture broth whilst the fungus was growing.

## EXPERIMENTAL

*Isolation. Botrytis cinerea* (GCRI strain 216) was grown for 10 days on surface culture on a Czapek Dox medium (10 l.) containing 0.1% yeast extract and 5% glucose. The broth was extracted with EtOAc and separated into acidic and neutral fractions with aq. $NaHCO_3$. The neutral fraction (4.0 g) was chromatographed on Si gel (250 g) (Merck, deactivated with 12% $H_2O$). Elution with 15% EtOAc–petrol gave a fraction which was further purified by PLC on Si gel in EtOAc–petrol (1:4) to afford norbotryal acetate (1) (476 mg) as an unstable oil. The material was homogeneous by TLC; in the above system it had $R_f$ 0.53 and gave a pink colouration with a MeOH–$H_2SO_4$ spray. It was also homogeneous by GLC on 1% OV17 at 170°. It had $[\alpha]_D^{20}$ + 102° (c 0.2 in $CHCl_3$); bp 84°/0.5 mm; MS 264, 204 (base peak), 189, metastable 175.1 (for 204–189), 161, 119, 105, 43, 41. Accurate mass: found 204.151481, $C_{14}H_{20}O^+$ (M − $MeCO_2H$) requires 204.151407.

*Oxidation.* The aldehyde (55 mg) in $Me_2CO$ (5 ml) was treated with the 8N $CrO_3$ reagent (0.5 ml) for 1 hr. MeOH was added, the soln conc *in vacuo* and the product recovered in EtOAc. It was methylated with $CH_2N_2$ in $Et_2O$ and purified by PLC to afford the methyl ester (3) as an oil, $\nu_{max}$ 1730, 1680, 1630 $cm^{-1}$, δ 0.80 (3H, *d*, *J* = 7 Hz), 0.95 (3H, *d*, *J* = 6 Hz), 1.05 (3H, *s*), 1.25 (3H, *s*), 2.00 (3H, *s*), 3.75 (3H, *s*), 4.8 (1H, *m*). MS 294, 250, 235, 208, 203, 193, 175, 43.

*Reaction of botrydial with alumina.* Botrydial (50 mg) in dry $C_6H_6$ (10 ml) was heated at 60° with $Al_2O_3$ (1 g) (dried in a vacuum oven at 120° overnight) for 1 hr. The soln was filtered, washed with aq. $NaHCO_3$, dried and evaporated. The residual gum was purified by PLC on Si gel in EtOAc–petrol (1:4) to afford norbotryal acetate (4 mg) identified by its IR spectrum.

*Acknowledgements*—We thank Dr. D. Price (Glasshouse Crops Research Institute, Littlehampton) for the strain of *Botrytis cinerea* and Miss Sharon Smith for growing the culture.

## REFERENCES

1. Hanson, J. R. and Nyfeler, R. (1976) *J. Chem. Soc. Chem. Commun.* 72.
2. Fehlhaber, H.-W., Geipal, R., Mercker, H.-J., Tschesche, R. and Welmar, K. (1974) *Chem. Ber.* **107**, 1720; Linder, H. J. and von Grosse, B. (1974) *Chem. Ber.* **107**, 3332.

---

*Phytochemistry*, 1977, Vol. 16, pp. 1062–1063. Pergamon Press. Printed in England

# HALOGENATED SESQUITERPENES FROM THE MARINE RED ALGA *MARGINISPORUM ABERRANS*

KEIICHI OHTA and MAKIKO TAKAGI
Department of Agricultural Chemistry, Shizuoka University, Shizuoka, Japan

(*Received* 12 *November* 1976)

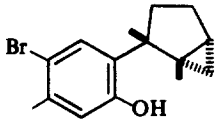
**Key Word Index**—*Marginisporum aberrans*; Corallinaceae; red alga; sesquiterpenes; laurinterol; isolaurinterol; aplysin; aplysinol; aplysinal.

In our previous paper [1], *p*-hydroxybenzaldehyde, dichloroacetamide and 3,5-dinitroguaiacol were identified as antimicrobial components of the marine red alga *Marginisporum aberrans*. Further study of the *n*-hexane extracts of the same plant has resulted in the isolation of five bromine-containing sesquiterpenes, which are described in the present communication.

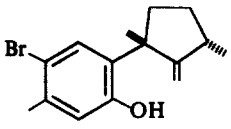
The *n*-hexane-soluble fraction of the MeOH extracts of the seaweed (15 kg) was chromatographed on Si gel. From fractions eluted with *n*-hexane–$Et_2O$ (3:1), there were obtained 10 mg laurinterol (1) [2–5] and a mixture of bromo-compounds (12 mg) from which isolaurinterol (2) [2], aplysin (3) [2,3,5,6], aplysinol (4) [3,6] and a new compound (5) were isolated by preparative GLC (2 m ×

5 mm, 5% Silicone OV-1, isothermal 190°, $N_2$ at 30 ml/min). 1–4 were identified by comparison of IR, NMR and MS with those reported in the literature.

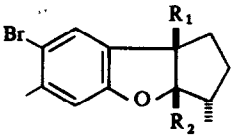
The new compound (5), named aplysinal, gave a positive



(1)



(2)



(3) $R_1 = R_2 = Me$
(4) $R_1 = Me$, $R_2 = CH_2OH$
(5) $R_1 = Me$, $R_2 = CHO$

2,4-DNP test. FTNMR spectrum (100 MHz, $CDCl_3$); 1.05 (3H, *d*, $J = 6$ Hz), 1.30 (3H, *s*), 1.60–1.90 (5H, *m*), (3H, *s*), 6.80 (1H, *s*), 7.16 (1H, *s*), and 9.74 (1H, *s*). MS; *m/e* 308 and 310 ($M^+$), 279 and 281 ($M^+ - CHO$), 237 and 239 ($M^+ - CHO - CH_2{=}CH{-}Me$), and 200 ($M^+ - CHO - Br$). From these data, structure 5 was deduced for this compound. Finally, 5 was transformed into 4 with $LiAlH_4$. The MS and $R_f$ value (TLC) of the synthetic material were identical to those of natural aplysinol (4).

We have now investigated *Amphiroa zonata* Yendo and *Corallina pilulifera* Postels et Ruprecht collected at Cape Omaezaki, Shizuoka, Japan. We note here that both algae contain all compounds 1–5. It is known that *Laurencia* species produces a large amount of bromosesquiterpenes including 1–4 [2–5]. In the vicinity of Cape Omaezaki, some *Laurencia* species grow; therefore, we cannot rule out the possibility that compounds 1–5 may be derived from these algae. An analysis of local *Laurencia* species and other algae growing around Cape Omaezaki is in progress.

Laurinterol (1) was found to display a marked antibiotic activity against *Staphylococcus aureus* [5]. We have also found both 1 and 2 to have a potent antimicrobial activity against *Bacillus subtilis*.

*Acknowledgement*—The identification of plant material was kindly carried out by Dr. T. Masaki, Faculty of Fisheries, Hokkaido University, Hakodate, Japan.

REFERENCES

1. Ohta, K. and Takagi, M. (1977) *Phytochemistry* **16**, 1085
2. Irie, T., Suzuki, M., Kurosawa, E. and Masamune, T. (1970) *Tetrahedron* **26**, 3271.
3. Irie, T., Suzuki, M. and Hayakawa, Y. (1969) *Bull. Chem. Soc. Japan* **42**, 843.
4. Sims, J. J., Fenical, W., Wing, R. M. and Radlick, P. (1971) *J. Am. Chem. Soc.* **93**, 3774.
5. Waraszkiewicz, S. M. and Erickson, K. L. (1974) *Tetrahedron Letters* 2003.
6. Yamamura, S. and Hirata, Y. (1963) *Tetrahedron* **19**, 1485.

*Phytochemistry*, 1977, Vol. 16, pp. 1063–1065. Pergamon Press. Printed in England.

# 4-HYDROXYDEHYDROMYOPORONE FROM INFECTED *IPOMOEA BATATAS* ROOT TISSUE*

HIROMASA INOUE, NATSUKI KATO and IKUZO URITANI
Department of Agricultural Chemistry, Nagoya University, Chikusa, Nagoya, Aichi 464, Japan

(*Revised received* 7 *January* 1977)

**Key Word Index**—*Ipomoea batatas*; *Ceratocystis fimbriata*; Convolvulaceae; sweet potato; sesquiterpene; 4-hydroxydehydromyoporone.

**Abstract**—A new sesquiterpenoid, 4-hydroxydehydromyoporone, was isolated from *Ceratocystis fimbriata*—infected root tissue of *Ipomoea batatas*. We showed that it was a derivative of myoporane with one hydroxyl group at C-8 and one double bond at C-12 by spectroscopic comparison with known compounds.

## INTRODUCTION

*Ipomoea batatas* root tissue infected by *Ceratocystis fimbriata* accumulates various sesquiterpenoids such as ipomeamarone (1a) [1, 2], dehydroipomeamarone (2) [3], and ipomeamaronol (1b) [4, 5].

Recently, Wilson's group isolated from diseased sweet potato a new sesquiterpenoid called 4-hydroxymyoporone (3) [6], and we have confirmed that 3 was also accumulated in response to the infection of *C. fimbriata*, by isolating this compound and comparing the structure with that of an authentic sample. We then

* This paper constitutes Part 129 of the Phytopathological Chemistry of Sweet Potato with Black Rot and Injury. This work was supported in part by a grant from the Ministry of Education.