Spherisorb 5 μm ODS. Elution was isocratic with either H_2O–MeOH (9:1) or H_2O–MeOH (7:3) containing 10^{-3} N HCl, flow rate 1 ml min^{-1} at 155 kg cm^2.

GLC. Carried out on ABA Me ester with an instrument equipped with an electron-capture detector and a 130 × 0.2 cm glass column packed with 3% DC-200 on Gas-Chrom Q. The carrier was Ar–CH_4 (19:1), flow rate 40 ml min^{-1}, oven temp. 165° and detector temp. 186°.

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NORBOTRYAL ACETATE, A NOR-SESQUITERPENOID ALDEHYDE FROM *BOTRYTIS CINEREA*

OLGA CUEVAS and JAMES R. HANSON
School of Molecular Sciences, University of Sussex, Brighton, Sussex BN1 9QJ, U.K.

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Key Word Index—*Botrytis cinerea*; Hyphomycetes; sesquiterpenoid; nor-sesquiterpenoid; botrydial; ^{13}C NMR.

In the course of biosynthetic studies [1] on the metabolites of the plant pathogen, *Botrytis cinerea*, we isolated an unstable oily acetoxy-aldehyde, $C_{16}H_{24}O_3$. The IR [ν_{max} 2740, 1670, 1625 (C=C.CHO) and 1735, 1235 (CH_3.CO.O) cm^{-1}] and NMR [δ 10.0 (1H, *s*) and 2.00 (3H, *s*)] revealed the presence of the aldehyde and acetate groupings. Oxidation with CrO_3 and methylation of the product with CH_2N_2 gave a monomethyl ester which was again an unstable oil. The NMR data (see Table 1) can be interpreted in terms of structure (1) for the compound which we have named norbotryal acetate. The fully substituted nature of the $\alpha\beta$-unsaturated aldehyde was confirmed by the UV [λ_{max} 253 nm (calc. 254 nm), ε 10300] and by the singlet character of the olefinic ^{13}C resonances. PMR decoupling experiments established the presence of a CH_2.CH(OAc).CH— and two CH.Me groups. The location of the other carbon atoms in two tertiary methyl groups, a methylene, a quaternary carbon atom and an acetoxyl group, was clear from the ^1H and ^{13}C NMR spectra.

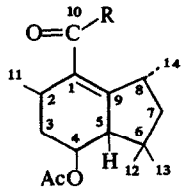
The co-occurrence of this compound with botrydial (2) [2] led to the proposed structure (1). This relationship

Table 1. The NMR spectra of norbotryal acetate

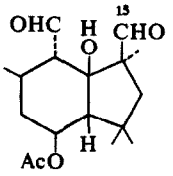
Position	^{13}C resonance*	^1H resonance
1	135.8	
2	32.5	2.85 (*m*)
3	37.5	1.38 and 2.14 (*m*)
4	70.2	4.75 (octet J = 3, 9, 10 Hz)
5	56.0	2.54 (*q* J = 2 and 9 Hz)†
6	40.9	
7	49.3	1.8 (*m*)
8	29.1	3.2 (*m*)†
9	169.0	
10	190.4	10.0 (*s*)
11	21.9	1.12 (*d*, J = 6 Hz)
12	28.3	1.25 (*s*)
13	20.6	0.75 (*s*)
14	24.2	1.28 (*d*, J = 7 Hz)
C=O	170.1	
Me	21.3	2.00 (*s*)

(determined in $CDCl_3$; values in ppm from TMS)
* Assigned by comparison with botrydial and derivatives.
† These signals showed a long-range coupling.

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



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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, ν_{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.

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HALOGENATED SESQUITERPENES FROM THE MARINE RED ALGA *MARGINISPORUM ABERRANS*

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

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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 ×