Tetrahedron Letters No. 33, pp.3137-3140, 1971. Pergamon Press. Printed in Great Britain.

STRUCTURE OF PESTALOTIN, A NEW METABOLITE FROM PESTALOTIA CRYPTOMERIAECOLA

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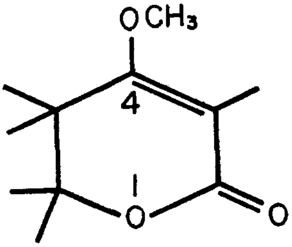
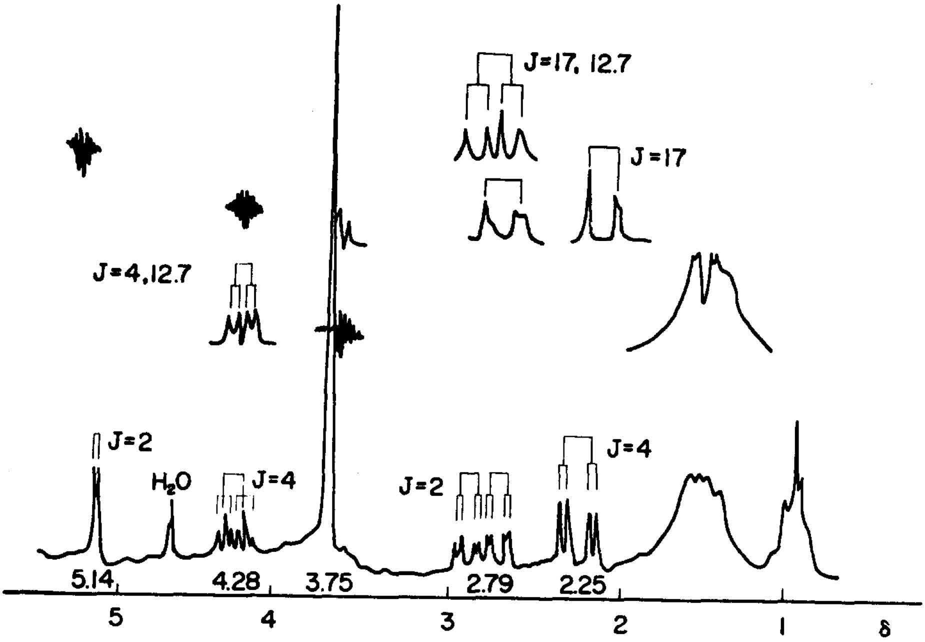
(Received in Japan 15 July 1971; received in UK for publication 20 July 1971)

During the course of our screening search for gibberellin synergists among microbial metabolites, we succeeded in isolating an active principle named pestalotin from culture filtrate of a phytopathogenic fungus, Pestalotia cryptomeriaecola. Here we wish to report the structure of this compound. Pestalotin (I), $C_{11}H_{18}O_4$, M^+ 214, mp 88-89°C, exhibited IR absorption bands at 1710 and 1635 cm^{-1} and an UV absorption maximum at 233 nm (ε=12200 in EtOH). The NMR spectrum of I showed the presence of an olefinic proton (δ 5.14, 1H; d, J=2 Hz) and a methoxyl group (δ 3.75, 3H; s). On the basis of these spectral data, I is considered to be a derivative of 4-methoxy-5,6-dihydro-α-pyrone (1, 2).



Treatment of I with acetic anhydride-pyridine gave an acetate with IR absorption bands at 1745 and 1240 cm^{-1}, accompanying the disappearance of absorption bands at 3480 and 1025 cm^{-1} observed in I. In the NMR spectrum of I, the signal at δ 2.22 (1H; s) was easily deuterized and the signal at δ 3.62 (1H; m) was deshielded to 5.08 (1H; m) on acetylation. Moreover, elimination of 18 mass units from the molecular ion of I was recognized in mass spectrometry. These data suggest the presence of a secondary hydroxyl group.

The signals at δ 0.91 (3H; t) and 1.30-1.60 (6H; m) were attributable to a n-butyl group, the presence of which was further confirmed by mass spectrometry as shown in Table 1.



NMR spectrum of I (in $CDCl_3$+D_2O)*

The signals at δ 2.25 (1H; q, J=4.0, 17.0 Hz) and 2.79 (1H; octet, J=2.0, 12.7, 17.0 Hz) were assigned to C-5 H on the basis of their chemical shifts and of the coupling constant 17.0 Hz indicative of their geminal relationship.

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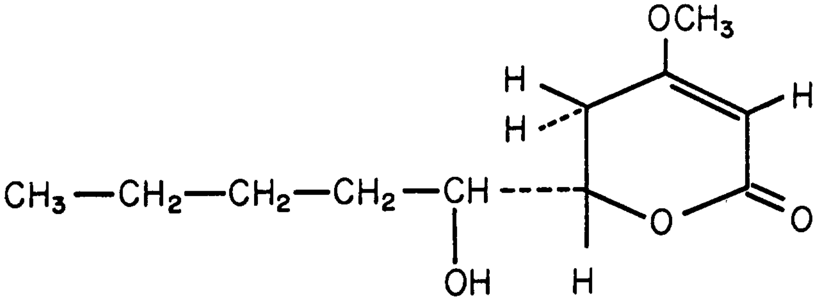
* NMR spectra (100 MHz) were recorded in $CDCl_3$ using TMS as an internal reference. The symbols "s", "d", "t" and "m" are used to refer to singlets, doublets, triplets and multiplets.

The signal at δ 4.28 (1H; sextet, J=4.0, 12,7 Hz) was assigned to C-6 H, because the peak exhibited coupling with C-5 H. Therefore, the side chain including the before-mentioned n-butyl group should be attatched to C-6. Thus, the structure of pestalotin has been assigned as 6-(1-hydroxylpent-1-yl)-4-methoxy-5,6-dihydro-α-pyrone (I).

Table 1. Mass spectrum of I**

m/e	
214	M^+
196	$M^+ - H_2O$
181	$M^+ - (H_2O + CH_3)$
167	$M^+ - (H_2O + C_2H_5)$
157	$M^+ - C_4H_9$
153	$M^+ - (H_2O + C_3H_7)$
139	$M^+ - (H_2O + C_4H_9)$
127	$M^+ - C_5H_{11}O$

The negative Cotton effect at 246 nm (Δε 12.0 in EtOH) in the circular dichroism curve (3, 4) of I suggests the absolute configuration at C-6 to be (R). However, the stereochemistry at C-1' has not been elucidated yet.



I

** Mass spectrum was measured with a Hitachi RMU-7 and the energy of the bombarding electrons was 70 eV.

Acknowledgement. We wish to express our thanks to Mr. K. Aizawa of our Department for the measurement of IR and NMR spectra.

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