Tetrahedron Letters No.45, pp. 3965-3968, 1969. Pergamon Press. Printed in Great Britain.

DIHYDROILLUDIN S, A NEW CONSTITUENT FROM LAMPTEROMYCES JAPONICUS

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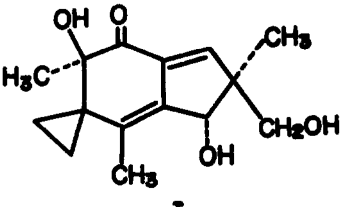
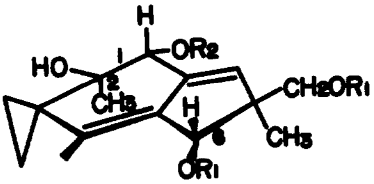
(Received in Japan 5 July 1969; received in UK for publication 25 August 1969)

Illudin S (lampterol, I), toxic constituent of Lampteromyces japonicus, which shows characteristic bioluminescence, was isolated,[1] and assigned the structure[2] and the stereochemistry[3] as in I. In this communication, we wish to report the isolation and structural elucidation of a new component, dihydroilludin S (II), which might be related to the luminescence,[4] from the same toadstool. Isolation of the component was carried out by the same procedure used as for illudin S and in the final stage, aqueous layer after extraction of illudin S with ethyl acetate was concentrated in vacuo to give a syrup. Column chromatography of the syrup on silica gel using dichloroethane-methanol (10%) as a solvent, yielded II (120 mg from ca. 60 kg of raw toadstool) as an amorphous powder, τ^{D_2O} 8.97 (3H, s, C-CH_3), 8.91 (3H, s, C-CH_3), 8.43 (3H, s, C-CH_3), 6.58 (2H, s, CH_2OH), 5.73 (1H, broad, -CH-O), 5.41 (1H, s, -CH-O), 4.38 (1H, broad, $\overset{H}{=/}$).



I



II R_1, R_2 = H
III R_1, R_2 = Ac
IV R_1=Ac, R_2=H

Acetylation of II gave a triacetate, M^+ 392, ν_{max}^{neat} 3480, 1745, 1655, 1230 cm^{-1}, τ^{CDCl_3} 8.98 (3H, s, C-CH_3), 8.85 (3H, s, C-CH_3), 8.60 (3H, s, =C-CH_3), 7.97. 7.93, 7.83 (each 3H, s, 3Ac), 5.88, 6.17 (2H, AB type quartet, J = 10.5Hz, -CH_2OAc), 4.63 (1H, broad, $=\!/^{H}$), 4.53 (1H, d, J=2Hz, CHOAc), 4.42 (1H, s, CHOAC). The n.m.r. and i.r. spectra of the triacetate were identical with those of the acetate derived by acetylation of dihydrodiacetylilludin S (IV) which was obtained from illudin S previously.[2] In addition, hydrolysis of the triacetate (III) with potassium carbonate gave, probably owing to the participation of the neighboring hydroxyl group,[5] partially hydrolyzed diacetate (IV) in good yield. Therefore, the structure and the stereochemistry of II except C-1 must be the same as for illudin S. The n.m.r. spectra of III and IV[7] showed respectively signals at 4.53 and at 5.67 with an allylic coupling (2Hz) which indicates that the angle between the plane of the double bond in the five membered ring and the C-H bond occupied a quasi-axial position.[8] Since the tertiary hydroxyl group is quasi-equatorial in illudin S,[3,9] the hydroxyl group on C-1 in dihydroilludin S should be trans to the tertiary hydroxyl group and the stereochemistry of dihydroilludin S could be described as II. Anti-tumor[1] activity for Ehrlich ascites tumor was negative after injection of 40 (10 4 days) of II into mice.

Acknowledgement: The authors are indebted to Dr. Hideya Saito, School of Medicine, Hokkaido University, for testing the antitumor activity.

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2) T. Matsumoto, H. Shirahama, A. Ichihara, Y. Fukuoka, Y. Takahashi, Y. Mori and M. Watanabe, Tetrahedron, 21, 2671 (1965); T.C. McMorris and M. Anchel, J. Am. Chem. Soc., 85, 831 (1963); K. Nakanishi, M. Ohashi, M. Tada and Y. Yamada, Tetrahedron, 21, 1231 (1965).

3) T. Matsumoto, Y. Fukuoka, A. Ichihara, Y. Mori, H. Shirahama, Y. Takahashi and M. Watanabe, Bull. Chem. Soc. Japan, **37**, 1716 (1964).

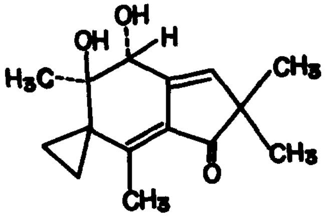
4) The authors wish to thank Prof. K. Nakanishi for his suggestion on this point.

5) For the examples of neighbouring hydroxyl group assistance in the alkaline hydrolysis of esters, see T. Yamanaka, A. Ichihara, K. Tanabe and T.Matsumoto, Tetrahedron, **21**, 1031 (1965). H. B. Henbest and B. J. Lovell, J. Chem. Soc., 1965 (1967); S. M. Kupchan, W. S. Johnson and S. Rajagopalan, Tetrahedron, **7**, 47 (1959); T. C. Bruice and T. H. Fife, J. Am. Chem. Soc., **84**, 1973 (1962).

6) N. S. Bhacca and D. H. Williams "Application of NMR Spectroscopy in Organic Chemistry" p. 108, Holden-Day, San Francisco (1964).

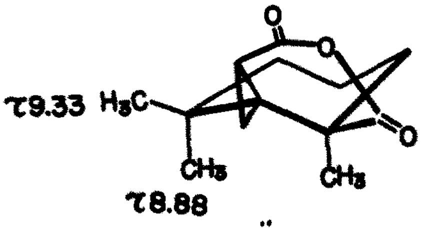
7) In the n.m.r. spectrum, dihydroilludin S (II) showed a broad signal (5.73) due to C-1 proton with a half-band width 4 Hz.

8) Another possibility of long range coupling of the C-1 proton with C-6 proton in compounds (III) and (IV) would be excluded by the fact that α proton to hydroxy group still couples with a vinylic proton (J=2Hz at τ 5.59) in compound (i) which was prepared by reduction of dehydroilludin M with sodium borohydride (Unpublished results).



i

9) Equatorial nature of the tertiary hydroxyl group in illudin S is shown by the large $\Delta\nu_{OH}$ value (133 cm^{-1}) of bonded hydroxyl group in the i.r. spectrum of I (M. Ōki, H. Iwamura, J. Aihara and H. Iida, Bull. Chem. Soc. Japan, **41**, 176 (1968)). Moreover, comparison of chemical shift of C-2 methyl group in II with that of the following compound (ii) (S. Forsen and T. Norin, Tetrahedron Letters, 2223 (1964) indicates that the methyl group of II is situated above the cyclopropane ring and confirms that the tertiary hydroxyl group in II is equatorial.



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