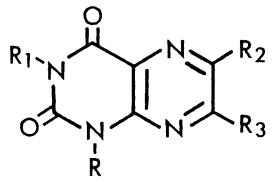
CHEMISTRY LETTERS, pp. 563-564, 1991 

# New Lumazines from the Marine Polychaete, Odontosyllis undecimdonta

Shoji INOUE,* Kunisuke OKADA, Hideo TANINO, Hisae KAKOI,
Yoshiko OHNISHI, and Naojiro HORII
Faculty of Pharmacy, Meijo University, Tenpaku, Nagoya 468

6-β-Methoxypropionyl-3-methyllumazine and 6-β-methoxypropionyl-1,3-dimethyllumazine, and 6-β-hydroxypropionyl-3-methyllumazine have been newly isolated from the swimming polychaete, Odontosyllis undecimdonta.

Previously we have reported the isolation of a new type of 6-propionyllumazines from the marine swimming polychaete, Odontosyllis undecimdonta.[1,2] In subsequent studies to isolate compounds related to the lumazine derivatives, additional three 6-propionyllumazines from the same polychaete were obtained by the following experiments: crude MeOH extracts of the freeze-dried worms (11 g, ca. 5500 individuals) obtained as previously described[2] were chromatographed on a silica-gel column using a MeOH-$CH_2Cl_2$ (1:10) solvent system into three fractions A, B, and C. Fraction B was further separated by preparative silica-gel TLC using MeOH-$CH_2Cl_2$ (1:10) to yield the previously reported 6-propionyllumazines **1**-**3**[2] along with a mixture of two unknown metabolites.



**1** : R=$R_1$=H, $R_2$=$COCH_2CH_3$, $R_3$=H

**2** : R=H, $R_1$=$CH_3$, $R_2$=$COCH_2CH_3$, $R_3$=H
**3** : R=$R_1$=$CH_3$, $R_2$=$COCH_2CH_3$, $R_3$=H
**4** : R=H, $R_1$=$CH_3$, $R_2$=$COCH_2CH_2OCH_3$, $R_3$=H
**5** : R=$R_1$=$CH_3$, $R_2$=$COCH_2CH_2OCH_3$, $R_3$=H
**6** : R=$R_1$=$CH_3$, $R_2$=$COCH_2CH_2OCH_3$, $R_3$=$SCH_3$
**7** : R=H, $R_1$=$CH_3$, $R_2$=$COCH_2CH_2OH$, $R_3$=H

The purification of these metabolites on silica-gel TLC plates using AcOEt-benzene-MeOH (10:6:1) for **4** and MeOH-$CH_2Cl_2$ (1:10 then 3:97) for **5** gave pure compounds **4** (0.8 mg) and **5** (0.6 mg), respectively. The UV spectral behavior of the new metabolites **4**[3] and **5**[4] in neutral and basic media were consistent with those of **2** and **3**, respectively, as reported in the previous paper.[2]

High resolution Mass spectra of **4** and **5** showed their molecular ion peaks: m/z 264.0868 for **4**[3] and 278.1027 for **5**.[4] These were attributable to the empirical formulas, $C_{11}H_{12}N_4O_4$ and $C_{12}H_{14}N_4O_4$, respectively. From these and the results of

$^1$H-NMR analysis of 4[3] and 5,[4] the structures of **4** and 5 were assinged as 6-β-methoxypropionyl-3-methyllumazine **4** and 6-β-methoxypropionyl-1,3-dimethyllumazine **5**, respectively. Compound **4** was methylated with MeI-$K_2CO_3$ in DMF (rt, 1 h) to give 1,3-dimethyl derivative **5** whose structure was established by comparison of physical data[4] with those of an authentic sample prepared from 6-β-methoxypropionyl-1,3-dimethyl-7-methylthiolumazine **6**[5] by a known method.[6]

In addition to the above 6-β-methoxypropionyllumazines, a trace amount of 6-β-hydroxypropionyl-3-methyllumazine **7**[7] was isolated from fraction C by successive purification on TLC using AcOEt-benzene-MeOH (10:6:1), AcOEt-MeOH-$H_2O$ (20:1:1) and finally MeOH-$CH_2Cl_2$ (1:10 then 1:20). The structure of compound **7** was elucidated by UV, MS, and NMR analysis and characterized by the following chemical conversion. By heating **7** in N HCl-MeOH at 50 °C for 1 h followed by the usual work up, the β-hydoxypropionyl substituent in **7** was easily converted to the β-methoxypropionyl substituent to form **4**.

Whether these lumazine derivatives are related to Odontosyllis bioluminescence or its particular biorhythm[1] is not yet known. Studies on the roles of 6-propionyllumazines in Odontosyllis and on the characterization of other metabolites are presently being conducted.

This work was supported by a Grant-in-Aid for Scientific Research No. 63571012 from the Ministry of Education, Science and Culture.

References

1) This swimming worm appears at the surface of the water in some abundance shortly after sunset and luminesces and spawns for a period of approximately 30 minutes. The spawning can be observed only once a year for about three weeks from the end of September to the middle of October at Toyama-Bay.
2) S. Inoue, K. Okada, H. Tanino, H. Kakoi, and N. Horii, Chem. Lett., 1990, 367.
3) **4**: Colorless crystalline solid, mp 193-196 °C (dec.); UV (MeOH) $\lambda_{max}$ 250, 273, 326 nm; UV (MeOH-NaOH) $\lambda_{max}$ 256, 315, 371 nm; $^1$H- NMR (400 MHz, $CDCl_3$) δ 3.36 (3H, s), 3.54 (3H, s), 3.54 (2H, t, J=6.0 Hz), 3.87 (2H, t, J=6.0 Hz), 9.24 (1H, s); High-resolution MS Found: m/z 264.0868. Calcd for $C_{11}H_{12}N_4O_4$: 264.0858.
4) **5**: Colorless needles, mp 129-130 °C; UV (MeOH) $\lambda_{max}$ 252 (log ε 4.09), 282 (4.07), 331 nm (3.97); UV (MeOH-NaOH) $\lambda_{max}$ 252 (log ε 4.09), 283 (4.07), 332 nm (3.97); $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.36 (3H, s), 3.55 (2H, t, J=5.9 Hz), 3.57 (3H, s), 3.76 (3H, s), 3.87 (2H, t, J=5.9 Hz), 9.29 (1H, s); $^{13}$C-NMR ($CDCl_3$) δ 29.2 (q), 29.8 (q), 38.0 (t), 58.8 (q), 67.4 (t), 125.7 (s), 143.3 (s), 147.2 (d), 149.8 (s), 150.4 (s), 159.2 (s), 197.9 (s); Anal. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.80; H, 5.07; N, 20.14. Found: C, 51.55; H, 5.05; N, 19.90; High-resolution MS Found: m/z 278.1027. Calcd for $C_{12}H_{14}N_4O_4$: 278.1014.
5) **6**: Pale yellow needles, mp 147-148 °C; UV (MeOH) $\lambda_{max}$ 257 (log ε 4.31), 311 (4.09), 366 nm (4.21); $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.58 (3H, s), 3.36 (3H, s), 3.53 (2H, t, J=5.9 Hz), 3.54 (3H, s), 3.75 (3H, s), 3.84 (2H, t, J=5.9 Hz); Anal. Calcd for $C_{13}H_{16}N_4O_4S$: C, 48.14; H, 4.97; N, 17.27. Found: C, 48.17; H, 4.94; N, 17.18.
6) R. Baur, E. Kleiner, and W. Pfleiderer, Liebigs Ann. Chem., 1984, 1798; W. Pfleiderer, Tetrahedron, 44, 3373 (1988).
7) **7**: Colorless solid ;UV (MeOH) $\lambda_{max}$ 250, 275, 327 nm; UV (MeOH-NaOH) $\lambda_{max}$ 257, 315, 371 nm; $^1$H-NMR (400 MHz, $CD_3OD$) δ 3.44 (2H, t, J=6.0 Hz), 3.45 (3H, s), 3.99 (2H, t, J=6.0 Hz), 9.15 (1H, s); High-resolution MS Found: m/z 250.0736. Calcd for $C_{10}H_{10}N_4O_4$: 250.0701.

(Received December 6, 1990)