4401-1 (C15 acetogenin)

Name: Laurencin {Acetic acid 1-(7-bromo-8-ethyl-3,6,7,8-tetrahydro-2*H*-oxocin-2-yl)-hex-3-en-5-ynyl ester}

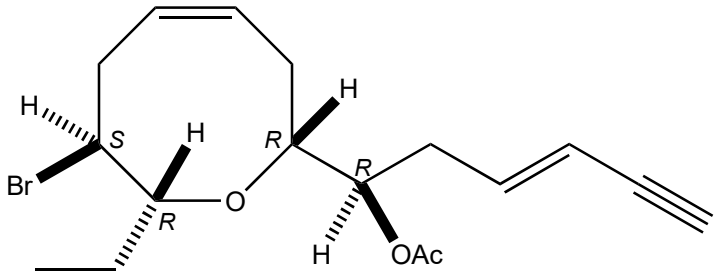
Origin: *Laurencia nipponica* (as *L. glandulifera*[(1)]) (Oshoro Bay, Otaru, Hokkaido, Japan)[(2-4)]; *Laurencia nipponica* (Bikuni, east Shakotan, Hokkaido, Japan)[(5)];

Formula: $C_{17}H_{23}BrO_3$

Mol. Wt.: 355.27

Opt. Rot.: $[\alpha]_D^{23}$ +70.2 ($CHCl_3$)

Mp.: 73-74



References and Notes

(1) *Laurencia nipponica* Yamada has been confused with the Adriatic species *Laurencia glandulifera* Kutzing. *Laurencia glandulifera* does not occur in Japanese water, and therefore *L. glandulifera* reported by Irie group shoud be revised to *L. nipponica*. Saito, Y. 1985. Jpn. J. Phycol., **33**, 167-171. So-called *Laurencia glandulifera* in Japan and *L. nipponica* (Rhodophyceae, Rhodomelaceae) (in Japanese).

(2) Irie, T., Suzuki, M., and Masamune, T. 1965. Tetrahedron Lett., **6**, 1091-1099. Laurencin, a constituent from *Laurencia* species. (**UV, IR, ^{1}H-NMR**)

(3) Irie, T., Suzuki, M., and Masamune, T. 1968. Tetrahedron, **24**, 4193-4205. Laurencin, a constituent of *Laurencia glandulifera* Kutzing. (**UV, IR, ^{1}H-NMR, MS**)

(4) (**X-ray crystallographic analysis**) (a) Cameron, A. F., Cheung, K. K., Ferguson, G, and Robertson, J. M. 1965. J. Chem. Soc. Chem. Commun., **1965**, 638-638. The crystal structure and stereochemistry of laurencin.; (b) Cameron, A. F., Cheung, K. K., Ferguson, G, and Robertson, J. M. 1969. J. Chem. Soc. B, **1969**, 559-564. *Laurencia* natural products. Part I. The crystal structure and absolute stereochemistry of laurencin.

(5) Suzuki, M. and Kurosawa, E. 1987. Bull. Chem. Soc. Jpn., **60**, 3791-3792. (3*E*)-Laureatin and (3*E*)-isolaureatin, halogenated C-15 non-terpenoid compounds from the red alga *Laurencia nipponica* Yamada. (**Laurencin from *L. nipponica* of several sites in Hokkaido**)

(Continue to 4401-2)

References and Notes

(Continue from 4401-1)

(6) **Synthesis**; (a) Murai, A., Murase, H., Matsue, H., and Masamune, T. 1977. Tetrahedron Lett., **18**, 2507-2510. The synthesis of (*dl*)-laurencin.; (b) Tsushima, K. and Murai, A. 1992. Tetrahedron Lett., **33**, 4345-4348. Total synthesis of (+)-laurencin.; (c) Rychnovsky, S. D. and Dahanukar, V. H. 1996. J. Org. Chem. **61**, 7648-7649. Carbon-carbon bond formation from small- and medium-ring lactol acetates via radical and oxonium ion intermediates. Synthesis of (*dl*)-laurencin.; (d) Burton, J. W., Clark, J. S., Derrer, S., Stork, T. C., Bendall, J. G., and Holmes, A. B. 1997. J. Am. Chem. Soc., **119**, 7483-7498. Synthesis of medium ring ethers. 5. The synthesis of (+)-laurencin.; (e) Kruger, J. and Hoffmann, R. W. 1997. J. Am. Chem. Soc., **119**, 7499-7504. Substituted oxocanes by intramolecular allylboration reactions. Entry to an efficient synthesis of (+)-laurencin.; (f) Crimmins, M. T. and Emmitte, K. A. 1999. Org. Lett., **1**, 2029-2032. Total synthesis of (+)-laurencin: An asymmetric alkylation-ring-closing metathesis approach to medium ring ehter.; (g) Baek, S., Jo, H., Kim, H., Kim, H., Kim, S., and Kim, D. 2005. Org. Lett., **7**, 75-77. Highly stereoselective and efficient total synthesis of (+)-laurencin.; (h) Fujiwara, K., Yoshimoto, S., Takizawa, A., Souma, S., Mishima, H., Murai, A., Kawai, H., and Suzuki, T. 2005. Tetrahedron Lett., **46**, 6819-6822. Synthesis of (+)-laurencin via ring expansion of a *C*-glycoside derivative.; (i) Ortega, N., Martin, V. S., and Martin, T. 2010. J. Org. Chem., **75**, 6660-6672. An approach to lauroxanes by interactive use of $Co_2(CO)_6$-acetylenic complexxes. A formal synthesis of (+)-laurencin.

(7) **Biosynthesis**; Suzuki, M., Takahashi, Y., Nakano, S., Abe, T., Masuda, M., Ohnishi, T., Noya, Y., and Seki, K. 2009. Phytochemistry, **70**, 1410-1415. An experimental approach to study the biosynthesis of brominated metabolites by the red algal genus *Laurencia*.