4708-1 (C15 acetogenin)

Name: Zagashimallene[4]; aplysiallene[5]
{2-(4-Bromo-hexa-1,3-dienyl)-5-(3-bromo-propa-1,2-dienyl)-hexahydro-furo[3,2-*b*]furan}

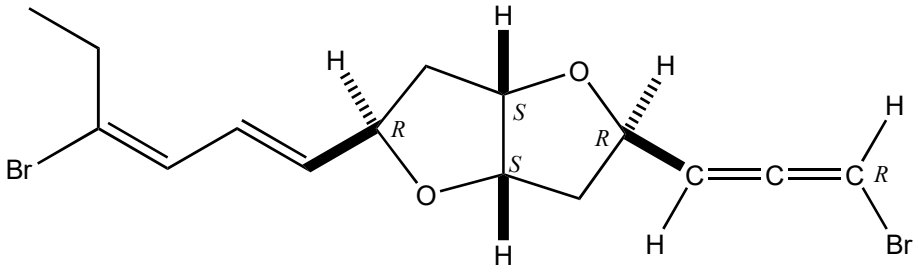
Origin: *Laurencia okamurae* (as *L. okamurai*) (Zagashima Island, Ago Bay, Mie, Japan)[1];
Laurencia sp. (Tsubota, Miyakejima Island, Tokyo, Japan)[2];
Laurencia sp. (Omaezaki, Shizuoka, Japan)[3];
Laurencia intricata (Katsuura, Chiba, Japan)[4];
Aplysia kurodai (Echizen Coast, Fukui, Japan)[5];

Formula: $C_{15}H_{18}Br_2O_2$

Mol. Wt.: 390.11

Opt. Rot.: $[\alpha]_D^{23}$ -215 ($CHCl_3$)[1]; $[\alpha]_D^{23}$ -168 ($CHCl_3$)[4]; $[\alpha]_D^{23}$ -160 ($CHCl_3$)[5]

Mp.: Oil



References and Notes

(1) Suzuki, M. and Kurosawa, E. 1985. Phytochemistry, **24**, 1999-2002. A C-15 non-terpenoid from the red alga *Laurencia okamurai*. (**UV, IR, ^{1}H-NMR, ^{13}C-NMR, MS**)

(2) **Revision of chemical shift values and assignment of carbon signals**; Suzuki, M., Kawamoto, T., Vairappan, C. S., Ishii, T., Abe, T, and Masuda, M. 2005. Phytochemistry, **66**, 2787-2793. Halogenated metabolites from Japanese *Laurencia* spp. (**^{13}C-NMR**)

(3) Umezawa, T., Oguri, Y., Matsuura, H., Yamazaki, S., Suzuki, M., Yoshimura, E., Furuta, T., Nogata, Y., Serisawa, Y., Matsuyama-Serisawa, K., Abe, T., Matsuda, F., Suzuki, M., and Okino, T. 2014. Angew. Chem. Int. Ed., **53**, 3909-3912. Omaezallene from red alga *Laurencia* sp.: Structure elucidation, total synthesis, and antifouling activity. (together with omaezallene, (12Z)-omaezallene, 12,13-dihydroomaezallene, zagashimallene, intricatetraol)

(4) Ishii, T., Shinjo, Y., Miyagi, M., Matsuura, H., Abe, T., Kikuchi, N.,, and Suzuki, M. 2019. Rec. Nat. Prod., **13**, 81-84. Investigation of insect repellent activity of cyclocolorenone obtained from the red alga *Laurencia intricata*. (**^{13}C-NMR**) (together with zagashimallene, intricatetraol, cyclocolorenone)

(5) **From the sea hare**; (a) Okamoto, Y., Nitanda, N., Ojika, M., and Sakagami, Y. 2001. Biosci. Biotechnol. Biochem., **65**, 474-476. Aplysiallene, a new bromoallene as an Na, K-ATPase inhibitor from the sea hare, *Aplysia kurodai.* (**UV, ^{1}H-NMR, ^{13}C-NMR**) (together with laurinterol, debromolaurinterol); (b) ERRATA, Biosci. Biotechnol. Biochem., **67**, 460 (2003).

(Continue to 4708-2)

References and Notes

(Continue from 4708-1)

(6) **Total synthesis**; (a) Wang, J. and Pagenkopf, B. L. 2007. Org. Lett., **9**, 3703-3706. First total synthesis and structural reassignment of (-)-aplysiallene.; (b) Yamakawa, M., Kurachi, T., Yoshikawa, Y., Arisawa, M., Okino, Y., Suzuki, K., and Fujioka, H. 2015. J. Org. Chem., **80**, 10261-10277. Stereoselective construction of 2,7-disubstituted *fused*-bis tetrahydrofuran skeletons: Biomimetic-type synthesis and biological evaluation of (*dl*)- and (-)-aplysiallene and their derivatives.; (c) Kobayashi, S., Yokoi, T., Inoue, T., Hori, Y., Saka, T., Shimomura, T., and Masuyama, A. 2016. J. Org. Chem., **81**, 1484-1488. Stereocontrolled synthesis of a possible stereoisomer of laurenidificin and a formal total synthesis of (+)-aplysiallene featuring a stereospecific ring contraction.; (d) Shin, I., Jang, H., Kwak, S. Y., Park, Y., Lee, D., Kim, H., and Kim, D. 2022. Org. Lett., **24**, 8780-8785. Highly stereodivergent construction of a C_2-symmetric *cis*,*cis*- and *trans*-,*trans*-2,6-dioxabicyclo[3.3.0]octane framework by double intramolecular amide enolate alkylation: Total synthesis of (+)-laurenidificin and (+)-aplysiallene.