4436-1 (C15 acetogenin)

Name: *trans*-Pinnatifidenyne; (*E*)-pinnatifidenyne {8-(1-Bromo-propyl)-3-chloro-2-pent-2-en-4-ynyl-3,4,7,8-tetrahydro-2*H*-oxocine}

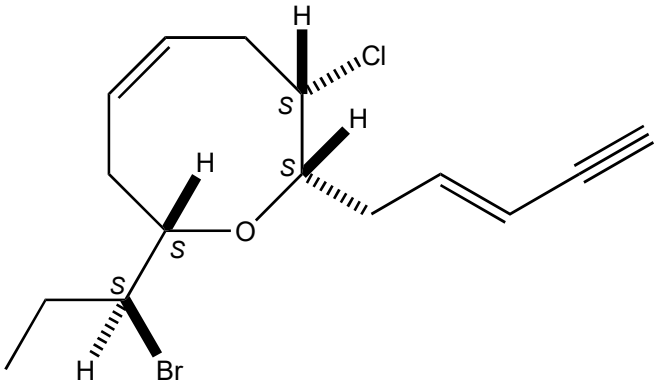
Origin: *Laurencia pinnatifida* (Los Cristianos, Tenerife, Canary Islands, Spain)(1);
Laurencia pinnatifida (Tenerife, Canary Islands, Spain)(2);
Laurenciella sp. (along the Sanguinaires Road, Ajaccio, Corsica, France)(3);
Aplysia dactylomela (Hainan Island in South China Sea, China)(4);

Formula: $C_{15}H_{20}BrClO$

Mol. Wt.: 331.68

Opt. Rot.: $[\alpha]_D^{25}$ +62 ($CHCl_3$)(1); $[\alpha]_D^{25}$ +4.6 ($CHCl_3$)(2); $[\alpha]_D$ +28.2 ($CHCl_3$)(4)

Mp.: 57-58(1); 54-56(2);



References and Notes

(1) Gonzalez, A. G., Martin, J. D., Martin, V. S., Norte, M., Perez, R., Ruano, J. Z., Drexler, S. A., and Clardy, J. 1982. Tetrahedron, **38**, 1009-1014. Non-terpenoid C-15 metabolites from the red seaweed *Laurencia pinnatifida*. (**X-ray crystallographic analysis**) (**IR, ^{1}H-NMR, ^{13}C-NMR, MS**)

(2) **Reassignment of the absolute configuration**; Norte, M., Gonzalez, A. G., Cataldo, F., Rodoriguez, M. L., and Brito, I. 1991. Tetrahedron, **47**, 9411-9418. New examples of acyclic and cyclic C-15 acetogenins from *Laurencia pinnatifida*. Reassignment of the absolute configuration for E and Z pinnatifidenyne. (**X-ray crystallographic analysis**)

(3) Sutour, S., Therrien, B., von Reuss, S. H., and Tomi, F. 2018. J. Nat. Prod., **81**, 279-285. Halogenated C_{15} acetogenin analogues of obtusallene III from a *Laurenciella* sp. collected in Corsica. (together with 4 obutusallene III derivatives, 1 marilzabicycloallene C derivative, 17 known compounds; **(3*E*)-laurenyne (main component)**, (3*Z*)-laurenyne, obtusallene I, 10-bromoobtusallene I, (*E*)-pinnadifidenyne, obtusin, 4-acetoxymarizallene, marizallene B, α-bromocuparene, α-isobromocuparene, α-snyderol, 1-deacetoxy-8-deoxyalgoane, cycloelatenene A, 9,15-dibromo-1,3(15)-chamigradien-11-ol, etcetera)

(4) Manzo, E., Ciavatta, M. L., Gavagnin, M., Puliti, R., Mollo, E., Guo, Y.-W., Mattia, C. A., Mazzarella, L., and Cimino, G. 2005. Tetrahedron, **61**, 7456-7460. Structure and absolute stereochemistry of novel C_{15}-halogenated acetogenins from the anaspidean mollusc *Aplysia dactylomela*. (together with (-)-3*E*,6*R*,7*R*-pinnatifidenyne, (+)-3*Z*,6*R*,7*R*-obtusenyne, (+)-3*E*,6*R*,7*R*-obtusenyne, three known compounds; (+)-3*E*-pinnatifidenyne, (+)-laurenyne, (+)-brasinelol)

(Continue to 4436-2)

References and Notes

(Continue from 4436-1)

(5) **Total synthesis**; (a) Kim, H., Choi, W. J., Jung, J., Kim, S., and Kim, D. 2003. J. Am. Chem. Soc., **125**, 10238-10240. Construction of eight-membered ether rings by olefin geometry-dependent internal alkylation: First asymmetric total synthesis of (+)-3-(*E*)- and (+)-3-(*Z*)-pinnatifidenyne.; (b) Snyder, S. A., Brucks, A. P., Treitler, D. S., and Moga, I. 2012. J. Am. Chem. Soc., **134**, 17714-17721. Concise synthetic approaches for the *Laurencia* family: Formal total syntheses of (*dl*)-laurefucin and (*dl*)-*E*- and (*dl*)-*Z*-pinnadifidenyne.; (c) Kim, H. S., Kim, T., Ahn, J., Yun, H., Lim, C., Jang, J., Sim, J., An, H., Surh, Y.-J., Lee, J., and Suh, Y.-G. 2018. J. Org. Chem., **47**, 1997-2005. Asymmetric total synthesis of (+)-(3*E*)-pinnatifidenyne via abnormally regioselective Pd(0)-catalyzed endocyclization.