CHEMISTRY LETTERS, pp. 1263-1264, 1985.

STRUCTURE OF A NEW BROMODITERPENE, PREPINNATERPENE, FROM THE MARINE RED ALGA LAURENCIA PINNATA YAMADA

Akio FUKUZAWA, Yoshiaki TAKAYA, Hideki MATSUE, and Tadashi MASAMUNE*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

The structure of a new bromoditerpene named prepinnaterpene, isolated from the title alga, is described.

In a continuing study on components of the alga, we isolated a new bromoditerpene named prepinnaterpene, which is regarded as one of the precursors of a group of bromoditerpenes with a unique skeleton, represented by pinnaterpenes[1] and irieols.[1b,2] We report herein the isolation and structure of this diterpene.

Neutral ether-soluble oil (30.8 g) obtained from the methanol extracts of the title alga (wet, 12 kg), collected at Onahama early in July (1982), was fractionated by chromatography over silica gel with benzene, ethyl acetate (EtOAc), and methanol as eluents. Fractions[3] early eluted with benzene:EtOAc (19:1) were separated by repeated chromatography [(i) column chromatography over silica gel, benzene, (ii) HPLC over Radial Pak Silica, hexane:EtOAc = 98:2 and then = 95:5, and (iii) HPLC over μ-Porasil, hexane:dichloromethane:acetonitrile = 80:18:2 and then = 74:25:1] to give prepinnaterpene (1) (7 mg) and irieol[2,4] (2) (9 mg).

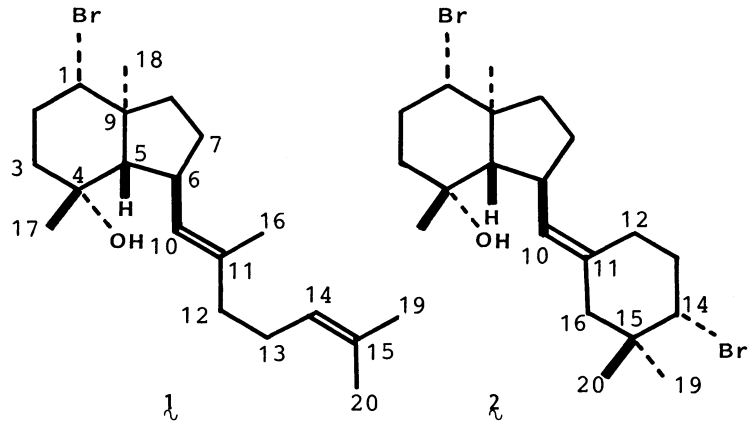
Prepinnaterpene (1), colorless oil, $[\alpha]_D$ -25.2° ($CHCl_3$), had molecular formula $C_{20}H_{33}OBr$ (Found: m/z 368.1695 and 370.1702. Calcd for $C_{20}H_{33}OBr$: M^+, 368.1716 and 370.1696) and exhibited the following spectra: EI-MS, m/z 370, 368, 352, 350, and 69 (base); IR ($CHCl_3$), 3500, 1460, 1395, and 1385 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ 3.99 (1H, dd, J = 4 and 13 Hz, 1β-H), 2.33 (1H, ddt, J = 5, 13, and 14, 2α-H), 1.47 (1H, dt, J = 5 and 14, 3β-H), 1.19 (1H, d, J = 11, 5β-H), 3.01 (1H, ddt, J = 6, 9.5, and 11, 6α-H), 2.05 and 1.23 (each 1H, m, 7β- and 7α-H), 5.10 (1H, br d, J = 9.5, 10-H), 1.97 (2H, t, J = 8, 12-H), 2.06 (2H, dt, J = 7 and 8, 13-H), 5.06 (1H, br t, J = 7, 14-H), 1.59 (3H, br s, 16-H), 1.21 and 1.13 (each 3H, s, 17- and 18-H), 1.66 and 1.64 (each 3H, d, J = 1, 19- and 20-H), and 0.98 (1H, s, OH); ^{13}C NMR ($CDCl_3$, 25.0 MHz) (Table 1). The ^1H NMR spectrum, coupled with spin-decoupling experiments and measurements of the decoupling difference spectra, indicated the presence of the following partial structures: 2 × CH_3-■ (i), HO-■ (ii), ■-CH(Br)CH_2CH_2-■ (iii), $(CH_3)_2$=■=CHCH_2CH_2-■ (iv), and ■-CH(-■)CH(CH_2CH_2-■)CH=■-CH_3 (v). Moreover, the ^{13}C NMR spectrum of 1, compared with that of 2, suggested that 1 would differ from 2 only in the C ring. Indeed, oxidation of 1 and 2 under the same Lemieux-Johnson conditions (OsO_4 and $NaIO_4$ in aqueous THF, room temp, 24 h) afforded the same aldehyde (3), colorless oil, $[\alpha]_D$ +10.2° and 9.8° ($CHCl_3$), in 23 and 54% yields (after purification by HPLC), respectively, which involves the partial structures (i), (ii), (iii), and (v).

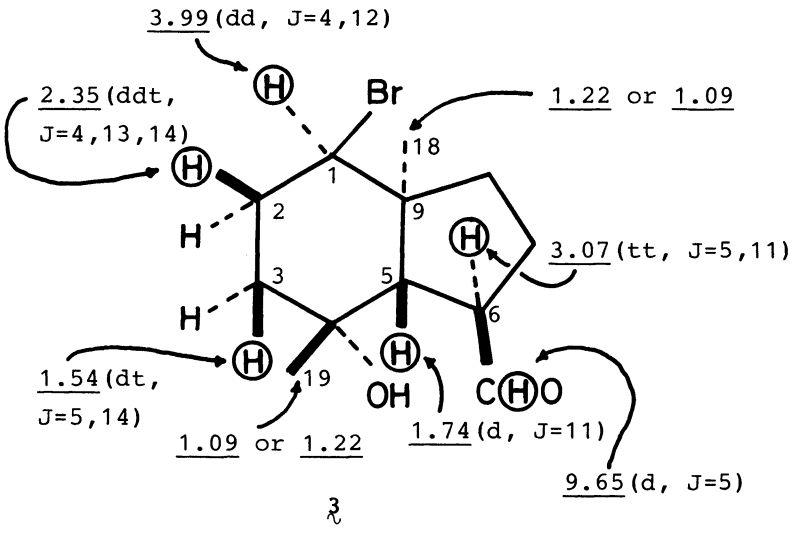
Combination of all the partial structures elucidates the structure of prepinnaterpene as shown in formula 1. The (E) configuration was assigned to the C-10-C-11 double bond by comparison of the chemical shift (Table 1) of C-11, C-12, and C-16 with the calculated values[6] (δ E 131.9, Z 137.3 for C-11; δ E 40.8, Z 33.9 for C-12; δ E 23.5, Z 17.5 for C-16).

Table 1. The ^{13}C NMR spectra

Carbon number	Chemical shift 1[a)]	2
1	65.3 (d)	64.9 (d)
2	31.2 (t)	31.2 (t)
3	40.8 (t)	40.6 (t)
4	71.7 (s)	71.7 (s)
5	60.8 (d)	60.9 (d)
6	36.3 (d)	35.7 (d)
7	28.6 (t)	28.0 (t)
8	42.8 (t)	42.9 (t)
9	47.8 (s)	48.0 (s)
10	132.0 (d)	132.4 (d)
11	132.3 (s)	131.9 (s)
17	30.8 (q)	31.2 (q)
18	16.3 (q)	16.3 (q)
12	39.7 (t)	33.6 (t)
13	26.3 (t)	29.2 (t)
14	124.3 (d)	66.1 (d)
15	132.2 (s)	38.3 (s)
16	25.7 (q)	48.7 (t)
19	16.3 (q)	23.0 (q)
20	17.7 (q)	29.6 (q)

a) Cited from Ref. 2.





3

References

1) a) A. Fukuzawa, Y. Kumagai, T. Masamune, A. Furusaki, T. Matsumoto, and C. Katayama, Chem. Lett., 1982, 1389; b) A. Fukuzawa, M. Miyamoto, Y. Kumagai, A. Abiko, Y. Takaya, and T. Masamune, ibid. (the preceding paper).

2) B. M. Howard and W. Fenical, J. Org. Chem., 23, 4401 (1978).

3) Pinnaterpene A, which had been one of the major components of these fractions (Ref. 1), was not isolated in the present experiment.

4) Irieol, mp 118.5-120 °C, $[\alpha]_D$ -38.9° ($CHCl_3$) [lit.,[2] oil, $[\alpha]_D$ -23.1° ($CHCl_3$)].

5) The abbreviation ■ denotes a quaternary carbon atom.

6) E. Pretsch, T. Clerc, J. Seibl, and W. Simon, "Tabellen zur Structuraufklarung organischer Verbindungen," Springer-Verlag, Berlin (1981), p. C10.

(Received May 27, 1985)