

THREE NEW SESQUITERPENOIDS CONTAINING BROMINE, MINOR CONSTITUENTS  
OF LAURENCIA GLANDULIFERA KÜTZING\*

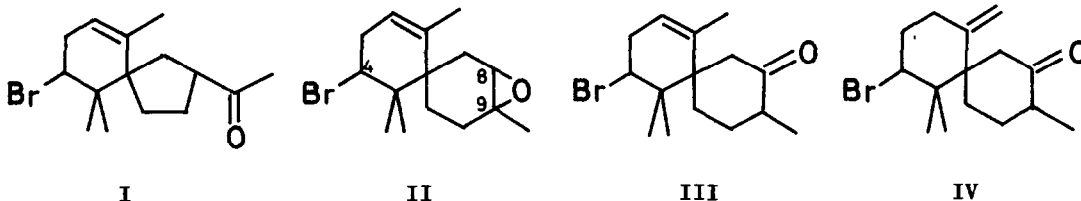
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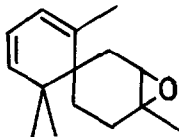
In a previous communication (1), we reported the structure of spiro-laurenone (I), a novel sesquiterpene ketone containing bromine, isolated from the neutral essential oil of Laurencia glandulifera Kützing ("Oosozo" in Japanese; Rhodomelaceae). Further studies searching other bromo-compounds from this alga have led to the isolation of three crystalline new bromine-containing sesquiterpenoids, having the same molecular formula  $C_{15}H_{23}OBr$ , isomeric with spiro-laurenone (I). The present paper describes the structure elucidation of these compounds.



One of the three bromo-sesquiterpenes, melted at  $53-54^{\circ}$ ,  $(\alpha)_D -92^{\circ}$ , was analyzed for  $C_{15}H_{23}OBr$  ( $M^+$  300, 298) (2). The UV, IR and NMR (3) spectra of this compound (II) ( $\lambda_{max}^{EtOH}$  only end absorption;  $\nu_{max}^{CHCl_3}$  1660, 1390, 1372, 1183, 1160, 1130, 1053, 1033, 965 and  $830\text{ cm}^{-1}$ ;  $\tau(CCl_4, 100\text{ MHz})$  9.07 (3H, s), 8.90 (3H, s), 8.75 (3H, s), 8.26 (3H, br. s), 8.02, 7.90 (each 1H, dd,  $J=16$  and 2.0 Hz, AB-type), 7.5 (2H, m), 7.16 (1H, t,  $J=2.0\text{ Hz}$ ), 5.48 (1H, t,  $J=8.0\text{ Hz}$ ) and 4.97 (1H, m)) showed the presence of two tertiary methyls (probably gem

dimethyl), an epoxide methyl ( $-\text{CH}^{\text{O}}\text{CMe}-$ ) and an olefinic methyl ( $-\text{CH}=\text{CMe}-$ ).

Similar in case of spiro-laurenone (I) (1), by the treatment with 1N KOH-EtOH (reflux 30 min), II afforded a conjugated cyclohexadiene (V),  $\text{C}_{15}\text{H}_{22}\text{O}$  ( $\text{M}^+$  218),  $(\alpha)_D +110^\circ$ ;  $\lambda_{\text{max}}^{\text{EtOH}}$  264 nm ( $\epsilon$  2900);  $\nu_{\text{max}}^{\text{CHCl}_3}$  1603, 1385, 1362, 1100 and  $840\text{ cm}^{-1}$ ;  $\tau$  9.04 (3H, s), 8.91 (3H, s), 8.78 (3H, s), 8.30 (3H, br. s), 7.21 (1H, d,  $J=4.0$  Hz), 5.0-4.3 (3H), and no absorption near  $\tau$  5.5.

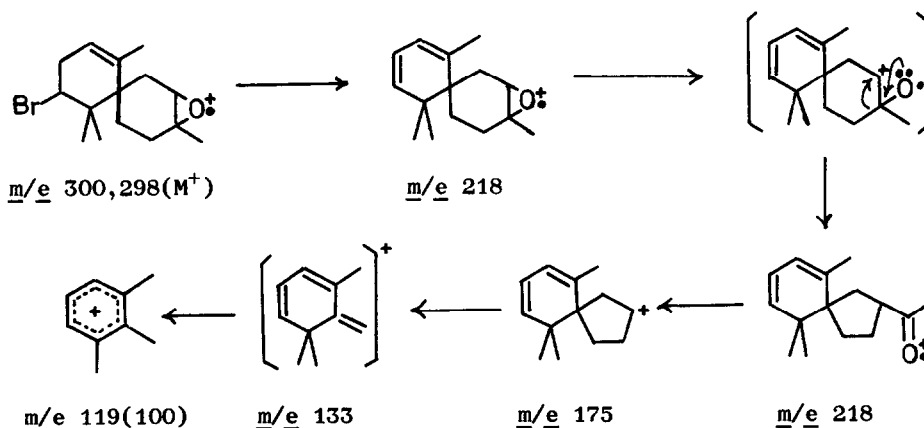


V

Double resonance experiments in the NMR spectrum of II provide additional information of the structure. One-proton triplet at  $\tau$  5.48 could be attributed to the proton on carbon bearing the bromine atom. Irradiation at  $\tau$  5.48 collapses the multiplet at  $\tau$  7.5 to a broad singlet. By irradiation at  $\tau$  7.5, the triplet at  $\tau$  5.48 and the multiplet at  $\tau$  4.97 are simplified to a sharp singlet and to a broad singlet, respectively. Irradiation at  $\tau$  8.26 collapses the multiplet at  $\tau$  4.97 to a triplet ( $J=4.0$  Hz). One-proton triplet at  $\tau$  7.16 is simplified to a sharp singlet by irradiation at ca.  $\tau$  7.9. Conversely, irradiation at  $\tau$  7.16 collapses the AB-type octet at  $\tau$  8.02 and  $\tau$  7.90 to a AB-type double doublet. Above results indicate the presence of  $-\text{CMe}=\text{CH}-\text{CH}_2-\text{CHBr}-$  and  $-\text{CH}_2-\text{CH}^{\text{O}}\text{CMe}-$  groupings in II.

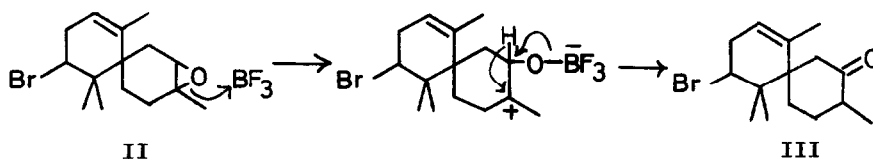
In view of above-mentioned data and the biogenetical considerations, the structure of II would be represented as 4-bromo- $\alpha$ -chamigren-8,9-epoxide. This was also supported by the mass spectra of II ( $\underline{m/e}$  (relative abundance) 300 and 298 ( $\text{M}^+$ , 3), 219 (19), 218 (40), 203 (20), 200 (38), 185 (41), 175 (19), 159 (38), 157 (44), 133 (74), 119 (100), 105 (74), 91 (65), 77 (43) and 69 (51)) and V (218 ( $\text{M}^+$ , 29), 203 (17), 200 (10), 185 (16), 175 (25), 159 (44), 157 (36), 133 (73), 119 (100), 105 (91), 91 (77), 77 (52) and 69 (35)).

The main fragmentations are reasonably explicable by the following scheme;



The second isomeric bromo-compound (III), m.p. 78-79°, ( $\alpha$ )<sub>D</sub> -88°, showed in its UV ( $\lambda_{\text{max}}^{\text{EtOH}}$  284 nm ( $\epsilon$  30)), IR and NMR spectra the presence of a secondary methyl ( $\tau$  9.00 (3H, d,  $J=6.0$  Hz)), two tertiary methyls ( $\tau$  9.13 and 8.80 (each 3H, s)), -CH=CMe- group ( $\nu_{\text{max}}^{\text{CHCl}_3}$  810  $\text{cm}^{-1}$ ;  $\tau$  8.45 (3H, br. s) and  $\tau$  4.9 (1H, m)), an allylic methylene ( $\tau$  7.45 (2H, m)), >CHBr group ( $\tau$  5.47 (1H, dd,  $J=9.7$  and 8.5 Hz)), and six or larger-membered ring ketone ( $\nu_{\text{max}}^{\text{CHCl}_3}$  1703  $\text{cm}^{-1}$ ). Moreover, two-proton singlet at  $\tau$  7.68 revealed the presence of a methylene group adjacent to both a quaternary carbon and the carbonyl group (4). These spectral data, NMR studies and mass spectrum ( $\underline{m/e}$  (rel. abundance): 300 and 298 ( $M^+$ , 15), 219 (100), 218 (22), 201 (42), 177 (50), 175 (14), 164 (56), 147 (55), 133 (45), 119 (46), 105 (55), 91 (53), 77 (42), 69 (89) and 55 (54)) suggested that III would have cyclohexene ring moiety as same as spiro-laurenone (I) and 4-bromo- $\alpha$ -chamigren-8,9-epoxide (II).

Treatment of II with  $\text{BF}_3$ -etherate in benzene at room temperature led to the formation of a rearranged product (about 50% yield), which was identified as natural ketone (III) by the mixed m.p. and by a comparison of the IR ( $\text{CHCl}_3$ ) and optical rotation with those of an authentic specimen.



From both this transformation and the spectral data, the structure of III would be represented as 4-bromo- $\alpha$ -chamigren-8-one.

The third isomer (IV), m.p. 114-116 $^{\circ}$ ,  $(\alpha)_D -57^{\circ}$ , exhibited in its IR spectrum absorption maxima at  $\nu_{\max}^{\text{CHCl}_3}$  1635 and 870  $\text{cm}^{-1}$  characteristic of terminal methylene group and at  $\nu_{\max}^{\text{CHCl}_3}$  1703  $\text{cm}^{-1}$  due to cyclohexanone. The NMR spectrum displayed the signals comparable to those of III at the higher magnetic field region ( $\tau$  9.05 (3H, d,  $J=6.0$  Hz), 9.02 (3H, s), 8.81 (3H, s), 7.65 (2H, br. s) and 5.48 (1H, dd,  $J=11.6$  and 5.1 Hz)) except the absence of signals due to an olefinic methyl and an allylic methylene groups. In the lower field region, however, the distinct difference was observed: e.g., in the spectrum of IV, absorptions due to two olefinic protons (terminal methylene protons) appeared at  $\tau$  5.30 and  $\tau$  5.01 (each 1H, s), instead of one-proton multiplet at  $\tau$  4.9 in the spectrum of III. The fragmentations in the mass spectrum of IV were found to correspond with those of III. On the basis of the above-mentioned spectral data compared with those of III and the standpoint of biogenesis (co-occurrence of III and IV), the structure of IV could be assigned to 4-bromo- $\beta$ -chamigren-8-one.

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#### References

- \* Part XXIV of "Constituents from Marine plants." Part XXIII, A. Furusaki, E. Kurosawa, A. Fukuzawa and T. Irie, Tetrahedron Letters, 4579 (1973).
- (1) M. Suzuki, E. Kurosawa and T. Irie, Tetrahedron Letters, 4995 (1970).
  - (2) Acceptable elemental analyses were obtained for all natural products.
  - (3) The NMR measurements were taken in  $\text{CCl}_4$  on Hitachi H-60 spectrometer with TMS as an internal reference, unless otherwise stated.
  - (4) Cf. N. S. Bhacca and D. H. Williams, "Application of NMR spectroscopy in organic chemistry," Holden-Day, San Fransisco (1964).