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α-BROMOCUPARENE AND α-ISOBROMOCUPARENE, NEW BROMO COMPOUNDS FROM LAURENCIA SPECIES [*]

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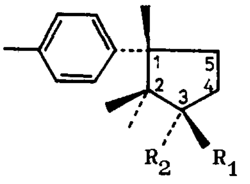
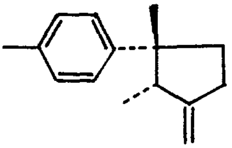
In recent years, the brominated or non-brominated laurane-type sesquiterpenoids have been isolated from seaweeds of genus Laurencia (1-4). Our further investigations of neutral essential oil from Laurencia species have led to the isolation of two new bromo compounds, α-bromocuparene (I) and α-isobromocuparene (II) from L. glandulifera Kützing, and II from L. nipponica Yamada, on the chromatography over neutral alumina with n-hexane. The compounds, I and II, appeared to be the first recognized cuparane-type sesquiterpenoid from seaweeds and the former seems to be the biogenetical precursor of laurene (III) (1), closely related to cuparane-type sesquiterpenoids.



I; R_1=Br, R_2=H
II; R_1=H, R_2=Br
IV; R_1=H, R_2=OH
V; R_1=OH, R_2=H



III

α-Bromocuparene (I). oil, $(\alpha)_D$ +23.0°(c, 0.95; $CHCl_3$); $C_{15}H_{21}Br$, m/e 282 and 280 (M^+), and 201 (M^+-Br); ν_{max} 1510, 1455, 1390, 1375, 1280, 1250, 1190, 1150, 1120, 1075, 1020, 830 and 815 cm^{-1}. The NMR spectrum displayed signals due to four methyl groups at δ 0.61 (3H, s), 1.08 (3H, s), 1.42 (3H, s) and 2.30 (3H, s), proton on carbon bearing bromine at 3.96 (1H, q, J=9.5, 8.5 Hz), and aromatic protons at 6.98 (4H, s).

α-Isobromocuparene (II). oil, $(\alpha)_D$ +91.0°(c, 0.87; $CHCl_3$); $C_{15}H_{21}Br$, m/e 282 and 280 (M^+), and 201 (M^+-Br); ν_{max} 1510, 1460, 1380, 1285, 1120, 1095, 1070, 1020, 900, 860 and 820 cm^{-1}. The NMR spectrum displayed signals due to four methyl groups at 0.63 (3H, s), 1.10 (3H, s), 1.29 (3H, s) and 2.32 (3H, s), proton on carbon bearing bromine at 4.36 (1H, dd, J=9.0, 9.0), and aromatic protons at 7.08 (4H, m).

The structures of I and II were confirmed by the bromination of α-isocuparenol (IV) and α-cuparenol (V) (5), respectively, whose absolute stereostructures have been definitely decided. Treatment of IV with CBr_4-$P(C_6H_5)_3$ in CH_2Cl_2 afforded monobromo compound which was identical with I in all respects, and similarly II was derived from V by the same procedure as I. The configurations at C-3 in I and II were concluded by comparison of the chemical shifts of methyl group at C-1 and proton at C-3 in the NMR spectra (Table 1).

Table 1. The chemical shifts (δ-value) of C-1 methyl and C-3 proton in I, II, IV and V.

	C-1 Me	C-3 H
α-bromocuparene (I)	1.42	3.96
α-isobromocuparene (II)	1.29	4.36
α-isocuparenol (IV)	1.19	4.00
α-cuparenol (V)	1.30	3.70

A 1,3-cis relationship between methyl group at C-1 and bromine at C-3 in I is strongly suggested, in the same way as V compared with IV, by the down field shift (0.13 ppm, compared with II) of methyl group which is caused by the 1,3-cis interaction of bromine, and consequently the high field shift (0.40 ppm, compared with II) of proton at C-3 could be ascribed to the magnetic anisotropy of benzene ring at C-1. From these observations, the absolute stereostructures of α-bromocuparene and α-isobromocuparene should be represented in terms of I and II, respectively.

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