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# STRUCTURE REVISION OF OKAMURALLENE AND STRUCTURE ELUCIDATION OF FURTHER $C_{15}$ NON-TERPENOID BROMOALLENES FROM *LAURENCIA INTRICATA**

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**Key Word Index**—*Laurencia intricata*; Rhodomelaceae; red alga; C-15 non-terpenoid; bromoallene; okamurallene; deoxyokamurallene; isookamurallene.

**Abstract**—The structures of okamurallene and related metabolites, which have previously been isolated from the red alga *Laurencia intricata*, have been revised. In addition, two new $C_{15}$ non-terpenoid bromoallenes with a halohydrin moiety have also been obtained, and their structures determined by chemical and spectroscopic methods.

## INTRODUCTION

In the course of our studies on the constituents of the Japanese red alga *Laurencia okamurai* Yamada [1], we reported [2] that a specimen collected early in August 1979 at Bikuni, Hokkaido, contained laurinterol and debromolaurinterol, typical rearranged cuparane-type sesquiterpenes, as major metabolites (20 and 10% of the extract, respectively). Furthermore, this specimen contained four unique $C_{15}$ non-terpenoids, okamurallene (**1**) [2], deoxyokamurallene (**2**) [3] and isookamurallene (**3**) [3] and neolaurallene (**4**) [4], as minor metabolites. However, examination of a specimen of *L. okamurai* collected at the same location early in August 1982 showed that laurinterol and debromolaurinterol were minor metabolites (4%) and that the $C_{15}$ non-terpenoids were the major metabolites (15%). The discrepancy was resolved when it was shown that the samples collected in 1979 and 1982 represent two *Laurencia* species, *L. okamurai* Yamada and *L. intricata* Lamouroux, respectively.

Freshly collected *L. okamurai* contained two sesquiterpenes, laurinterol and debromolaurinterol as the major metabolites. On the other hand, freshly collected *L. intricata* contained a trace of both sesquiterpenes and a large quantity of $C_{15}$ non-terpenoids. Furthermore, the major metabolite of this species was found to be a triterpene alcohol, the structure of which had not been determined. In this paper, we describe the structure revision of okamurallene (**1**) and the related metabolites **2** and **3** as well as the isolation and structure elucidation of two new $C_{15}$ non-terpenoids, **5** and **6**, both of which possess a halohydrin moiety.

## RESULTS AND DISCUSSION

In previous papers [2, 3] formulae **1′**, **2′** and **3′** have been proposed for okamurallene, deoxyokamurallene and isookamurallene, respectively, on the basis of spectroscopic data. However, the stereochemical and connectivity relationships, in addition to the presence of a cyclopropane ring, have remained, in part, ambiguous. Thus, in order to clarify this ambiguity, further structural analysis of okamurallene (**1**) has been carried out by means of 2D-NMR and NOE difference techniques.

A $^1H$–$^{13}C$ shift-correlated 2D-NMR spectrum of okamurallene (**1**) indicated that our initial assignments [2] for the epoxide carbons are incorrect and should be reversed. Two different 2D-INADEQUATE spectra [5, 6] of okamurallene (90 mg) were measured in $CDCl_3$ using propagation times ($\tau = 1/4J_{cc}$) of 25 msec and 7.1 msec optimized for $J_{cc} = 10$ Hz and $J_{cc} = 35$ Hz, respectively. The results gave correlation peaks for all of the $^{13}C$–$^{13}C$ pairs except for those between C-1 and C-2, C-2 and C-3, C-8 and C-9, and C-9 and C-10, and established the partial sequences shown in Fig. 1. The existence of a six-carbon unit containing 1,2-disubstituted cyclopropane and oxirane rings was unambiguously confirmed, but, contrary to our expectation, the methylene carbon at $\delta$ 40.8 was not connected to the quaternary carbon at $\delta$ 91.2 but to the methine carbon at $\delta$ 83.6, thus indicating that the proposed formula (**1′**) for okamurallene is incorrect and should be revised. Furthermore, as described previously [2], in the 200 MHz $^1H$ NMR spectrum ($CDCl_3$) the signal due to one of the methylene protons at C-5, which overlapped with that of the cyclopropyl methine proton at C-10, was observed at about $\delta$ 1.9 as a complex multiplet. However, in the 500 MHz $^1H$ NMR spectrum ($CDCl_3$) those signals were slightly resolved, and the $^1H$–$^1H$ 2D-COSY spectrum indicated that one of the methylene protons at about $\delta$ 1.9 is further coupled to the methine proton at $\delta$5.06. This was further supported by the measurements obtained in $C_6D_6$, the results of which revealed that the overlapped signals are well resolved and all protons can be assigned as shown in Table 1. These

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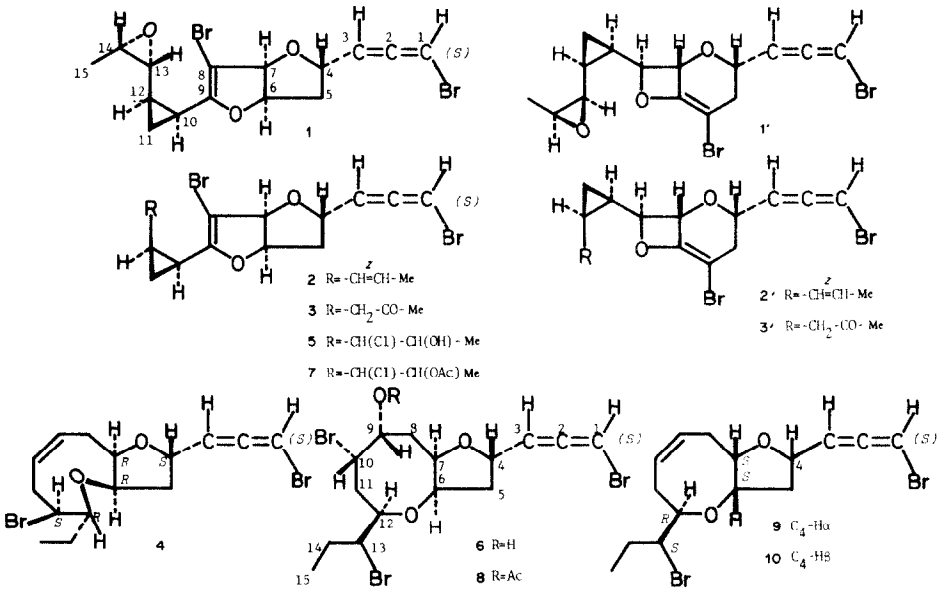

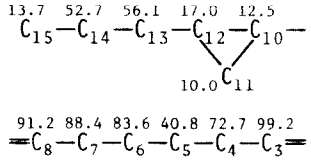

Fig. 1. Partial sequences of C atoms.

data unequivocally showed that the planar structure of okamurallene should be revised to formula **1**.

The relative stereochemistry of the eight chiral centres was partly determined as follows. Since the splitting patterns of the protons at C-4, C-5, C-6 and C-7 are very similar to those of the $C_{15}$-bromoallenes with a 2,6-dioxabicyclo [3.3.0] octane skeleton [1, 7], the bromoallenic side chain in **1** is in the *exo*-configuration. This was further supported by NOE experiments. The NOESY and NOE difference spectra provided all of the stereochemical relationships except for the configuration between C-3/C-4 and C-12/C-13, leading to formula **1** for okamurallene (Fig. 2). Therefore, the structures of deoxyokamurallene and isookamurallene should also be revised to formulae **2** and **3**, respectively. In view of the strong positive rotations of **1**–**3**, the absolute configuration of the bromoallene moiety in each of these compounds was assigned as *S* by application of Lowe's rule [8].

One of the new metabolites, compound **5**, had a molecular formula $C_{15}H_{17}O_3Br_2Cl$. Its IR spectrum showed hydroxyl absorption at 3444 $cm^{-1}$ and no carbonyl absorption. Treatment of **5** with acetic anhydride and pyridine gave the corresponding acetate **7**, $C_{17}H_{19}O_4Br_2Cl$; $\nu_{max}$ 1740 and 1238 $cm^{-1}$; $\delta$ 2.02 (3H, *s*). The $^1H$ NMR spectra (Table 1) of **5** and **7** were

Table 1. $^1H$ NMR data for compounds **1**, **5** and **7** (270 MHz, in $C_6D_6$, TMS as int. standard.)

| C | 1 | 5 | 7 |
|---|---|---|---|
| 1 | 5.58 *dd* (5.8, 1.5) | 5.55 *dd* (5.8, 1.8) | 5.53 *dd* (5.9, 1.8) |
| 3 | 5.10 *dd* (5.8, 5.8) | 5.19 *dd* (5.8, 5.8) | 5.17 *dd* (5.9, 5.9) |
| 4 | 4.2 *m* | 4.71 *m* | 4.70 *m* |
| 5 | 1.19 *ddd* (13.5, 10.6, 5.8) Hα | 1.31 *m* Hα | 1.33 *ddd* (13.9, 11.0, 6.2) Hα |
| | 1.72 *dd* (13.5, 4.7) Hβ | 1.88 *dd* (13.7, 4.8) Hβ | 1.93 *dd* (13.9, 4.8) Hβ |
| 6 | 4.23 *dd* (6.2, 5.8) | 4.24 *dd* (6.6, 6.6) | 4.25 *dd* (6.6, 6.2) |
| 7 | 4.94 *d* (6.2) | 5.00 *d* (6.6) | 5.00 *d* (6.6) |
| 10 | 1.59 *ddd* (8.4, 8.4, 5.8) | 1.81 *ddd* (8.4, 8.4, 5.8) | 1.82 *ddd* (8.4, 8.4, 5.8) |
| 11 | 0.62 *ddd* (8.4, 8.4, 4.8) Hα | 0.52 *ddd* (8.4, 8.4, 4.8) Hα | 0.54 *ddd* (8.4, 8.4, 5.1) Hα |
| | 1.10 *m* Hβ | 0.77 *ddd* (5.8, 5.8, 4.8) Hβ | 0.79 *ddd* (5.8, 5.8, 5.1) Hβ |
| 12 | 0.80 *dddd* (8.4, 8.4, 5.9, 5.8) | 1.25 *m* | 1.15 *m* |
| 13 | 2.71 *dd* (5.9, 4.0) | 3.70 *dd* (11.0, 5.1) | 3.90 *dd* (11.0, 5.1) |
| 14 | 2.79 *dq* (4.0, 5.5) | 3.59 *m* | 5.17 *m* |
| 15 | 1.13 *d* (5.5) | 1.03 *d* (6.2) | 1.14 *d* (6.2) |
| | | | 1.68 *s* OAc |

*J* in Hz in parenthesis.

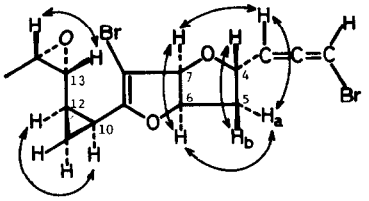

Fig. 2. NOE (⟵⟶).

very similar to that of okamurallene (**1**) except for the signals due to the protons at C-13 and C-14, thus indicating that **5** has the same carbon framework as **1**. This was further supported by the $^{13}C$ NMR spectrum (Table 2) of **7**, which was also very similar to that of **1** except for the signals due to C-10–C-15 in addition to those of acetoxyl group. The above results coupled with the $^1H$–$^1H$ and $^1H$–$^{13}C$ 2D-COSY spectra showed that the structure of compound **5** must be represented by formula **5**. This was confirmed by the following reaction. Treatment of the acetate **7** with potassium carbonate in methanol gave okamurallene (**1**).

Another new metabolite, compound **6**, $C_{15}H_{21}O_3Br_3$, showed in its $^1H$ NMR spectrum the presence of a bromoallenic side chain and seven protons on the carbons bearing a hetero atom. Acetylation of **6** with acetic anhydride and pyridine gave the corresponding acetate **8**, $C_{17}H_{23}O_4Br_3$, $\nu_{max}$ 1735 and 1238 $cm^{-1}$; $\delta$ 2.07 (3H, *s*), which generated the original alcohol on mild saponification with potassium carbonate in methanol. The $^1H$–$^1H$ 2D-COSY spectra of **6** and **8** provided the partial formula shown in Fig. 3. As judged from the chemical shift ($\delta$ 60.0) of the carbon at C-13 in the $^{13}C$ NMR spectrum of **8**, the hetero atom on C-13 is not an oxygen atom but a bromine atom. The $^1H$ NMR spectra of **6** and **8** contained no signals due to methine protons on an oxirane ring [9] or to methylene protons on a 1,2-disubstituted oxetane ring [10, 11]. Moreover, comparisons of the $^1H$ and $^{13}C$ NMR data of **6** and **8** with those of laurallene (**9**) [12], epilaurallene (**10**) [13], neolaurallene (**4**) [4] and isolaurallene [14] indicated that compound **6** has the same 2,6-dioxabicyclo[6.3.0]undecane skeleton as **9** and **10** and this leads to the planar formula **6**. The relative configurations, except for those between C-3/C-4 and C-12/C-13, were determined by NOE difference spectra on the $^1H$ NMR spectrum of **8** (Fig. 4). Furthermore, NOE experiments indicated that the oxocane ring in compounds **6** and **8** adopts the conformation depicted in Fig. 4. In the $^1H$ NMR spectra of **6** and **8**, the signals of H-9 ($\delta$ 4.39 and $\delta$ 5.49, respectively) appear in a considerably low field region. These low field chemical shifts are due to deshielding caused by the oxocane oxygen atom which is situated close to H-9. Accordingly, the structure of **6** must be represented by formula **6**, in which the absolute configuration of the bromoallene moiety was assigned by application of Lowe's rule [8].

The structure of the major metabolite is currently under investigation.

Table 2. $^{13}C$ NMR data for compounds **1** and **7** (67.9 MHz, in $C_6D_6$, TMS as int. standard.)

| C | 1 | 7 |
|---|---|---|
| 1 *d* | 73.8 | 73.9 |
| 2 *s* | 202.5 | 202.4 |
| 3 *d* | 99.7 | 99.8 |
| 4 *d* | 72.6 | 72.6* |
| 5 *t* | 40.7 | 40.8 |
| 6 *d* | 83.6 | 83.9 |
| 7 *d* | 88.3 | 88.2 |
| 8 *s* | 91.6 | 92.8 |
| 9 *s* | 157.7 | 156.6 |
| 10 *d* | 12.6 | 14.0 |
| 11 *t* | 9.8 | 12.6 |
| 12 *d* | 17.4 | 23.7 |
| 13 *d* | 55.3 | 64.3 |
| 14 *d* | 53.0 | 72.7* |
| 15 *q* | 13.7 | 17.2 |
| *s* | | 169.4† |
| *q* | | 20.5† |

* Assignments may be reversed.

† OAc.

## EXPERIMENTAL

$^1H$ NMR: 270 MHz, TMS as int. standard; LRMS and HRMS: 70 eV; CC: silica gel (Merck, Kieselgel 60, 70–230 mesh); TLC: silica gel $60F_{254}$ (Merck).

*Collection.* The *Laurencia intricata* Lamouroux samples were collected during 1983–1988 (early August) at Bikuni, Hokkaido. The extracts of the algal samples gave almost identical patterns on TLC.

*Isolation.* Half-dried alga (*L. intricata*, collected in 1986) (90 g) was extracted with MeOH, and the neutral MeOH extract (1 g) obtained by conventional methods was fractionated by CC. The early $C_6H_6$ fraction gave deoxyokamurallene (**2**) (10 mg) by further TLC. The next $C_6H_6$ fraction yielded neolaurallene (**4**) (30 mg) by further CC. The last $C_6H_6$ fraction consisted of a mixture of $C_{15}$ non-terpenoids and triterpene alcohols, which was further subjected to repeated CC and TLC to give okamurallene (**1**) (70 mg), compound **5** (10 mg) and crude **6** (3 mg) which was purified via its acetate.

*Compound* **5**. Mp 71–72° ($Et_2O$–hexane); $[\alpha]_D^{18}$ + 205° ($CCl_4$; *c* 0.328); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3444, 3060, 1961, 1656, 1365, 1351, 1313, 1281, 1245, 1226, 1199, 1183, 1141, 1110, 1049, 1035, 1005, 991, 938, 900, 863, 831, 738 and 660; MS *m/z*: (rel. int.): 444, 442, 440, 438 $[M]^+$ (0.7:4.2:6.0:2.6), 406, 404, 402 $[M-HCl]^+$ (0.8:1.6:0.8), 363, 361, 359 $[M-Br]^+$ (0.5:2.2:1.6), 325, 323, 321 $[M-C_3H_2Br]^+$ (2.0:3.2:1.5), 305 (2.0), 279 (2.4), 265 (2.1), 257 (2.4), 255 (2.7), 239 (5.7), 237 (5.6), 229 (5.0), 227 (6.9), 203 (6.0), 201 (9.4), 199 (6.2), 187 (5.3), 185 (6.4), 161 (6.5), 159 (6.7), 133 (7.0), 125 (5.2), 119 (12), 117 (8.4), 115 (7.1), 107 (5.5), 105 (7.5), 97 (6.0), 95 (5.4), 91 (13), 89 (7.1), 83 (5.5), 81 (9.2), 79 (8.2), 78 (8.3), 77 (12), 67 (8.1), 65 (12), 55 (12), 53 (9.0), 51 (12), 45 (46), 43 (100), 41 (8.0) and 39 (20). HRMS *m/z*: 439.9197. Calc. for $C_{15}H_{17}O_3{}^{79}Br{}^{79}Br{}^{35}Cl$: 439.9205.

*Compound* **6**. Oil; $[\alpha]_D^{21}$ + 95.8° ($CHCl_3$; *c* 0.600); IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3560, 3440, 3060, 1955, 1381, 1332, 1315, 1282, 1191, 1103, 1087, 1062, 1020 and 897: $^1H$ NMR ($CDCl_3$): $\delta$ 1.09 (3H, *t*, *J* = 7.3 Hz, $H_3$-15), 1.76 (1H, *m*, H-14), 2.00 (1H, *m*, H-14), 2.05 (1H, *m*, H-5), ~ 2.1 (1H, *m*, H-8), 2.23 (1H, *m*, H-5), 2.50 (2H, *br t*, *J* = 4.7 Hz, H-11), 2.55 (1H, *m*, H-8), 3.77 (1H, *m*, H-12), 3.85 (1H, *m*, H-13), 4.08–4.16 (2H, *m*, H-6 and H-7), 4.39 (1H, *br dd*, *J* = 6.6, 6.6 Hz, H-9), 4.71 (1H, *ddd*, *J* = 5.4, 5.4, 1.1 Hz, H-10), 4.82 (1H, *m*, H-4), 5.45 (1H, *dd*, *J* = 5.5, 5.5, H-3) and 6.10 (1H, *dd*, *J*

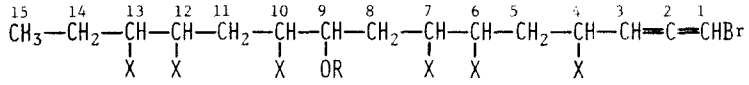

Fig. 3. Partial structure (X = Br or O; R = H or Ac).

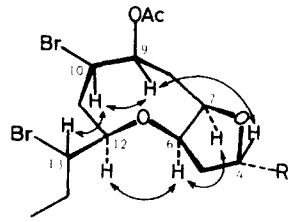

Fig. 4. NOE (⟷).

= 5.5, 1.5 Hz, H-1); MS *m/z*: 474, 472, 470, 468 $[M-H_2O]^+$ (0.3:1.1:1.1:0.3), 410, 408, 406 $[M-HBr]^+$ (0.3:0.6:0.4), 392, 390, 388 $[M-H_2O-HBr]^+$ (0.9:1.8:1.0), 372, 370, 368 $[M-C_3H_2Br]^+$ (18:39:18), 273 (14), 271(22), 191 (40), 189 (12), 165 (34), 163 (13), 161 (11), 149 (10), 147 (19), 127 (14), 123 (13), 121 (19), 119 (15), 111 (26), 109 (34), 107 (20), 105 (16), 99 (12), 95 (30), 93 (18), 91 (14), 85 (31), 83 (46), 82 (11), 81 (99), 80 (11), 79 (32), 78 (22), 77 (28), 71 (41), 69 (30), 67 (53), 66 (22), 65 (42), 57 (58), 55 (100), 53 (28), 45 (17), 43 (60), 41 (88) and 39 (56); HRMS *m/z*: 470.8979. Calc. for $C_{15}H_{20}O_2{}^{79}Br^{79}Br^{81}Br$ $[M-OH]$: 470.8975.

*Acetylation of* **5**. Acetylation of **5** (2 mg) was carried out with $Ac_2O$ (0.1 ml) and pyridine (0.1 ml) at room temp. in the usual manner to give the corresponding acetate **7** in almost quantitative yield.

*Compound* **7**. Mp 85–86° ($C_6H_{14}$); $[\alpha]_D^{18}$ + 203° ($CCl_4$; *c* 0.443); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3050, 1964, 1740, 1658, 1373, 1344, 1315, 1281, 1269, 1238, 1202, 1186, 1114, 1083, 1055, 1035, 1000, 985, 966, 952, 905, 862, 842, 759, 724 and 657; MS *m/z*: 486, 484, 482, 480 $[M]^+$ (0.4:2.2:3.1:1.4), 405, 403, 401 $[M-Br]^+$ (0.3:1.1:0.8), 367, 365, 363 $[M-C_3H_2Br]^+$ (0.2:0.8:0.6), 345, 343, 341 $[M-Br-HOAc]^+$ (0.6:2.3:1.8), 307, 305, 303 $[M-C_3H_2Br-HOAc]^+$ (2.6:5.2:2.9), 227 (3.3), 225 (4.3), 223 (3.1), 161 (3.9), 159 (3.9), 145 (3.8), 119 (3.5), 117 (3.9), 115 (5.6), 105 (4.7), 91 (5.2), 89 (4.2), 81 (4.3), 79 (4.6), 78 (4.0), 77 (6.0), 71 (3.4), 67 (5.2), 65 (5.9), 55 (7.3), 53 (4.8), 51 (5.2), 44 (48) and 43 (100); HRMS *m/z*: 479.9357. Calc. for $C_{17}H_{19}O_4{}^{79}Br^{79}Br^{35}Cl$: 479.9340.

*Conversion of* **7** *into okamurallene* (**1**). To a soln of **7** (3 mg) in MeOH (0.5 ml) was added $K_2CO_3$ (10 mg). The mixture was stirred at room temp. for 70 min and then worked-up in the usual manner. The resulting oil was subjected to TLC to give a colourless gum (2 mg), $[\alpha]_D^{18}$ + 190° ($CHCl_3$; *c* 0.214), whose spectral data were consistent with those of okamurallene (**1**).

*Acetylation of* **6**. Acetylation of **6** (4 mg) was carried out with $Ac_2O$ (0.2 ml) and pyridine (0.2 ml) in the usual manner to afford the acetate **8** in almost quantitative yield.

*Compound* **8**. Oil; $[\alpha]_D^{17}$ + 134° ($CHCl_3$; *c* 1.01); IR $\nu_{max}^{film}$ $cm^{-1}$: 3060, 1953, 1735, 1370, 1319, 1284, 1238, 1198, 1105, 1088, 1069, 1045, 1032 and 999; $^1H$ NMR ($CDCl_3$): $\delta$ 1.09 (3H, *t*, *J* = 7.0 Hz, $H_3$-15), 1.77 (1H, *m*, H-14), 1.95 (1H, *m*, H-14), 2.05 (1H, *m*, H-5$\alpha$), 2.07 (3H, *s*, Ac), 2.13 (1H, *br dd*, *J* = 14.5, 5.8 Hz, H-8), 2.28 (1H, *ddd*, *J* = 13.8, 6.6, 0.7 Hz, H-5$\beta$), 2.32 (1H, *ddd*, *J* = 15.0, 5.8, 1.8 Hz, H-11), 2.61 (1H, *ddd*, *J* = 15.0, 7.3, 4.8 Hz, H-11), 2.67 (1H, *ddd*, *J* = 14.5, 7.3, 1.8 Hz, H-8), 3.80 (1H, *m*, H-12), 3.85 (1H, *m*, H-13), 4.04 (1H, *m*, H-7), 4.19 (1H, *br dd*, *J* = 3.3, 3.3 Hz, H-6), 4.69 (1H, *m*, H-10), 4.86 (1H, *m*, H-4), 5.44 (1H, *dd*, *J* = 5.5, 5.5 Hz, H-3), 5.49 (1H, *br d*, *J* = 7.7 Hz, H-9) and 6.09 (1H, *dd*, *J* = 5.5, 1.5 Hz, H-1); $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ 201.8 (*s*, C-2), 170.2 (*s*, Ac), 101.9 (*d*, C-3), 82.0 (*d*, C-6), 79.2 (*d*, C-12), 78.4 (*d*, C-7), 74.4 (*d*, C-4), 74.0 (*d*, C-1), 70.3 (*d*, C-9), 60.4 (*d*, C-13), 57.1 (*d*, C-10), 40.3 (*t*, C-11), 40.0 (*t*, C-5), 32.9 (*t*, C-8), 27.0 (*t*, C-14), 21.3 (*q*, Ac) and 12.4 (*q*, C-15); MS *m/z*: 453, 451, 449 $[M-Br]^+$ (0.2:0.4:0.2), 415, 413, 411 $[M-C_3H_2Br]^+$ (7:14:8), 355, 353, 351 $[M-C_3H_2Br-HOAc]^+$ (2:4:2), 273, 271 $[M-C_3H_2Br-HOAc-HBr]^+$ (15:16), 191 $[M-C_3H_2Br-HOAc-2\times HBr]^+$ (12), 109 (12), 107 (10), 81 (39), 79 (11), 77 (10), 67 (13), 65 (12), 55 (18), 43 (100), 41 (18) and 39 (10); HRMS *m/z*: 412.9771. Calc. for $C_{14}H_{21}O_4{}^{79}Br^{81}Br$ $[M-C_3H_2Br]$: 412.9787.

*Saponification of* **8**. A soln of **8** (7 mg) and $K_2CO_3$ (10 mg) in MeOH (0.5 ml) was stirred at room temp. for 20 min and then worked-up in the usual manner. The crude product was purified by TLC to afford **6** (5 mg), whose spectral data were identical with those of the natural **6**.

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