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(5*S*,7*R*,10*R*)-SELIN-4(14)-EN-5α-OL, A SESQUITERPENE ALCOHOL FROM THE RED ALGA *LAURENCIA NIPPONICA**

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Key Word Index—*Laurencia nipponica*; Rhodomelaceae; red alga; sesquiterpene alcohol; halochamigrene derivatives; C-15 non-terpenoid.

Abstract—A new sesquiterpene alcohol isolated from the red alga *Laurencia nipponica* has been characterized as (5*S*,7*R*,10*R*)-selin-4(14)-en-5α-ol by spectral and chemical methods.

INTRODUCTION

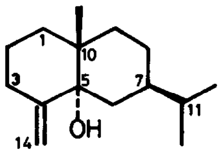
Specimens of *Laurencia nipponica* Yamada collected at various locations in the warm and cold current regions of Hokkaido contain diverse terpenoid and non-terpenoid C-15 metabolites [1–4]. The major components from the specimens collected in the warm current regions (Japan Sea) are composed of halogenated C-15 non-terpenoids with the exception of Atsuta's specimen [1]. As part of our studies on the constituents of specimens grown in Northern Hokkaido [4], belonging to the warm current region, we have sampled at Rumoi, Tomamae, Shosanbetsu (near Haboro) and Bakkai (near Wakkanai). Contrary to our expectations, the specimens collected at the last three locations contained as major metabolites the same halogenated sesquiterpenoids, prepacifenol [5] and pacifenol [6], as those specimens collected at several locations [K. Kurata, unpublished work; 7], on the Pacific Coast of Hokkaido which belongs to the cold current region. On the other hand, Rumoi's specimen contained the halogenated C-15 non-terpenoids laureatin and isolaureatin [8, 9] as the major metabolites. In this paper we describe the isolation and characterization of a new sesquiterpene alcohol, (5*S*,7*R*,10*R*)-selin-4(14)-en-5α-ol (**1**), along with known metabolites.

RESULTS AND DISCUSSION

The sesquiterpene alcohol **1**, colourless oil, $[\alpha]_D^{20}$ +97.2° (*c* 3.01; $CHCl_3$), was analysed for $C_{15}H_{26}O$ by HR-MS. Its IR and ^1H NMR spectra showed the presence of an isopropyl group [ν_{max} 1382 and 1363 cm^{-1}; δ0.90 (3H, *d*, $J = 6.5$ Hz) and 0.92 (3H, *d*, $J = 6.5$ Hz)], a tertiary methyl group [δ0.90 (3H, *s*)], an exomethylene group [ν_{max} 1645 and 895 cm^{-1}; δ4.67 (1H, *dd*, $J = 1.7$ and 1.7 Hz) and 4.77 (1H, *dd*, $J = 1.7$ and 1.7 Hz)] and a hydroxyl group [ν_{max} 3450 and 1155 cm^{-1}]. The tertiary nature of the hydroxyl group was indicated by its resistance to acetylation with acetic anhydride and pyridine. Furthermore, the ^{13}C NMR spectrum showed that there was no double bond present, apart from the one in the exomethylene group, and hence **1**, having three degrees of unsaturation, had to be a bicyclic sesquiterpene alcohol.

Treatment of **1** with *p*-toluenesulphonic acid in refluxing benzene gave (+)-δ-selinene (**2**) [10, 11] in 71 % yield. Thus, both the eudesmane skeleton for **1** and the absolute configuration at C-10 were established. In view of the aforementioned data, two formulae **1** and **3**, the configurations at C-5 and C-7 of which remained unsettled, could be proposed as possible structures for this sesquiterpene alcohol. Placement of the hydroxyl group at C-5 and the stereochemistries at C-5 and C-7 was deduced from the LIS ^1H NMR spectra [in the presence of shift reagent, $Eu(dpm)_3$] as follows.

In the normal ^1H NMR spectrum, irradiation at δ4.72 collapsed the multiplet at δ2.60 to a double double doublet with coupling constants 13, 13 and 6.5 Hz. Conversely irradiation at δ2.60 collapsed two double doublets at δ4.77 and 4.67 to doublets ($J = 1.7$ Hz) respectively. This fact established that the signal at δ2.60 was ascribable to the axial proton at C-3. In the LIS ^1H NMR spectra, the signal at δ2.60 was largely shifted, whereas those of the methyl group at C-10 and the isopropyl group at C-7 were slightly shifted, thus indicat-



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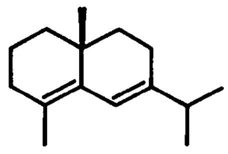

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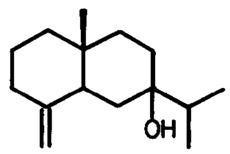

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*Part 60 in the series "Constituents of Marine Plants". For Part 59 see Suzuki, M., Kurosawa, E., Furusaki, A., Katsuragi, S. and Matsumoto, T. (1984) *Chem. Letters* 1033.

ing that the hydroxyl group was attached to C-5 (not C-7). Furthermore, the hydroxyl group at C-5 was shown to be *cis* to the axial proton at C-3 and *trans* both to the angular methyl group at C-10 and to the isopropyl group at C-7. Therefore, the structure, including the absolute configuration, of the sesquiterpene alcohol would be represented by formula **1**. (5*S*,7*R*,10*R*)-Selin-4(14)-en-5α-ol (**1**) is widely distributed in *L. nipponica* which produce a halogenated C-15 non-terpenoid as the major component.

EXPERIMENTAL

^1H and ^{13}C NMR: $CDCl_3$, TMS as int. standard; Low and high resolution MS: 70 eV; Optical rotations: $CHCl_3$. All known compounds were identified by comparison of the spectral data with those of the authentic specimens. Yields are based on the weights of the extracts.

Collection, extraction and isolation. Samples were collected at Rumoi (July 16, 1980), Tomamae (July 30, 1982), Shosanbetsu (*ca* 20 km north of Haboro, July 30, 1982) and Bakkai (*ca* 15 km southwest of Wakkanai, August 2, 1981) in Hokkaido. Extraction and isolation were carried out by conventional methods as described in refs [1, 4].

Rumoi specimen contained isodihydrolaurene (1.4 %) [1], 10-bromo-α-chamigrene (0.1 %) [12], laurene (1.5 %) [13], α-bromocuparene (0.5 %) [14, 15], 2,10-dibromo-3-chloro-α-chamigrene (0.2 %) [12], selin-4(14)-en-5α-ol (**1**) (1.3 %) [4], laureatin (23 %) [8], isolaureatin (16 %) [8], spirolaurenone (2.7 %) [16], laurenisol (0.2 %) [17, 18] and 2,10-dibromo-3-hydroxy-α-chamigrene (6.6 %) [4].

Tomamae, Shosanbetsu and Bakkai specimens contained laurene (1.2 %, 1.1 % and 2.1 %, respectively), *trans*-laurencenyne (2.6 %, 2.5 % and 6.8 %) [19], 2,10-dibromo-3-chloro-α-chamigrene (1.4 %, 1.4 % and 2.5 %), deoxyprepacifenol (6.1 %, 2.3 % and 2.9 %) [20], prepacifenol (29 %, 3.2 % and 13 %) [5] and pacifenol (6.1 %, 19 % and 9.1 %) [6].

Purification of **1**. Crude **1** [4] was purified by HPLC on JASCO Finepak SIL-C_{18} with MeOH–H_2O (9:1).

(5*S*,7*R*,10*R*)-*Selin*-4(14)-*en*-5α-*ol* (**1**). Colourless oil; $[\alpha]_D^{20}$ + 97.2° (*c* 3.01); IR ν_{max}^{film} cm^{-1}: 3450, 3060, 1645, 1382, 1363, 1155, 1020, 1008, 965, 895, 867 and 858; ^1H NMR (200 MHz): δ0.90 (3H, *s*), 0.90 (3H, *d*, *J* = 6.5 Hz), 0.92 (3H, *d*, *J* = 6.5 Hz), 0.9–2.2 (14H), 2.60 (1H, *m*), 4.67 (1H, *dd*, *J* = 1.7 and 1.7 Hz) and 4.77 (1H, *dd*, *J* = 1.7 and 1.7 Hz); ^{13}C NMR (25.0 MHz): δ152.6 (*s*), 106.9 (*t*), 76.4 (*s*), 40.8 (*d*), 38.1 (*s*), 34.8 (*t*), 31.5 (*t*), 30.8 (*t*), 30.4 (*t*), 29.0 (*d*), 22.7 (*t*), 22.3 (*t*), 22.2 (*q*), 22.1 (*q*) and 20.2 (*q*); MS *m/z* (rel. int.): 222 $[M]^+$ (100), 207 $[M-Me]^+$ (4), 204 $[M-H_2O]^+$ (3), 189 $[M-Me-H_2O]^+$ (4), 179 $[M-C_3H_7]^+$ (18), 164 $[M-Me-C_3H_7]^+$ (17), 161 $[M-H_2O-C_3H_7]^+$ (46), 95 (95), 81 (81) and 43 (66); HR-MS *m/z*: 222.1986. Calc. for $C_{15}H_{26}O$: 222.1984.

Dehydration of **1**. To a soln of **1** (23 mg) in C_6H_6 (10 ml) was added a piece of *p*-TsOH, and the mixture was refluxed for 5 min and then, after cooling, extracted with Et_2O. The ethereal soln was washed with 5 % aq. $NaHCO_3$ and H_2O, dried (Na_2SO_4) and evaporated. The residual oil was chromatographed on silica gel to give **2** (15 mg); colourless oil; $[\alpha]_D^{20}$ + 251° (*c* 1.93); IR ν_{max}^{film} cm^{-1}: 1620, 1380, 1368, 1290, 1265, 1225, 1210, 1170, 1155, 1110, 1060, 1030, 990, 952, 915, 873 and 757; ^1H NMR (100 MHz): δ0.94 (3H, *s*), 1.05 (6H, *d*, *J* = 6.5 Hz), 1.2–1.6 (6H), 1.69 (3H, *s*), 1.9–2.5 (5H) and 6.14 (1H, *br s*); MS *m/z*: 204 $[M]^+$ (95), 189 $[M-Me]^+$ (100), 161 $[M-C_3H_7]^+$ (97), 133 (28), 105 (35), 91 (31) and 41 (29). The spectral properties were consistent with those reported [10, 11] for δ-selinene.

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