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(*E*)-2-Tridecyl-2-heptadecenal, an Unusual Metabolite from the Red Alga *Laurencia* Species[1]

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Synopsis. The structure of an unusual α,β-unsaturated aldehyde isolated from the red algae *Laurencia undulata* and *L. papillosa* was established as (*E*)-2-tridecyl-2-heptadecenal by synthetic method.

In connection with our interest on the halogenated metabolites of the marine seaweeds, we have investigated various Japanese species of the genus *Laurencia* (Rhodomelaceae; Rhodophyta) and found as the major metabolites many halogenated compounds with unique structural features in the extracts of *L. nipponica* Yamada (Ura-sozo),[2] *L. okamurai* Yamada (Mitsude-sozo),[3,4] *L. venusta* Yamada (Hime-sozo),[5] *L. majuscula* Harvey (Aka-sozo),[6] and *L. pinnata* Yamada (Hane-sozo).[7] On the other hand, *L. intermedia* Yamada (Kuro-sozo),[3a] *L. capituliformis* Yamada (Maru-sozo),[3a] and *L. cartilaginea* Yamada (Kata-sozo)[8] displayed no halogenated metabolite in their extracts. Furthermore, *L. undulata* Yamada (Kobu-sozo) and *L. papillosa* (Forsk.) Greville (Papira-sozo) also contained no halogenated compound and instead an unusual α,β-unsaturated aldehyde **1**, whose structure is described in this note.

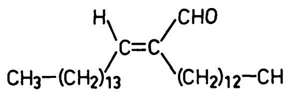
The neutral methanol extract was subjected to repeated column and thin-layer chromatography to give a new aldehyde **1** in 5% yield of the extract along with fatty acid esters.

Compound **1**, $C_{30}H_{58}O$, showed in its ^1H NMR spectrum the signals due to two methyl groups at $\delta=0.88$ (6H, br t, $J=7$ Hz), a vinyl proton at $\delta=6.43$ (1H, dd, $J=7$, 7 Hz), and an aldehyde proton at $\delta=9.35$ (1H, s). The presence of a disubstituted α,β-unsaturated aldehyde moiety was evident on the basis of UV (λ_{max} 230 nm (ε 10800)), IR (ν_{max} 2730, 1680, and 1640 cm^{-1}), and ^{13}C NMR ($\delta=195.3$ (s), 155.2 (d), and 143.9 (s)) spectra. Furthermore, ^{13}C NMR spectrum (INEPT method) revealed the presence of methyl groups at $\delta=14.1$, methylene groups at $\delta=22.7$—32.0, and no methine group and no other double bonds except for the abovementioned trisubstituted double bond. Therefore, compound **1**, having two degrees of unsaturation, must be composed of branched-chain carbon skeleton, permitting a formula **2** ($m+n=25$) to be assigned to this unique aldehyde.

At this stage we noticed the previous report[9] that 2-dodecyl-2-hexadecenal (formula **2**: $m=12$ and $n=11$) was isolated as the major constituent from *L. spectabilis* collected from Southern California along with other α,β-unsaturated aldehydes (range from C_{22} to C_{34}). Thus, formula **2** ($m=13$ and $n=12$) could be assigned to our aldehyde. The stereochemistry of the double bond was established as *E*-configuration by the observation of a strong NOE between the aldehyde proton and the vinyl proton on the NOE difference spectra. Confirmation of the structure of **1**, 2-tridecyl-2-heptadecenal, was obtained by synthesis from pentadecanal.

Aldol condensation of pentadecanal, which was obtained from commercially available 1-pentadecanol by oxidation with the chromium trioxide-pyridine complex,[10] gave (*E*)-2-tridecyl-2-heptadecenal[11] in 83% yield which was identical with natural aldehyde **1** in all respects.

Consequently, the structure of the unique aldehyde is represented by formula **1**.



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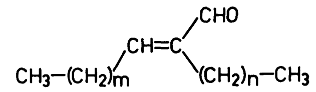

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Experimental

The IR spectra were measured on a JASCO IR-S or a JASCO A-102 spectrophotometer. The UV spectrum was taken with a Shimadzu UV-240 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 or a JEOL JNM-GX 270 spectrometer, using tetramethylsilane as an internal standard. The low and high resolution mass spectra were measured by a JEOL JMS-D300 spectrometer. Silica gel (Merck, Kieselgel 60, 70—230 mesh) and silica gel 60 F_{254} (Merck) were used for column and thin-layer chromatography, respectively.

Collection. *Laurencia undulata* Yamada were collected at Zagashima, Ago Bay, Mie Prefecture, late in June 1983, and at Shirahama, Wakayama Prefecture, late in May 1976. *Laurencia papillosa* (Forsk.) Greville was collected at Hedomisaki, Okinawa Prefecture, late in May 1976. These three specimens showed almost identical thin-layer chromatogram.

Isolation of (*E*)-2-Tridecyl-2-heptadecenal (1). Half-dried alga (40 g) collected at Ago Bay was extractcd with methanol, and the methanol extract was percolated with ether. The ethereal solution was shaken with 0.5M aqueous KOH ($1\,M=1\,mol\,dm^{-3}$) and saturated brine. After drying over anhydrous Na_2SO_4, the ether was evaporated to give a neutral brown oil (160 mg) which was chromatographed on silica-gel column. The earlier benzene fraction was further subjected to preparative thin-layer chromatography to yield **1** (10 mg) as white crystals. Recrystallization of **1** has been unsuccessful.

1: UV (C_2H_5OH), λ_{max} 230 nm (ε 10800); IR ($CHCl_3$), ν_{max} 2730, 1680, and 1640 cm^{-1}; ^1H NMR (100 MHz; $CDCl_3$), $\delta=0.88$ (6H, br t, $J=7$ Hz), 1.0—1.7 (46H, br s), 2.0—2.5 (4H, m), 6.43 (1H, dd, $J=7$, 7 Hz), and 9.35 (1H, s); ^{13}C NMR (67.9 MHz; $CDCl_3$) (INEPT), CH_3: $\delta=14.1$; CH_2: $\delta=22.7$, 24.1, 28.7, 28.8, 29.0, 29.4, 29.5, 29.6, 29.7, and 32.0; CH: $\delta=155.2$; C: $\delta=143.9$ and 195.3; LR-EI-MS (70 eV), m/z (rel intensity)

434 (19; M^+), 265 (9), 255 (11), 237 (20), 169 (16), 149 (11), 135 (17), 123 (14), 121 (19), 119 (15), 111 (21), 109 (25), 98 (38), 97 (38), 95 (41), 83 (46), 81 (48), 71 (40), 69 (55), 67 (46), 57 (93), 55 (78), and 43 (100). HR-EI-MS; Found: m/z 434.4481. Calcd for $C_{30}H_{58}O$: M, 434.4487.

Aldol Condensation of Pentadecanal. To a solution of pentadecanal (100 mg) in ethanol (1 ml) was added saturated methanolic KOH solution (4 ml), and the mixture was stirred at room temperature for 1 h, acidified with 6M HCl, and extracted with ether. The ethereal solution was washed with 1M HCl and water. After drying over anhydrous Na_2SO_4, the ether was evaporated to give an oily substance which was chromatographed on silica-gel column to yield (*E*)-2-tridecyl-2-heptadecenal (**1**) (42 mg) as crystals, whose spectral properties were consistent with those of natural **1**.

We are grateful to Dr. Yuzuru Saito, Faculty of Fisheries, Hokkaido University, and Dr. Washiro Kida, Mie University, for collection and identification of *L. undulata*, and also to Dr. Hiroshi Yabu, Faculty of Fisheries, Hokkaido University, for collection and identification of *L. papillosa*.

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4) *L. okamurai* Y., collected in Kyūshū at Hananose and Sakurajima, Kagoshima Prefecture, late in March 1986, also contained laurinterol[3a] as the major metabolite.

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7) Contrary to the previous reports,[12] *L. pinnata* Y., collected in Kyūshū at Matsushima, Nagasaki Prefecture, in April 1, 1986, contained as the main component (10% of the extract) a unique sesquiterpene, cupalaurenol, which has recently been isolated from the sea hare *Aplysia dactylomela.*[13] We thank to Prof. Tatsuo Higa, University of the Ryukyus, for providing us with preprint and spectral data.

8) *L. cartilaginea* Y. was collected at Sakurajima, Kagoshima Prefecture, late in March 1986.

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11) It is well-known that the α,β-unsaturated aldehydes derived from aldols are trans isomers with trans disposition of the β-alkyl group and the α-formyl group.[14]

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