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KUMAUSYNES AND DEACETYLKUMAUSYNES, FOUR NEW HALOGENATED C-15 ACETYLENES FROM THE RED ALGA *LAURENCIA NIPPONICA* YAMADA[1]

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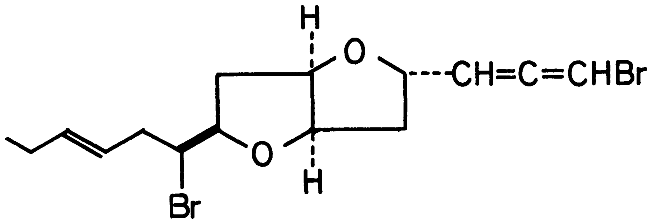
Four new halogenated C_{15}-nonterpenoids which are unusual oxolane derivatives have been isolated from the red alga *L. nipponica* Yamada, and their structures were determined by spectral and chemical evidence.

In the preceding paper[2] we reported the structure of kumausallene (1) which has been isolated from the red alga *Laurencia nipponica* Yamada collected at Kumausu, near Otaru, Hokkaido. In this communication we wish to describe the isolation and structures of four acetylenic metabolites, kumausynes and deacetylkumausynes, which were also obtained from this alga and contain unusual oxolane ring with pentenynyl and hexenyl side chains not yet observed in the halogenated C_{15}-nonterpenoids from the genus *Laurencia*.

The neutral methanol extracts were fractionated by a combination of column chromatography on alumina and silica gel to yield a mixture of *trans*-kumausyne (2) (7% of the extracts) and *cis*-kumausyne (3) (0.7%) and also a mixture of *trans*-deacetylkumausyne (4) (5%) and *cis*-deacetylkumausyne (5) (0.5%). Separation of the geometrical isomers was successfully carried out by HPLC.[3]

trans-Kumausyne (2), $C_{17}H_{23}O_3Br$ (m/z 356 and 354; M^+), oil, $[\alpha]_D^{26}$ -2.3° (c 0.62; $CHCl_3$), showed the presence of an acetoxyl group [ν_{max} 1740 and 1230 cm^{-1}; δ 2.08 (3H, s)] and a conjugated *trans*-2-penten-4-ynyl side chain [ν_{max} 3300 and 2100; λ_{max}^{EtOH} 223 nm (ε 12,300); δ 2.82 (1H, d, J=2 Hz), 5.55 (1H, dd, J=16, 2 Hz), and 6.25 (1H, ddd, J=16, 7.5, 7.5 Hz)] which was supported by spin decoupling experiments in ^1H NMR spectrum. Furthermore, spin decoupling results indicated that 2 possesses the same 1-bromo-*trans*-3-hexenyl side chain as kumausallene (1). *cis*-Kumausyne (3), $C_{17}H_{23}O_3Br$, oil, $[\alpha]_D^{25}$ -3.2° (c 1.03), reveals very similar spectral properties[4] to those of 2 and is shown to be the geometrical isomer of



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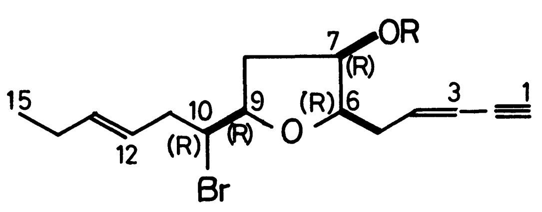
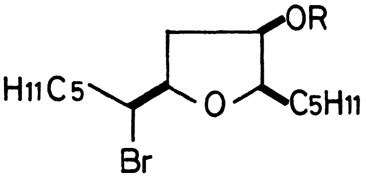


2: R=Ac, trans at C-3
3: R=Ac, cis at C-3
4 : R=H, trans at C-3
5 : R=H, cis at C-3



6: R=Ac
7: R=H

the double bond at C-3 of **2** by the chemical shift (δ 3.10) of the acetylenic proton and the coupling constant (J=10 Hz) between the olefinic protons at C-3 and C-4. This was confirmed by the hydrogenation of **2** and **3** with PtO_2 in ethyl acetate to give the same octahydro compound (**6**). Saponification of *trans*-kumausyne (**2**) with K_2CO_3 in methanol afforded the corresponding alcohol, which regenerated the parent acetate on acetylation with acetic anhydride in pyridine, and the spectral data of the alcohol were identical with those of *trans*-deacetylkumausyne (**4**), $C_{15}H_{21}O_2Br$, oil, $[\alpha]_D^{20}$ +6.5° (c 1.08). Correlation of *trans*-deacetylkumausyne (**4**) and *cis*-deacetylkumausyne (**5**), $C_{15}H_{21}O_2Br$, oil, $[\alpha]_D^{20}$ +10.8° (c 1.88), was carried out by hydrogenation. Hydrogenation of **4** and **5** gave the same octahydro derivative (**7**) which was found to be identical with one of the hydrogenation product (**7**) of kumausallene (**1**).[2] Moreover, treatment of kumausallene (**1**) with Zn-AcOH in methanol yielded *trans*-deacetylkumausyne (**4**) in 44% yield. Therefore, the structures, including the absolute configuration, of *trans*- and *cis*-kumausyne, and *trans*- and *cis*-deacetylkumausyne are represented by formulae **2**, **3**, **4**, and **5**, respectively.

References

1) Part 57 of "Constituents of Marine Plants". Part 56; T. Suzuki, K. Koizumi, M. Suzuki, and E. Kurosawa, Chem. Lett., 1983, preceding paper.

2) Part 56 of this series.

3) Conditions: JASCO Finepak SIL-C_{18}, hexane-isopropyl ether·methanol (100:10:0.75).

4) **2**: λ_{inf}^{EtOH} 216 (ε 10,950) and 230 (ε 9,290) nm; ν_{max}^{film} 3300, 3050, 2100, 1740, 1230, 1050, and 960 cm^{-1}; δ (400 MHz, $CDCl_3$) 0.99 (3H, t, J=7.5 Hz), 2.04 (2H, dq, J=6.5, 7.5 Hz), 2.08 (3H, s), 2.82 (1H, d, J=2 Hz), 3.84 (1H, ddd, J=7.5, 6, 4.5 Hz), 4.0 (2H, m), 5.24 (1H, ddd, J=7.5, 4.5, 2.5 Hz), 5.46 (1H, ddd, J=15, 6.5, 6.5 Hz), 5.55 (1H, dd, J=16, 2 Hz), 5.61 (1H, dt, J=15, 6.5 Hz), and 6.26 (1H, ddd, J=16, 7.5, 7.5 Hz); MS, m/z (rel intensity) 356, 354 (0.3; M^+), 291, 289 (29; $M^+-C_5H_5$), 249, 247 (16; $M^+-C_5H_5-C_2H_2O$), 146 (9; $M^+-C_6H_{10}Br-C_2H_3O_2$), and 43 (100); HR-MS, m/z 354.0839 (calcd for $C_{17}H_{23}O_3{}^{79}Br$, 354.0832).
3: ν_{max} 3300, 3050, 2100, 1740, 1230, 1050, 963, and 730 cm^{-1}; δ 3.11 (1H, d, J=2 Hz), 5.48 (1H, ddd, J=15, 7, 7 Hz), 5.54 (1H, dd, J=10, 2 Hz), 5.60 (1H, dt, J=15, 6 Hz), and 6.04 (1H, ddd, J=10, 7, 7 Hz); MS, m/z 356 and 354 (M^+).
4: ν_{max} 3450, 3300, 3050, 2100, 1060, and 960 cm^{-1}; δ 0.99 (3H, t, J=7 Hz), 2.04 (2H, dq, J=6, 7 Hz), 2.83 (1H, d, J=2 Hz), 3.62 (1H, dt, J=7, 3.5 Hz), 3.99 (1H, ddd, J=9, 6, 3.5 Hz), 4.04 (1H, ddd, J=8, 6, 3.5 Hz), 4.2 (1H, m), 5.43 (1H, br ddd, J=15, 7, 7 Hz), 5.61 (1H, dd, J=16, 2 Hz), 5.61 (1H, dt, J=15, 6 Hz), and 6.30 (1H, dt, J=16, 7 Hz); MS, m/z 314 and 312 (M^+); HR-MS, m/z 314.0674 (calcd for $C_{15}H_{21}O_2{}^{81}Br$, 314.0704).
5: ν_{max} 3450, 3300, 3050, 2100, 1060, 960, and 730 cm^{-1}; δ 3.10 (1H, d, J=2 Hz), 5.33 (1H, ddd, J=15, 7, 7 Hz), 5.53 (1H, dt, J=15, 6 Hz), 5.56 (1H, dd, J=10, 2 Hz), and 6.06 (1H, ddd, J=10, 6, 6 Hz); MS, m/z 314 and 312 (M^+).

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