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NEW BROMO ACETAL FROM THE MARINE ALGA, LAURENCIA NIPPONICA YAMADA (1)

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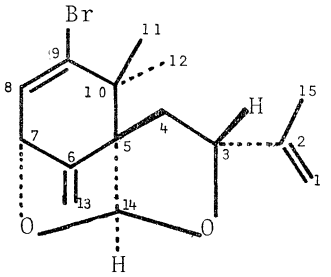
The novel skeletal component, laureacetal-B, having bromine and cyclic acetal, has been isolated from the marine alga, Laurencia nipponica Yamada (Japanese name;Urasozo). Its structure was established by its physical properties and the chemical transformations.

We have recently reported the isolation and the structure, including the absolute configuration, of bromo acetal (1, designated as laureacetal-A) (2), a novel carbon skeletal metabolite having cyclic acetal group, isolated from the marine red alga, L. nipponica Yamada (Rhodomelaceae). In our continuing study of the neutral essential oil from this alga, collected at Usujiri, Hokkaido, Japan, we have isolated the several new halogenated compounds on the repeated neutral alumina column chromatography (Merck, activity II-III) with benzene and ethyl acetate (10:1). We wish to report herein the structural elucidation of a new alcoholic bromo acetal (2, designated as laureacetal-B, 1% yield based on the neutral essential oil), having the same carbon skeleton as that of 1, on the basis of its spectral properties and the chemical transformations.



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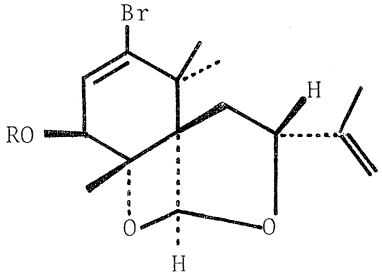


2; R=H
3; R=$COCH_3$

Laureacetal-B (2), mp, 105-106° (isopropyl ether/n-hexane), $[\alpha]_D$ +8.4° ($CHCl_3$, c; 1.0), $C_{15}H_{21}O_3Br$, m/e 330 and 328 (M^+), ν_{max} 3420, 1655, 1630, 1124, 1018, 910, 900 and 860 cm^{-1}. The treatment of 2 with acetic anhydride in pyridine gave monoacetate (3) which showed neither hydroxyl nor carbonyl absorption in IR spectrum and the oxidation of 2 with CrO_3 in pyridine afforded an α,β-unsaturated ketone, [$C_{15}H_{19}O_3Br$, ν_{max} 1675 cm^{-1}, λ_{max} 250 nm (ε; 11.000)]. Thus it is clear that the hydroxyl group in 2 is secondary and allylic, and two of three oxygen

functions are involved in ether link. The ^{13}C and ^{1}H NMR spectra of 2 (Table 1) are similar to those of 1 (Table 2), except at C-6 and C-13, and in consideration of the proton spin decoupling studies, the structure of laureacetal-B seems to be represented as formula 2 and the confirmation of the structure, including absolute configuration, has been obtained by the following chemical transformations of 2 to 1.

Table 1. ^{13}C and ^{1}H NMR spectra of laureacetal-B (2); ppm (TMS=0), $CDCl_3$

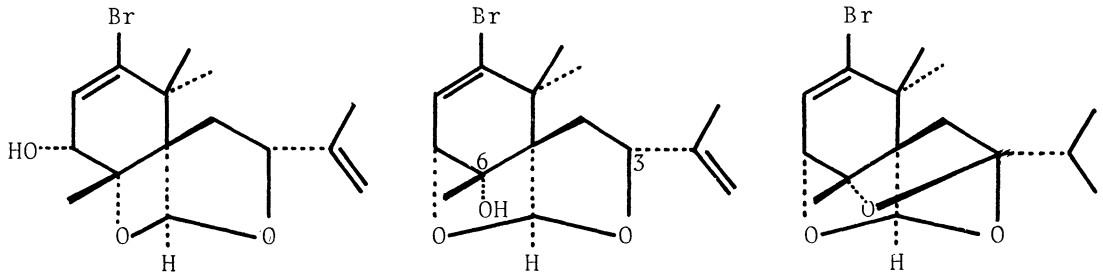
	^{13}C		^{1}H	
Carbon No.	δ	Multiplicity	δ	Multiplicity, J (Hz)
1	111.9	t	4.97	br. s
			5.13	br. s
2	140.3	s		
3	84.3	d	ca. 5.0	m
4	33.0	t	1.78	dd, J=14, 9
			2.24	dd, J=14, 7
5	62.9	s		
6	81.2	s		
7	71.9	d	3.98	d, J=7
8	130.3	d	6.60	d, J=7
9	142.8	s		
10	40.5	s		
11	17.9	q	1.12	s
12	24.1	q	1.17	s
13	25.5	q	1.51	s
14	105.6	d	5.55	s
15	21.2	q	1.81	s

Table 2. ^{13}C and ^{1}H NMR spectra of laureacetal-A (1); ppm (TMS=0), $CDCl_3$

	^{13}C		^{1}H	
Carbon No.	δ	Multiplicity	δ	Multiplicity, J (Hz)
1	111.6	t	4.76	br. s
			4.91	br. s
2	139.1	s		
3	82.1	d	ca. 4.4	m
4	33.0	t	ca. 1.7	m
			1.96	dd, J=12, 4
5	63.0	s		
6	146.5	s		
7	77.5	d	4.38	d, J=6
8	131.2	d	6.23	d, J=6
9	143.4	s		
10	47.2	s		
11	18.0	q	1.10	s
12	22.5	q	1.25	s
13	102.0	t	4.80	s
			5.08	s
14	108.3	d	5.52	s
15	21.8	q	1.72	s

Oxidation of 2 with CrO_3 in pyridine followed by the reduction with $NaBH_4$ in methanol provided the corresponding epimeric alcohol (4) in quantitative yield, [δ 0.91, 1.17 and 1.51 (each 3H, s), 1.80 (3H, br. s), ca. 1.80 (1H, m), 2.28 (1H, dd, J=14, 7 Hz), 3.91 (1H, d, J=1.5), ca. 4.90 (1H, m), 4.94 (1H, br. s), 5.12 (1H,

br. s), 5.49 (1H, s) and 6.32 (1H, d, J=1.5)]. Being contrary to the stability of 2, 4 easily isomerized under stirring with silica gel (Merck, Kieselgel 60) in benzene at 35-40° for 16 hr. to 5, $C_{15}H_{21}O_3Br$, [δ 1.23 (6H, s), 1.42 (3H, s), 1.71 (3H, br. s), ca. 1.7 (1H, m), 2.48 (1H, dd, J=13, 8), 4.08 (1H, d, J=7), 4.80 (1H, br. s), ca. 4.9 (1H, m), 4.98 (1H, br. s), 5.78 (1H, s) and 6.25 (1H, d, J=7); ^{13}C NMR, 17.9 (q), 19.6 (q), 23.8 (q), 26.1 (q), 31.6 (t), 45.7 (s), 65.2 (s), 78.5 (s), 83.8 (d), 85.7 (d), 109.6 (t), 109.7 (d), 129.5 (d), 138.6 (s) and 145.7 (s)]



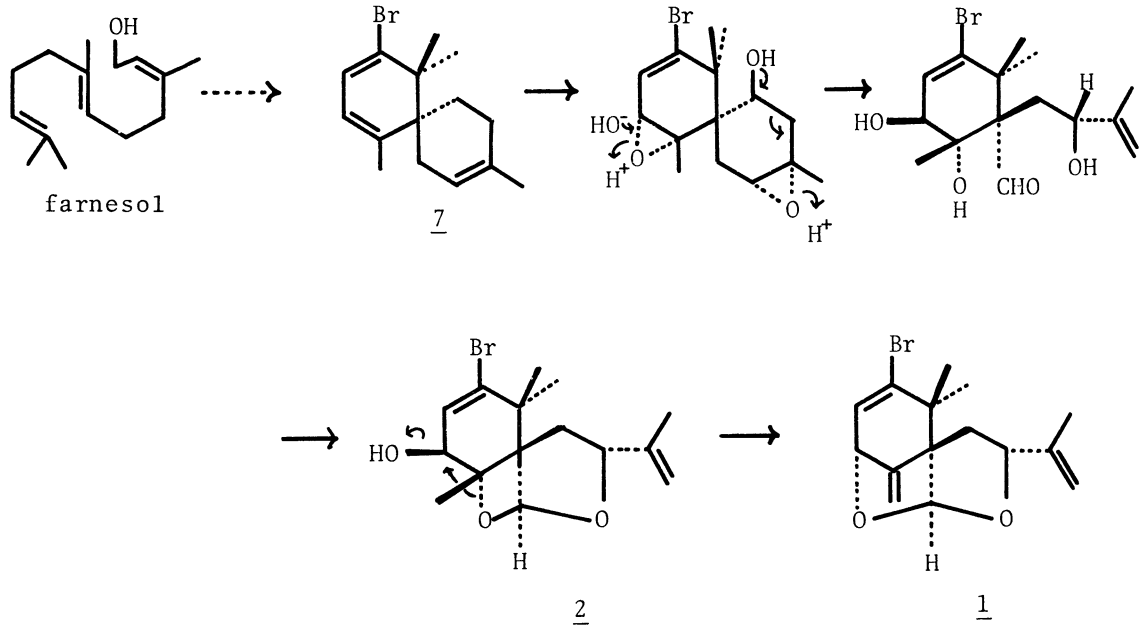
4 5 6

Successively, 5 was submitted to the treatment with $SOCl_2$ in pyridine at -10° for 6 hr. to give the dehydration product, $C_{15}H_{19}O_2Br$, which was identified with the natural product, laureacetal-A (1), by the mixed melting point and a comparison of IR, NMR and Mass spectra and the optical rotation with those of an authentic specimen. The above-mentioned results concluded that the structure of the isomerized product from 4 should be represented as 5, excluding the stereochemistry at C-6, and the remaining stereochemistry at C-6 was clarified by the following chemical transformation.

Treatment of 5 with p-toluenesulfonic acid in refluxing benzene for 30 min., in an attempt to generate 1, resulted in quantitative yield of the isomeric diacetal (6), $C_{15}H_{21}O_3Br$, [δ 1.04 (6H, d, J=7 Hz), 1.24 (6H, s), 1.42 (3H, s), 1.79 and 1.87 (each 1H, d, J=12), 2.16 (1H, septet, J=7), 4.12 (1H, d, J=6), 5.62 (1H, s) and 6.42 (1H, d, J=6); ^{13}C NMR, 17.6 (q), 19.2 (q), 24.0 (q), 25.9 (q), 29.8 (d), 35.4 (t), 42.4 (s), 62.0 (s), 78.0 (d), 85.4 (s), 106.5 (d), 111.9 (s), 132.5 (d) and 137.9 (s)]. The IR spectrum of 6 did not show the presence of hydroxyl or carbonyl groups and the ^{13}C and ^{1}H NMR spectral studies of 6 gave much the structural informations. The signals due to the proton at C-3 (ca. 4.9) and isopropenyl group (1.71, 4.80 and 4.98) and the signal due to C-3 (83.8 or 85.7) in 5 disappeared during the isomerization of 5 to 6. On the other hand, the signal due to C-3 (111.9, probably due to acetal carbon) newly appeared as singlet in 6 and moreover the proton spin decoupling studies clearly showed the presence of the partial structure of ■-$CH(CH_3)_2$ at 1.04 and 2.16 in 6. These spectral experiments strongly supported the formula 6 for the acid-rearranged product from 5, and the configuration at C-6 in 5 would be undoubtedly represented as in formula 5, since the alternative configuration was sterically impossible to produce the ether ring between C-3 and C-6 on the Dreiding model.

Consequently, the isomerization of 4 to 5 should arrise from the reformation between 4-membered ring acetal and hydroxyl group, preserving the stereochemistry of two oxygen functions at C-6 and C-7.

The above-mentioned chemical transformations strongly supported the assigned stereochemistry of laureacetal-B as formula 2, epimeric alcohol of 4, and its carbon skeleton is second example among the naturally occurring sesquiterpenes. The biogenesis of these interesting metabolites, 1 and 2, from farnesol via intermediate 7 (2), is proposed in the following scheme.



References

(1) Part XXXII of "Constituents of Marine Plants". Part XXXI, M. Suzuki and E. Kurosawa, Tetrahedron Letters, in press.

(2) T. Suzuki, A. Furusaki, N. Hashiba, and E. Kurosawa, Tetrahedron Letters, 3731 (1977).

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