Constituents of a Fern, *Davallia mariesii* MOORE. III.[1] Revised Structure and Absolute Configuration of Davallialactone

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The structure of davallialactone (1), obtained from the rhizomes of a fern, *Davallia mariesii* MOORE, was revised on the basis of chemical and spectroscopic evidence. Also, the absolute stereochemistry of 1 was determined to be 5′*R*,6′*S* from a circular dichroism (CD) study of dihydrodavallialactone (2).

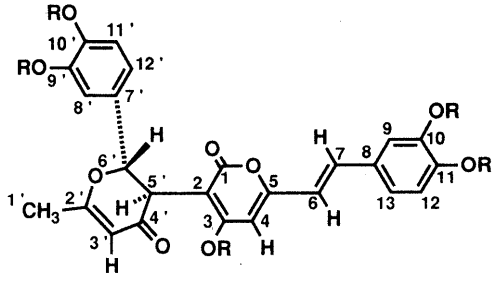
Keywords *Davallia mariesii*; fern; davallialactone; penta-*O*-methyldavallialactone; penta-*O*-methyltetrahydrodavallialactone; dihydrodavallialactone; two dimensional NMR; CD spectrum; absolute configuration

In a previous paper,[2] we reported the isolation and structure of a new compound, davallialactone, from the rhizomes of *Davallia mariesii* MOORE. However, there was a question about the acetyl group in the proposed structure (**1a**), because the carbon-13 nuclear magnetic resonance (^{13}C-NMR) signal that was assigned to the carbonyl carbon in this acetyl group had an unusually high-field shift value (δ 173.1 in deuterio-dimethyl sulfoxide (DMSO-d_6)). Recently, we reexamined the structure of this compound and this led to a revised structure (**1**). The absolute configuration of **1** was also determined on the basis of the circular dichroism (CD) spectrum of dihydrodavallialactone (**2**). This paper deals with the revised structure and the absolute stereochemistry of davallialactone (**1**).

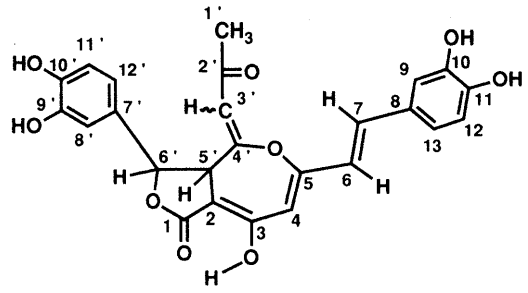
Catalytic hydrogenation of davallialactone (**1**) over 10% palladium–carbon gave a dihydro compound (**2**) as the sole product, $C_{25}H_{22}O_9$, $[\alpha]_D^{22}$ +153.5° (MeOH), which showed ^{1}H-NMR signals due to an ethylene group at δ 2.59 and 2.71 (each 2H, t, J=7.3 Hz) instead of the *trans*-olefin protons in **1**, while an attempt at reduction of **1** with sodium borohydride afforded an intractable mixture.

On the other hand, treatment of **1** with diazomethane gave a penta-*O*-methyl ether (**3**) as a yellow amorphous solid, $C_{30}H_{30}O_9$, $[\alpha]_D^{22}$ +291.7° (MeOH), which showed five *O*-methyl signals at δ 3.77, 3.79, 3.81, 3.83, and 3.84 in the ^{1}H-NMR spectrum. Reduction of the latter (**3**) with sodium borohydride in methanol–isopropanol (1 : 1) yielded an alcohol (**4a**), amorphous solid, $[\alpha]_D^{22}$ +207.5° ($CHCl_3$), ν 3592 cm^{-1} (OH), together with an epimeric alcohol (**4b**), $[\alpha]_D^{23}$ +218.1° ($CHCl_3$), ν 3400 cm^{-1} (OH). Both **4a** and **4b** showed the molecular ion peak at m/z 538 ($C_{30}H_{34}O_9$) in the mass spectrum (MS), indicating that both are tetrahydro derivatives of **2**.

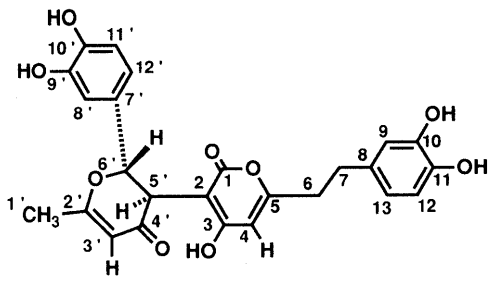
As expected, the ^{1}H-NMR spectrum of **4a** (in acetone-d_6) exhibited a signal due to a *sec*-methyl group at δ 1.22 (d, J=6.1 Hz) instead of the singlet methyl signal (δ 2.01) in



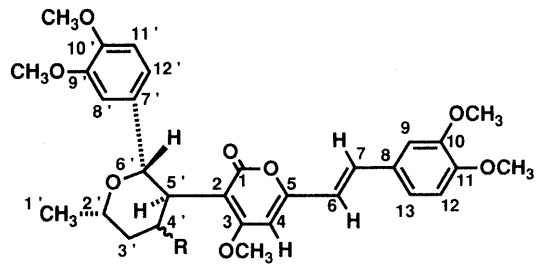
1 : R = H
3 : R = CH_3



1a



2



4a : R = ····OH
4b : R = —OH

Chart 1

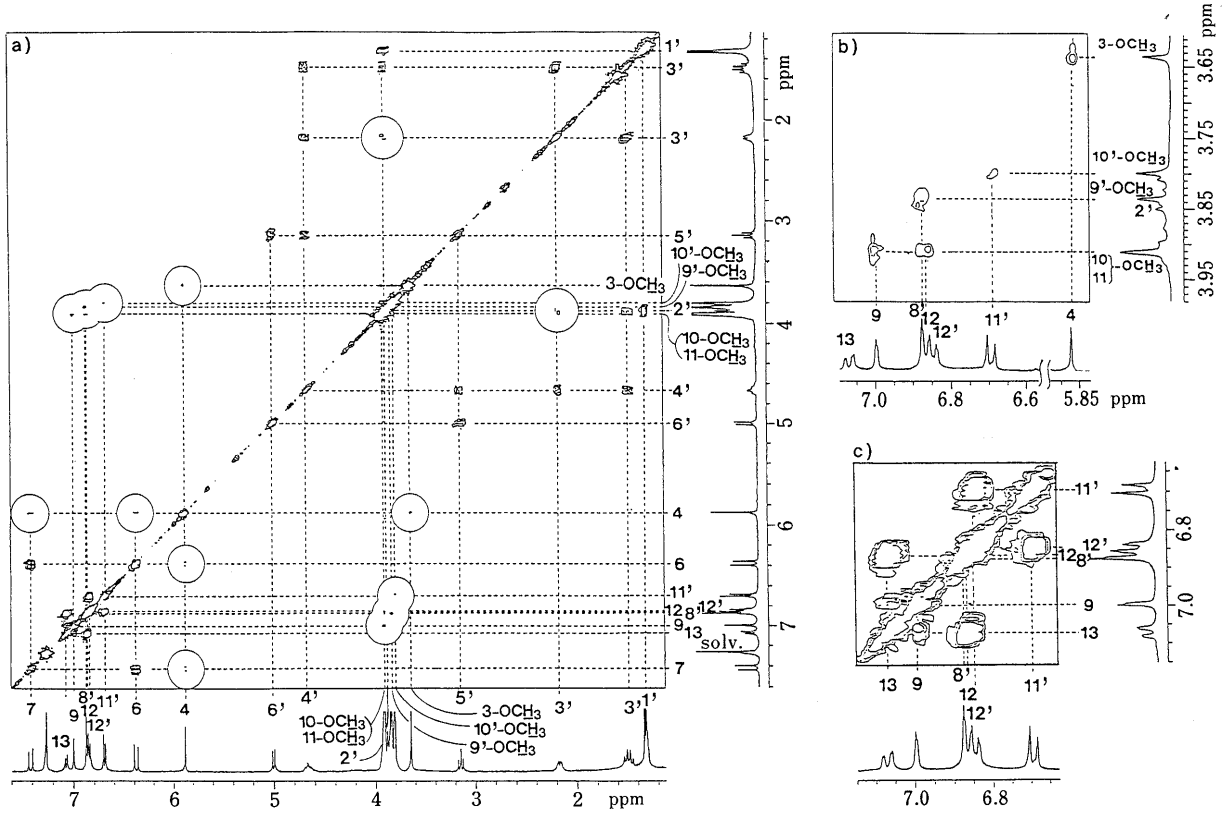


Fig. 1. ^{1}H–^{1}H COSY Spectrum of **4a** in $CHCl_3$-*d*

a) Whole region. b) Cross peaks between aromatic or olefinic protons and methoxy protons. c) Cross peaks between aromatic protons. Open circles indicate significant but weak peaks at this threshold level.

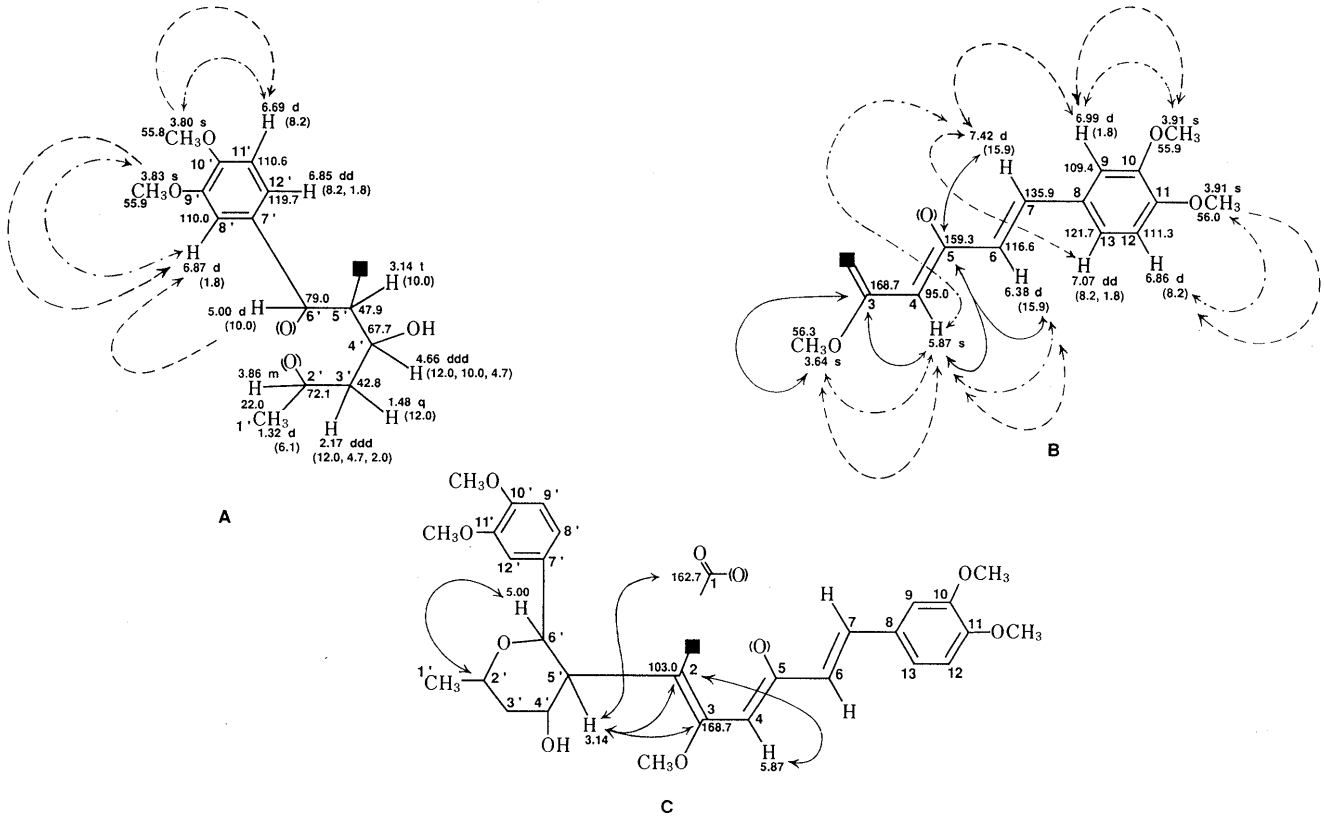


Fig. 2. Partial Structures and NMR Data for **4a**

Long-range ^{1}H–^{1}H coupling observed in ^{1}H–^{1}H COSY. NOE observed in difference NOE experiments. Long-range ^{1}H–^{13}C coupling observed in HMBC spectrum.

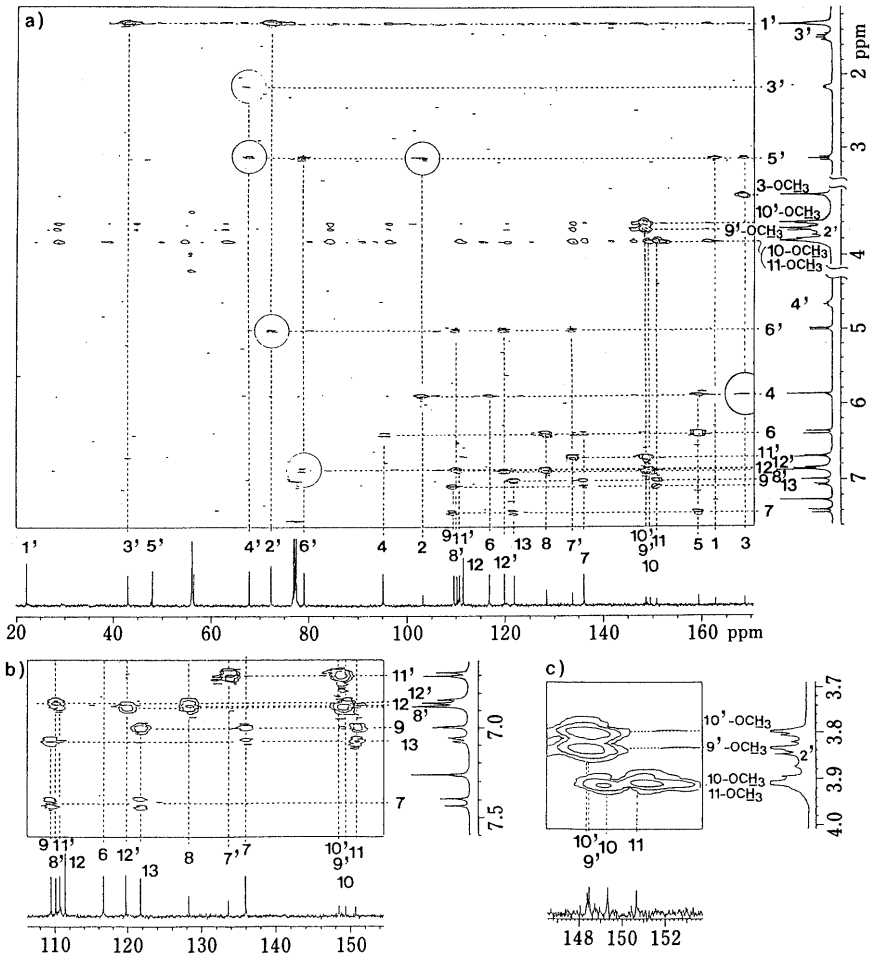


Fig. 3. HMBC Spectrum of **4a** in $CHCl_3$-*d* (Sample: 3.3 mg, Long-range J_{CH} = 8.3 Hz, 36 h run)

a) Whole region. b) Low-field region. c) δ_C 147—153 and δ_H 3.7—4.0 region. Open circles indicate significant but weak peaks at this threshold level.

TABLE I. 400 MHz ^{1}H-NMR Data for **1**, **2**, **3**, **4a**, and **4b** (Coupling Constants in Parenthesis)

^{1}H	**1**[a,c]	**2**[a]	**3**[a]	**4a**[b]	**4b**[b]
4-H	5.93 s	5.68 s	6.38 s	5.87 s	5.91 s
6-H	6.43 d (15.9)	2.59 2H, t (7.3)	6.66 d (15.9)	6.38 d (15.9)	6.38 d (15.9)
7-H	7.18 d (15.9)	2.71 2H, t (7.3)	7.29 d (15.9)	7.42 d (15.9)	7.42 d (15.9)
9-H	6.97[d] d (1.8)	6.57[d] d (2.1)	7.13[d] d (1.9)	6.99 d (1.8)	6.98 d (2.1)
12-H	6.74 d (8.2)	6.63 d (7.9)	6.92 d (8.5)	6.86 d (8.2)	6.87 d (8.2)
13-H	6.873[d] dd (8.2, 1.8)	6.36[d] dd (7.9, 2.1)	7.08[d] dd (8.5, 1.9)	7.07 dd (8.2, 1.8)	7.07 dd (8.2, 2.1)
1′-H_3	2.08 s	2.07 s	2.10 s	1.32 d (6.1)	1.27 d (6.4)
2′-H	—	—	—	3.86 m	4.37 dqd (12.5, 6.4, 2.5)
3′-H	5.48 s	5.46 s	5.50 s	2.17 ddd (12.0, 4.7, 2.0)	1.92 ddd (12.5, 3.0, 2.5)
				1.48 q (12.0)	1.65 br t (12.5)
4′-H	—	—	—	4.66 ddd (12.0, 10.0, 4.7)	4.29 br s
5′-H	4.28 d (13.7)	4.23 d (13.7)	4.39 d (13.7)	3.14 t (10.0)	3.43 dd (10.7, 2.1)
6′-H	5.77 d (13.7)	5.74 d (13.7)	5.80 d (13.7)	5.00 d (10.0)	5.48 d (10.7)
8′-H	6.867[e] d (1.8)	6.84[e] d (1.5)	7.05 d (1.8)	6.87 d (1.8)	6.88 br s
11′-H	6.67 d (8.2)	6.67 d (8.0)	6.84 d (8.2)	6.69 d (8.2)	6.68 d (8.2)
12′-H	6.71[e] dd (8.2, 1.8)	6.65[e] dd (8.0, 1.5)	6.89 dd (8.2, 1.8)	6.85 dd (8.2, 1.8)	6.89 dd (8.2, 2.0)
3-OC$\underline{H}_3$[f]	—	—	3.79 s	3.64 s	3.74 s
10-OC$\underline{H}_3$[g]	—	—	3.84 s	3.91 s	3.91 s
11-OC$\underline{H}_3$[h]	—	—	3.83 s	3.91 s	3.91 s
9′-OC$\underline{H}_3$[i]	—	—	3.81 s	3.83 s	3.83 s
10′-OC$\underline{H}_3$[j]	—	—	3.77 s	3.80 s	3.78 s

a, b) Values in MeOH-d_4 and $CHCl_3$-*d*, respectively. *c)* Data were reexamined for the revised structure **1**. *d, e)* Long-range (LR) couplings were observed with 7-H and 6′-H, respectively, in the ^{1}H–^{1}H COSY. *f—j)* NOE's were observed with 4-H, 9-H, 12-H, 8′-H, and 11′-H, respectively, in the difference NOE experiments.

1a and a characteristic signal assignable to a newly introduced carbinol methine proton at δ 4.53 (dddd, J = 11.3, 10.1, 5.0, 4.5 Hz; changed to ddd on addition of deuterium oxide, J = 11.3, 10.1, 4.5 Hz), but it was proved by decoupling experiments that these *sec*-methyl and carbinol methine groups were not adjacent to each other.

TABLE II. 100 MHz ^{13}C-NMR Data for **1**, **2**, **3**, and **4a**

Compound ^{13}C	**1**[a,c]			**2**[a]			**3**[a]			**4a**[b]		
	δ	^{1}H LR coupled ($^3J_{CH}$	$^2J_{CH}$)[d]	δ	^{1}H LR coupled ($^3J_{CH}$	$^2J_{CH}$)[d]	δ	^{1}H LR coupled ($^3J_{CH}$	$^2J_{CH}$)[d]	δ	^{1}H LR coupled ($^3J_{CH}$	$^2J_{CH}$)[d]
1	167.5 s	5′		168.2 s	5′		166.1 s	5′		162.7 s	5′	
2	99.1 s	4, 6′	5′	98.3 s	4	5′	101.4 s	4	5′	103.0 s	4	5′
3	171.8 s	5′	4	171.6 s	5′	4	171.4 s	5′	4	168.7 s	3-OC$\underline{H}_3$, 5′	4
4	102.5 d	6		102.8 d	6		97.5 d	6		95.0 d	6	
5	160.9 s	7	4, 6	166.3 s	7	4, 6	162.4 s	7	4, 6	159.3 s	7	4, 6
6	117.7 d	4	7	37.5 t	4	7	118.8 d	4	7	116.6 d	4	
7	137.5 d	9, 13	6	34.1 t	9, 13	6	138.0 d	9, 13	6	135.9 d	9, 13	
8	129.8 s	6, 12	7	133.8 s	6, 12	7	130.6 s	6, 12	7	128.2 s	6, 12	
9	115.6 d	7, 13		117.2 d	7, 13		112.0 d	7, 13		109.4 d	7, 13	
10	147.4 s	12	9	145.4 s	12	9	151.5 s	10-OC$\underline{H}_3$, 12	9	149.3 s	10-OC$\underline{H}_3$, 12	
11	149.2 s	9, 13	12	147.0 s	9, 13	12	153.0 s	11−OC$\underline{H}_3$, 9, 13	12	150.7 s	11-OC$\underline{H}_3$, 9, 13	
12	117.3 d			117.2 d			113.5 d			111.3 d		
13	122.6 d	7, 9		121.5 d	7, 9		124.1 d	7, 9	12	121.7 d	7, 9	
1′	21.9 q	3′		21.9 q	3′		21.9 q	3′		22.0 q		
2′	177.9 s		1′, 3′	177.8 s		1′, 3′	177.9 s		1′, 3′	72.1 d	1′, 6′	
3′	105.7 d	1′		105.7 d	1′		105.8 d	1′		42.8 t	1′	
4′	196.8 s	6′	5′	196.7 s	6′	5′	195.8 s	6′	5′	67.7 d		3′, 5′
5′	48.7 d	3′	6′	48.5 d	3′	6′	48.8 d	3′		47.9 d		
6′	85.2 d	8′, 12′	5′	85.1 d	8′, 12′	5′	85.0 d	8′, 12′	5′	79.0 d	12′	5′
7′	131.0 s	5′, 11′	6′	131.0 s	5′, 11′	6′, 8′, 12′	131.8 s	5′, 11′	6′, 8′	133.6 s	11′	6′
8′	116.5 d	6′, 12′		116.5 d	6′, 12′		112.87 d	6′, 12′		110.0 d	6′, 12′	
9′	146.7 s	11′	8′	146.7 s	11′	8′	151.0 s	9′-OC$\underline{H}_3$, 11′	8′	148.5[e] s	9′-OC$\underline{H}_3$, 11′	8′
10′	147.7 s	8′, 12′	11′	147.7 s	8′, 12′	11′	151.9 s	10′-OC$\underline{H}_3$, 8′, 12′	11′	148.4[e] s	10′-OC$\underline{H}_3$, 8′	11′
11′	116.6 d		12′	116.6 d		12′	112.94 d			110.6 d		12′
12′	121.4 d	6′, 8′		121.4 d	6′, 8′		122.8 d	6′, 8′	11′	119.7 d	6′, 8′	
3-OC$\underline{H}_3$	—			—			58.3 q			56.3 q		
10-OC$\underline{H}_3$	—			—			57.22 q			55.9 q		
11-OC$\underline{H}_3$	—			—			57.27 q			56.0 q		
9′-OC$\underline{H}_3$	—			—			57.33 q			55.9 q		
10′-OC$\underline{H}_3$	—			—			57.15 q			55.8 q		

a, b) Values in MeOH-d_4 and $CHCl_3$-*d*, respectively. *c*) Data were reexamined for the revised structure **1**, and the previous assignments[2] of C-1 and C-4′ were interchanged. *d*) $^2J_{CH}$ and $^3J_{CH}$ indicate the protons which are coupled with the carbon through two and three bonds, respectively, and are observed in the HMBC spectrum. *e*) Assignments may be interchanged.

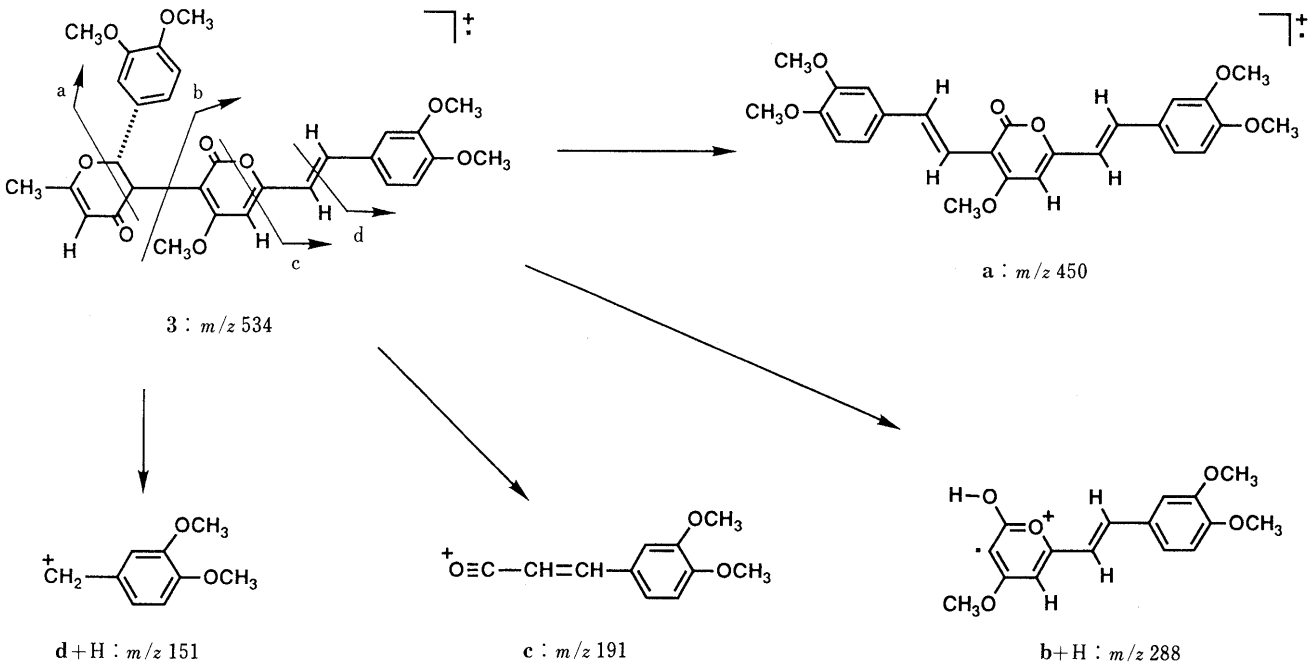


Chart 2

This finding led to the conclusion that no acetyl group was present in the molecule of davallialactone.

Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of **4a** with the aid of ^{1}H–^{1}H shift correlated spectroscopy (COSY) (Fig. 1), ^{1}H–^{13}C COSY, and difference nuclear Overhauser effect (NOE) experiments indicated the presence

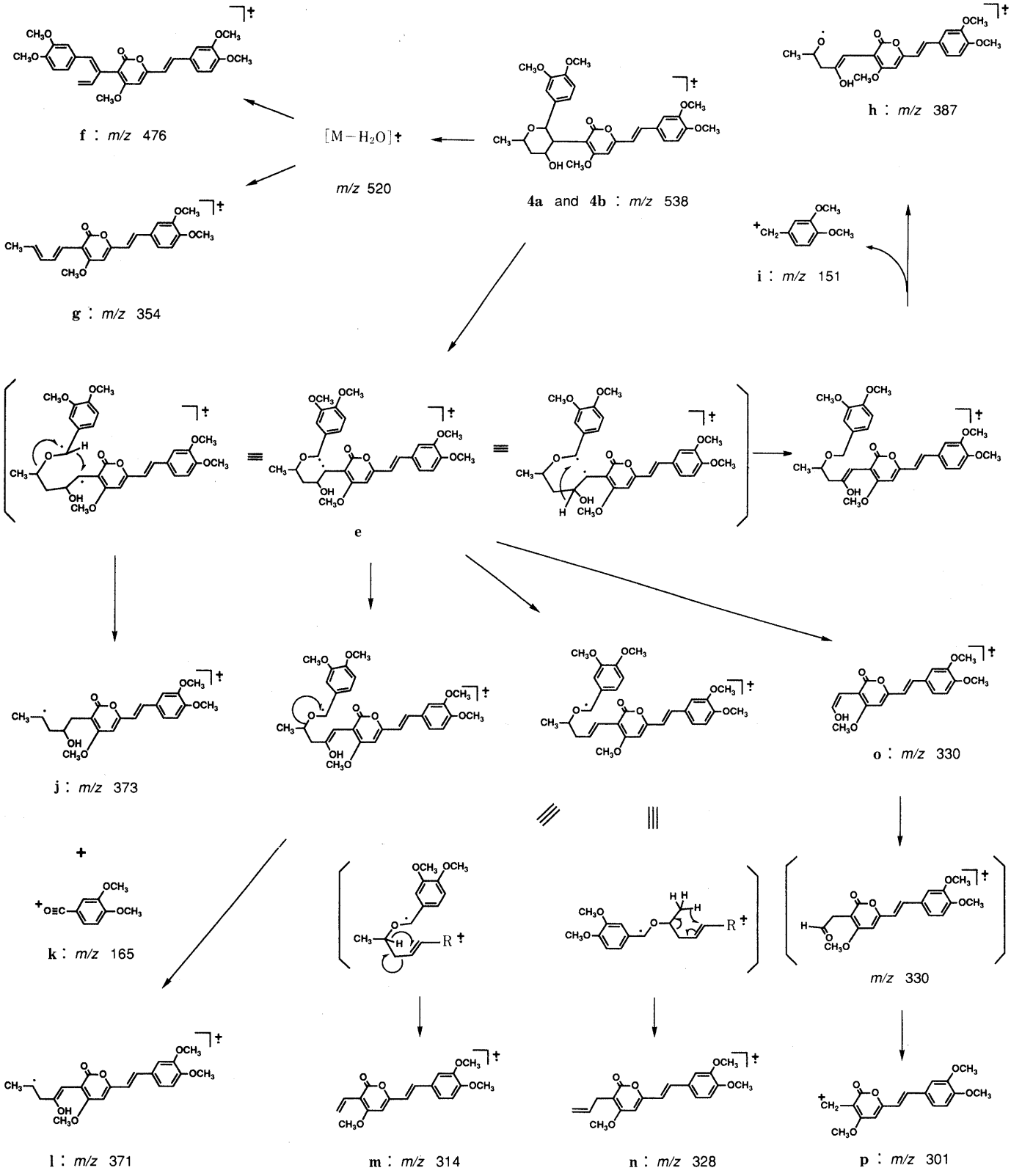


Chart 3

of partial structures A and B in **4a** (Fig. 2).

Then, we measured the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) spectrum[3] of **4a** in order to obtain more detailed information about the total structure. As can be seen in Fig. 3, the quaternary carbon at δ 159.3 (C-5 in the partial structure B) shows long-range correlations with the protons at δ 5.87 (4-H), 6.38 (6-H), and 7.42 (7-H), while the quaternary carbon at δ 168.7 (C-3 in the partial structure B) shows long-range correlations with the ^{1}H-signals due to 3-OC$\underline{H}_3$ (δ 3.64) and 4-H. Therefore these signals could be assigned to C-3 and C-5, respectively.

Then, our attention was turned to the benzylic methine proton at δ 5.00 (6′-H in the partial structure A), which

shows a long-range correlation with the oxygenated methine carbon at δ 72.1 (C-2′ in the partial structure A). This suggested that C-2′ and C-6′ are connected across an oxygen atom, forming a tetrahydropyran ring.[4] Furthermore, the methine proton at δ 3.14 (5′-H in the partial structure A) shows a long-range correlation with C-3 (in the partial structure B, δ 168.7) and also with the quaternary sp^2 carbon at δ 103.0 (C-2). Since the latter carbon (C-2) is also correlated with the olefinic proton at δ 5.87 (4-H in the partial structure B), it is reasonable to assume that the partial structure A is combined at the C-5′ position with the partial structure B across the quaternary carbon at δ 103.0 (C-2) to form the expanded structure C. The remaining carbon, which corresponds to the ^{13}C-signal at δ 162.7, was considered to be a conjugated ester carbonyl in view of the chemical shift value and the infrared (IR) absorption at 1693 cm^{-1}. This carbon shows a long-range correlation with 5′-H in the HMBC spectrum (Fig. 3), and it may be considered that this carbon is linked to C-2 to form a 6-membered lactone ring with C-5.[5]

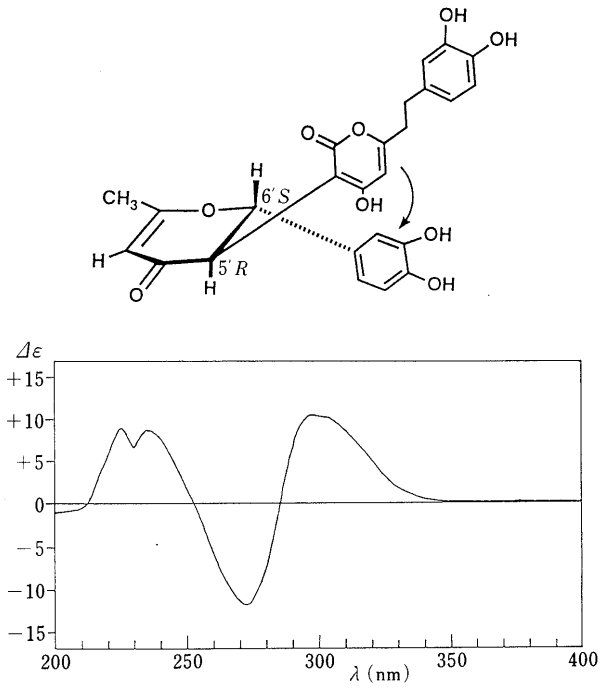


Fig. 4. CD Spectrum of **2** in MeOH

The relative stereochemistry of **4a** was determined on the basis of the coupling constants of each proton ($J_{2',3'ax.} = J_{3'ax.,4'} = 12$ Hz, $J_{4',5'} = J_{5',6'} = 10$ Hz) and it was confirmed by the difference NOE experiments, where irradiation of 6′-H (δ 5.00) increased the intensities of 2′-H (δ 3.86) and 4′-H (δ 4.66) and irradiation of 4′-H increased the intensities of 2′-H and 6′-H, indicating that 2′-H, 4′-H, and 6′-H are all axial and in the *cis*-relation.

From these findings, the structure of the alcohol **4a** was determined to be as shown in Chart 1. The other alcohol (**4b**) showed ultraviolet (UV) and IR spectra closely similar to those of **4a**, and its ^{1}H-NMR spectrum also resembled that of **4a**, except for the signals assignable to the protons of the tetrahydropyran group. These ^{1}H-signals could easily be analyzed with the aid of ^{1}H–^{1}H COSY (see Table I), leading to the structure **4b**.

Because the alcohols **4a** and **4b** were considered to be formed by sequential reduction of the α,β-unsaturated ketone moiety of penta-*O*-methyldavallialactone (**3**), the structure of davallialactone should be revised to the formula **1**.[6] This conclusion was supported by the MS of **3**, which revealed characteristic ions at *m/z* 450 (**a**) and at *m/z* 288 (**b**+H) due to the retro-Diels–Alder type fragmentation at the dihydro-γ-pyrone ring and the McLafferty type fragmentation, respectively. Other significant fragment ions were observed at *m/z* 191 (**c**) and 151 (**d**+H) (Chart 2), which were considered to have arisen from the trimethylhispidin moiety.[5c] On the other hand, alcohols **4a** and **4b** showed more complicated fragmentation patterns in the

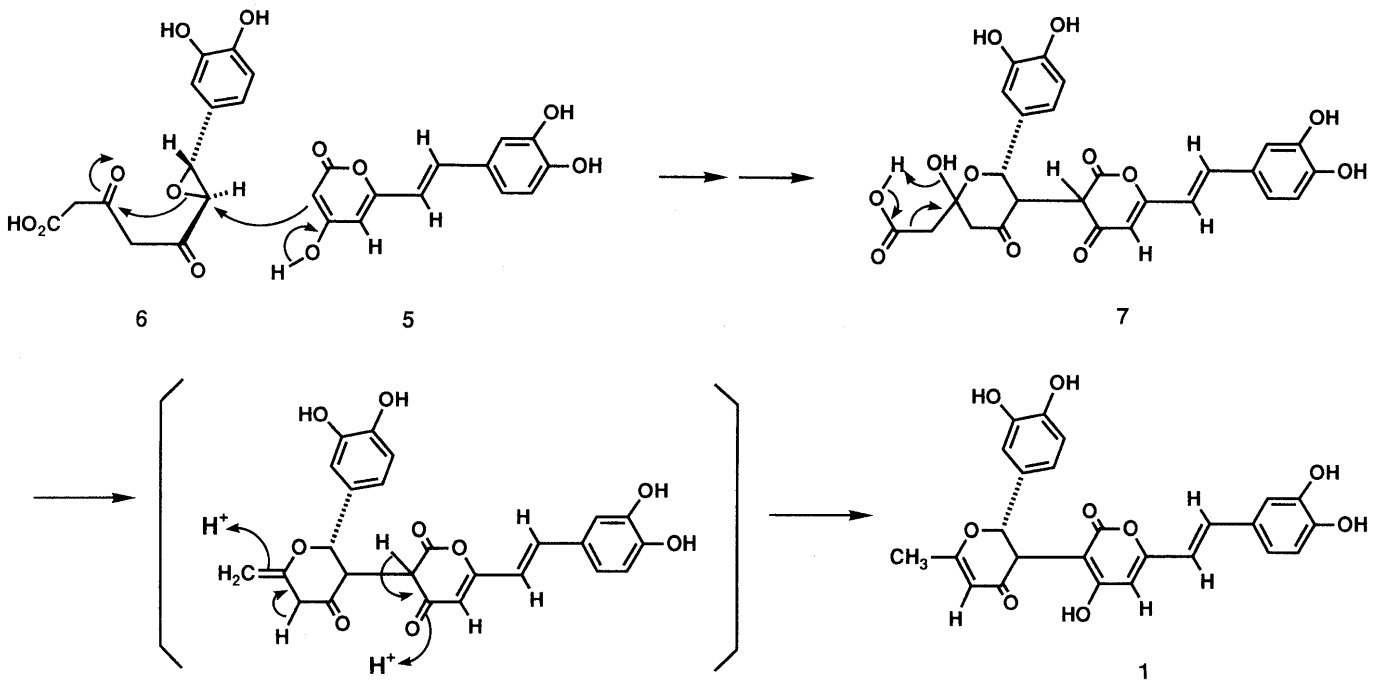


Chart 4

MS. The most characteristic reaction occurring in **4a** and **4b** may be radical fission at the 5′–6′ bond, giving an ion **e**, which undergoes further fragmentations with or without hydrogen migration to afford several significant fragment ions as shown in Chart 3. Another important reaction was dehydration followed by retro-Diels–Alder fragmentation to yield ions **f** and **g**.

Next, we examined the CD spectrum of dihydrodavallialactone (**2**). It showed a positive Cotton effect at 297 nm ($\Delta\varepsilon$, +11.05) and a negative one at 272.5 nm ($\Delta\varepsilon$, −12.18), which may be ascribed to the exciton–coupling interaction between the benzene and α-pyrone chromophores.[7] This indicated that these chromophores are arranged in a clockwise disposition (Fig. 4).[8] Thus, the absolute stereochemistry of **2**, and also **1**, was concluded to be 5′*R*,6′*S*.

Davallialactone (**1**) may be biosynthesized by dimerization of hispidin (**5**)[5c] or its congeners. A plausible precursor is the epoxide **6**, which may be produced by oxidation of 7-(3,4-dihydroxyphenyl)-3,5-dioxo-6-heptenoic acid. Nucleophilic attack of **5** on **6**, accompanied with concomitant acetalization, would give a dimeric precursor (**7**). This may be decarboxylated to yield **1** (Chart 4).

Experimental

Optical rotations were measured on a JASCO DIP-140 digital polarimeter in MeOH solutions. UV spectra were taken with a Shimadzu 202 UV spectrophotometer in MeOH solutions and IR spectra were recorded on a Nicolet 5DX FT-IR spectrometer in $CHCl_3$ solutions unless otherwise noted. Electron impact (EI)-MS (ionization voltage, 70 eV; accelerating voltage, 3 kV), high resolution (HR)-MS, and fast atom bombardment (FAB)-MS were obtained with a JEOL D-300 spectrometer using a direct inlet system and glycerol was used as a matrix in FAB-MS measurements. ^{1}H-, ^{13}C-, and 2D NMR spectra were taken on a JEOL JNM-GX400 spectrometer by the use of JEOL standard pulse sequences and collected data were treated by JEOL standard software.

Davallialactone (**1**) used in this study was obtained from the air-dried rhizomes (17 kg) of *Davallia mariesii* Moore, collected at Pusan, South Korea, as described in the previous paper.[2]

Preparative thin-layer chromatography (preparative TLC) was carried out on precoated Merck Kieselgel 60 F_{254} plates (0.5 mm) and the plates were examined under UV light. Extraction of substances from silica gel was done with $CHCl_3$–MeOH (90:10 or 85:15) and solutions were concentrated *in vacuo*.

Catalytic Hydrogenation of 1 A mixture of **1** (15 mg), 10% Pd/C (2 mg), and EtOH (6 ml) was stirred under a hydrogen atmosphere for 12 h at room temperature. The catalyst was removed by filtration, and the filtrate was concentrated *in vacuo* to give 6,7-dihydrodavallialactone (**2**) (15 mg) as an amorphous solid, $[\alpha]_D^{22}$ +153.5° (c=0.5, MeOH). UV λ_{max} nm (log ε): 284 (4.31). IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 1675, 1650 (conjugated CO), 1595, 1518 (aromatic ring). ^{1}H- and ^{13}C-NMR: Tables I and II. FAB-MS m/z: 537 $[M+H]^+$. CD (c=0.005, MeOH) $\Delta\varepsilon^{25}$ (nm): +9.09 (225), +8.77 (235), 0 (253), −12.18 (272.5), 0 (285), +11.05 (297).

Methylation of 1 with CH_2N_2 Excess CH_2N_2 (ether solution) was added to a solution of **1** (30 mg) in MeOH (0.5 ml), and the mixture was left for 2 h at room temperature. The mixture was subjected to preparative TLC with $CHCl_3$–MeOH (96:4) to give penta-*O*-methyldavallialactone (**3**) (17.5 mg) as an amorphous solid, $[\alpha]_D^{22}$ +291.7° (c=0.5, MeOH). UV λ_{max} nm (log ε): 226 (4.39), 260 (4.33), 318 (3.95), 382 (4.32). IR ν_{max} cm^{-1}: 1696, 1665 (conjugated CO), 1640 (C=C), 1610, 1544, 1517, 1464 (aromatic ring). ^{1}H- and ^{13}C-NMR: Tables I and II. EI-MS m/z (%): 534 (M^+, 17), 450 (**a**, 100), 288 (**b**+H, 52), 191 (**c**, 38), 151 (**d**+H, 7). HR-MS Found (Calcd for) m/z: 534.1900 [$C_{30}H_{30}O_9$ (M^+), 534.1890], 450.1681 ($C_{26}H_{26}O_7$, 450.1679), 288.0986 ($C_{16}H_{16}O_5$, 288.0997), 191.0712 ($C_{11}H_{11}O_3$, 191.0708).

Reduction of 3 with $NaBH_4$ A solution of **3** (10 mg) in MeOH–isopropanol (1:1) (0.2 ml) was stirred with $NaBH_4$ (10 mg) for 1.5 h at room temperature. The reaction mixture was subjected to preparative TLC with $CHCl_3$–MeOH (98:2) to give two fractions. The more polar fraction gave an alcohol **4a** (3.3 mg), while the less polar fraction afforded another alcohol **4b** (not very pure, 3.9 mg).

4a: An amorphous solid, $[\alpha]_D^{22}$ +207.5° (c=0.53, $CHCl_3$), +183.4° (c=0.53, MeOH). UV λ_{max} nm (log ε): 228 (4.26), 257 sh (3.94), 275 (3.99), 383 (4.01). IR ν_{max} cm^{-1}: 3592 (OH), 1693 (conjugated CO), 1635 (C=C), 1595, 1539, 1515, 1465 (aromatic ring). ^{1}H- and ^{13}C-NMR: Tables I and II. EI-MS m/z (%): 538 (M^+, 62), 520 (M^+-H_2O, 12), 502 (22), 476 (**f**, 16), 450 (**a**, 7), 387 (**h**, 28), 373 (**j**, 42), 371 (**l**, 24), 354 (**g**, 41), 330 (**o**, 79), 328 (**n**, 73), 314 (**m**, 100), 301 (**p**, 35), 191 (**c**, 65), 165 (**k**, 20), 151 (**i**, 77). HR-MS Found (Calcd for) m/z: 538.2237 [$C_{30}H_{34}O_9$ (M^+), 538.2202], 450.1665 ($C_{26}H_{26}O_7$, 450.1678), 387.1425 ($C_{21}H_{23}O_7$, 387.1443), 373.1678 ($C_{21}H_{25}O_6$, 373.1651), 354.1461 ($C_{21}H_{22}O_5$, 354.1466), 330.1110 ($C_{18}H_{18}O_6$, 330.1103), 328.1310 ($C_{19}H_{20}O_5$, 328.1310), 314.1141 ($C_{18}H_{18}O_5$, 314.1153), 301.1057 ($C_{17}H_{17}O_5$, 301.1075), 191.0690 ($C_{11}H_{11}O_3$, 191.0707), 151.0762 ($C_9H_{11}O_2$, 151.0759).

4b: An amorphous solid, $[\alpha]_D^{23}$ +218.1° (c=0.78, $CHCl_3$). UV λ_{max} nm (log ε): 228 (4.14), 258 sh (3.80), 276 (3.80), 383 (3.95). IR ν_{max} cm^{-1}: 3400 (OH), 1672 (conjugated CO), 1638 (C=C), 1598, 1515, 1465 (aromatic ring). ^{1}H-NMR: Table I. EI-MS m/z (%): 538 (M^+, 67), 520 (M^+-H_2O, 11), 502 (5), 476 (**f**, 6), 450 (**a**, 23), 387 (**h**, 12), 373 (**j**, 34), 354 (**g**, 17), 330 (**o**, 60), 328 (**n**, 85), 314 (**m**, 100), 301 (**p**, 20), 191 (**c**, 76), 165 (**k**, 12), 151 (**i**, 16). HR-MS Found (Calcd for) m/z: 538.2215 [$C_{30}H_{34}O_9$ (M^+), 538.2202], 450.1678 ($C_{26}H_{26}O_7$, 450.1678), 387.1416 ($C_{21}H_{23}O_7$, 387.1443), 354.1455 ($C_{21}H_{22}O_5$, 354.1466), 330.1133 ($C_{18}H_{18}O_6$, 330.1103), 328.1305 ($C_{19}H_{20}O_5$, 328.1310), 314.1146 ($C_{18}H_{18}O_5$, 314.1153), 301.1075 ($C_{17}H_{17}O_5$, 301.1075), 165.0585 ($C_9H_9O_3$, 165.0552).

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References and Notes

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3) *a*) A. Bax and M. F. Summers, *J. Am. Chem. Soc.*, **108**, 2093 (1986); *b*) M. F. Summers, L. G. Marzilli, and A. Bax, *ibid.*, **108**, 4285 (1986).
4) The long-range correlation peak between 2′-H and C-6′ was not observed, because it was obscured by strong F1-noises due to neighboring *O*-methyl signals.
5) The UV and IR spectra of **4a** resembled those of trimethylhispidin. This supported the presence of a trimethylhispidin moiety in **4a**. See *a*) R. L. Edwards, D. G. Lewis, and D. V. Wilson, *J. Chem. Soc.*, **1961**, 4995; *b*) J. D. Bu'Lock, P. R. Leeming, and H. G. Smith, *ibid.*, **1962**, 2085; *c*) M. Klaar and W. Steglich, *Chem. Ber.*, **110**, 1058 (1977); *d*) *Idem*, *ibid.*, **110**, 1063 (1977).
6) Reexamination of the ^{1}H- and ^{13}C-NMR spectra of davallialactone (reference 2) showed that they are in good agreement with the structure **1** and that the previous assignments of the ^{13}C-signals for C-1 and C-4′ must be interchanged (C-1, δ 162.9 and C-4′, δ 191.2 in DMSO-d_6).
7) The 4-hydroxy-α-pyrone group shows a UV maximum at around 280 nm. See K. Yamada, *Bull. Chem. Soc. Jpn.*, **35**, 1323 (1962).
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