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Studies on the Diterpenoids of *Rabdosia longituba* (MIQ.) HARA: Structure of a New Bitter Diterpenoid, Rabdolongin A, and the Absolute Stereochemistry of Rabdolongin B (=Maoecrystal D)

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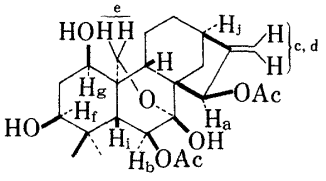
From the dried aerial parts of *Rabdosia longituba* (MIQ.) HARA, a new bitter diterpenoid, rabdolongin A (**1**), was isolated and its structure was elucidated on the basis of spectroscopic and chemical evidence. The absolute stereochemistry of rabdolongin B (=maoecrystal D) (**6**) was chemically established by correlation with trichokaurin (**8**) possessing known absolute stereochemistry.

Keywords——*Rabdosia longituba*; Labiatae; rabdolongin A; rabdolongin B; *ent*-kaurenoid; structure elucidation

Many diterpenoids have been isolated from the plants of the genus *Rabdosia* (Labiatae).[1] From *Rabdosia longituba* (MIQ.) HARA (Japanese name: akichôji),[2] several biologically active diterpenoids such as longikaurins,[3] oridonin, lasiokaurin, isodocarpin, and nodosin[4] have already been isolated. In a continuation of our studies on biologically active diterpenoids from the *Rabdosia* plants, we examined the constituents of the aerial parts of *R. longituba* (MIQ.) HARA collected in the suburbs of Hiroshima city, Japan, and isolated a new diterpenoid, rabdolongin A (**1**), together with rabdolongin B (=maoecrystal D) (**6**),[5,6] trichokaurin (**8**),[7] odonicin (**9**),[8] and rabdosianin B (**10**).[9] This paper deals with the structure elucidation of the new diterpene, rabdolongin A (**1**), and the chemical confirmation of the structure of rabdolongin B (=maoecrystal D) (**6**).



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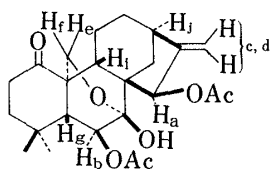

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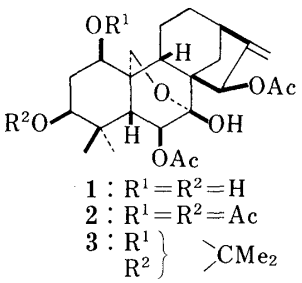
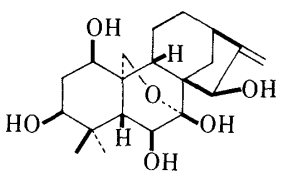
Rabdolongin A (**1**), mp 134—137 °C (from MeOH), $[\alpha]_D$ −75.5° (MeOH) was obtained as colorless prisms. The molecular formula was determined as $C_{24}H_{34}O_8 \cdot 1/2H_2O$ on the basis of the elemental analysis and high-resolution mass spectrum (High-MS). This compound did not show any absorption maximum above 220 nm in the ultraviolet (UV) spectrum. In addition to two tertiary methyl groups [δ_H 1.20 and 1.25 (each 3H, s); δ_C 21.7 and 28.7] and two acetyl groups [δ_H 2.13 and 2.19 (each 3H, s); δ_C 22.3, 23.6, 171.5 and 171.7], rabdolongin A (**1**) contains an *exo*-methylene group [δ_H (C_5D_5N) 5.09 (H_d) and 5.21 (H_c) (each 1H, br s); δ_C (C_5D_5N) 109.1 (t) and 160.1 (s)], three hydroxy groups [ν_{max} 3360 cm^{-1}; δ_H 6.27 (1H, br d, J=8 Hz), 7.07 (1H, br d, J=6 Hz) and 7.78 (1H, m), disappeared on addition of D_2O], an

oxygenated methylene group [δ_H 4.11 (2H, s) (H_e); δ_C 66.5 (t)] and a ketalic carbon (δ_C 96.1) as partial structures as judged from the infrared (IR) spectrum, and proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra. The ^{1}H-NMR spectrum of **1** showed the presence of two methine protons [δ_H 3.72 (1H, t, J=3 Hz, on addition of D_2O) (H_g) and 3.77 (1H, t, J=3 Hz, on addition of D_2O) (H_f)] on the carbons having a hydroxy group and two methine protons [δ_H 5.90 (1H, d, J=7 Hz) (H_b) and 6.20 (1H, t, J=2 Hz) (H_a)] on the carbons having an acetoxyl group. The ^{13}C-NMR signals at δ_C 77.2, 75.7, 75.1 and 68.1 ppm support the presence of four secondary carbinyl carbons. The presence of two secondary hydroxy groups was confirmed by the fact that rabdolongin A (**1**) gave the diacetate (**2**) [mp 206—209 °C (from MeOH); δ_H ($CDCl_3$) 2.21 (3H, s), 2.08 (3H, s), 2.06 (6H, s), 4.61 (1H, t, J=3 Hz) and 4.76 (1H, t, J=2.5 Hz)]. The ^{13}C-NMR spectrum of **1** further showed signals due to four methylenes, three methines and three quaternary carbons in addition to the signals mentioned above. Consideration of the structures of diterpenoids isolated so far from the genus Rabdosia[1] in relation to the above-mentioned spectral data suggests that rabdolongin A (**1**) has a pentacyclic *ent*-7β,20-epoxykaur-16-en-7α-ol (**7**) nucleus as the basic skeleton, as in the case of trichokaurin (**8**) which was isolated at the same time. The locations of two secondary hydroxy groups and two secondary acetoxyl groups were elucidated on the basis of the results of spin–spin decoupling experiments and nuclear Overhauser effect (NOE) experiments in the ^{1}H-NMR spectrum. On irradiation at the frequency of H_a, the signal of H_c became sharp and the signal of H_d collapsed to a singlet. When the frequency of H_c was irradiated, the signal of H_a changed to a doublet (J=2 Hz) and the signal of H_d became sharp. Both signals due to H_c and H_a became sharp on irradiation at the frequency of H_d. When the frequency of either H_c or H_d was irradiated, the signal H_j became sharp. On the other hand, the signals of H_c and H_d changed to a doublet (J=2 Hz) and a doublet (J=2 Hz), respectively, on irradiation at the frequency of H_j. On the basis of these findings, H_c and H_d were assigned as 17-H_2 and H_j was assigned as 13-H. Accordingly, an acetoxyl group is located at C-15. The acetoxyl group was presumed to take β-configuration since the proton signal [δ_H ($CDCl_3$) 5.65 (1H, t, J=2 Hz)] is very similar to that [δ_H ($CDCl_3$) 5.62 (1H, t, J=2 Hz)] of trichokaurin (**8**).[7] The presumption was confirmed by the following chemical reactions. Lithium aluminum hydride reduction of rabdolongin A (**1**) gave the deacetylated compound (**4**), which was then subjected to the conditions for the garryfoline-cuauchichicine rearrangement[10] to give the dihydroketone (**5**), indicating the β-configuration of the acetoxyl group at C-15. Compound **5** showed a negative Cotton effect in the optical rotatory dispersion (ORD) spectrum. Thus, the absolute stereochemistry was



1 : R^1=R^2=H
2 : R^1=R^2=Ac
3 : R^1, R^2 } >CMe$_2$



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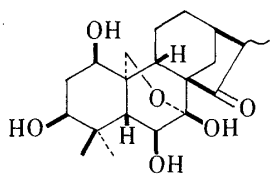

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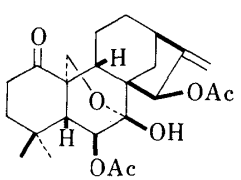

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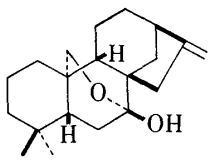

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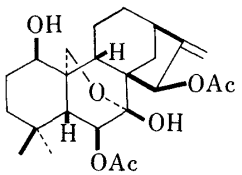

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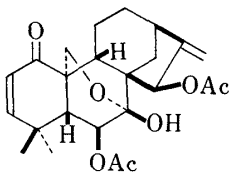

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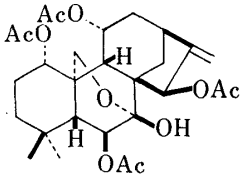

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verified to be as shown. On irradiation at the frequency of H_b, the signal of H_i [δ_H 2.65 (1H, d, $J=7$ Hz), 5-H] collapsed to a singlet. On the other hand, the signal of H_b collapsed to a singlet on irradiation at the frequency of H_i. When the signals at δ 1.25 (18-H_3) and 1.20 (19-H_3) were irradiated, respectively, NOE's for H_i (11.6%) and H_b (14.6%), and NOE for H_b (19.4%) were observed. On the basis of the results, H_b was assigned as 6α-H. Consequently, another acetoxyl group is located at C-6β. The remaining two secondary hydroxy groups were deduced to be located at C-1β and C-3β based on the following discussion. On irradiation at δ 1.20 and 1.25, NOE's for H_f (9.6 and 7.6%, respectively) were observed, indicating the location of a β-axial hydroxy group at C-3. NOE (13%) was observed for H_g when the frequency of H_e (20-H_2) was irradiated, suggesting the location of a β-axial hydroxy group at C-1β. The arrangement of two secondary hydroxy groups in a 1,3-diaxial relationship was confirmed by the fact that treatment of rabdolongin A (**1**) with 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-toluenesulfonic acid in *N*,*N*-dimethylformamide gave an acetonide (**3**) [δ_H 1.44 and 1.57 (each 3H, s)]. On the basis of these findings, the structure of rabdolongin A should be represented as *ent*-7β,20-epoxy-1α,3α,6α,7α,15α-pentahydroxykaur-16-ene 6,15-diacetate (**1**).

Rabdolongin B (=maoecrystal D) (**6**),[5,6] mp 185—187 °C (MeOH), $[\alpha]_D$ +14.3° (MeOH) was obtained as colorless prisms. The molecular formula was determined as $C_{24}H_{32}O_7$ on the basis of the elemental analysis and High-MS, and was 2 mass units less than that of trichokaurin (**8**). In addition to two tertiary methyl groups [δ_H 0.90 and 0.95 (each 3H, s); δ_C 21.1 and 29.5] and two acetyl groups [δ_H 2.14 and 2.33 (each 3H, s)]; δ_C 21.9 23.0 170.5 and 170.7], rabdolongin B (**6**) contains a hydroxy group [ν_{max} 3380 cm^{-1}; δ_H 8.57 (1H, s)], an *exo*-methylene group [δ_H 5.16 (2H, m), H_c and H_d; δ_C 109.6 (t) and 158.6 (s)], an oxygenated methylene group [δ_H 4.17 (1H, dd, $J=10$ and 1.5 Hz), H_f and 4.63 (1H, dd, $J=10$ and 1 Hz), H_e; δ_C 64.8], two secondary carbinyl functional groups having an acetyl group on them [δ_H 5.69 (1H, d, $J=9.5$ Hz), H_b and 6.17 (1H, t, $J=2.5$ Hz), H_a; δ_C 73.9 and 75.2], a ketal (δ_C 96.2), and an isolated ketone (δ_C 212.2) as partial structures. The ^{13}C-NMR spectrum of **6** showed, in addition to the above-mentioned signals, signals due to five methylenes, three methines and three quaternary carbons. Based on the findings mentioned above, rabdolongin B (**6**) was presumed to have the structure which corresponds to the 1-dehydro derivative of trichokaurin (**8**). Jones oxidation of trichokaurin (**8**) gave rabdolongin B (**6**). Thus, the structure of rabdolongin B was determined as *ent*-7β,20-epoxy-6α,7α,15α-trihydroxy-kaur-16-en-1-one 6,15-diacetate (**6**).

Experimental

Melting points were obtained on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. ^{1}H- and ^{13}C-NMR spectra were taken with a JEOL JNM FX 200 spectrometer (^{1}H, 200 MHz; ^{13}C, 50.1 MHz). Tetramethylsilane was used as the internal standard and chemical shifts were given in δ (ppm) values. MS were determined with a JEOL D-300 spectrometer. Optical rotations were measured with a Union Giken PM-201 digital polarimeter. ORD spectra were taken with a JASCO ORD/UV-5 spectrophotometer. Kiesel gel 60 (0.063—0.200 mm, Merck) was used for column chromatography and precoated silica gel plates F_{254} (0.25 mm and 0.5 mm in thickness) were used for thin layer and preparative layer chromatography, respectively. Extracts were dried over anhydrous magnesium sulfate.

Isolation of Diterpenoids from *Rabdosia longituba*.——Dried aerial parts of *R. longituba* (Miq.) Hara (3.4 kg) were extracted with MeOH (80 l) at room temperature for 2 weeks. The methanolic extract was concentrated *in vacuo* to give a residue which was partitioned between 90% MeOH (2.5 l) and *n*-hexane (2.3 l × 3). The 90% methanolic layer was concentrated under reduced pressure. The residue was suspended in water (900 ml) and extracted with AcOEt (900 ml × 3). The AcOEt extract was washed with water, dried and evaporated under reduced pressure to give a residue (61 g), which was chromatographed on a silica gel (1.5 kg) column. Elution was carried out with $CHCl_3$–Me_2CO with increasing Me_2CO content: $CHCl_3$ (8 l), $CHCl_3$–Me_2CO (19:1) (10 l), $CHCl_3$–Me_2CO (9:1) (8 l), $CHCl_3$–Me_2CO (85:15) (8.8 l), $CHCl_3$–Me_2CO (8:2) (8.8 l), $CHCl_3$–Me_2CO (7:3) (9.2 l) and Me_2CO (5 l) were passed successively, and 500 ml fractions were collected.

Fractions 19—21 were combined and evaporated under reduced pressure to give a residue (8.18 g) which was separated by a repeated silica gel chromatography (solvent: $CHCl_3$–Me_2CO; *n*-hexane–AcOEt) to give rabdolongin B (=maoecrystal D) (**6**)[5,6] (96.5 mg), trichokaurin (**8**)[7] (542 mg), odonicin (**9**)[8] (2.043 g) and rabdosianin B (**10**)[9] (6.5 mg).

Fractions 22—24 were combined and evaporated under reduced pressure to give a residue (9.848 g), which was separated by repeated silica gel chromatography (solvent: $CHCl_3$–Me_2CO; *n*-hexane–AcOEt) to give further **8** (1.053 g), **9** (1.187 g) and **10** (26.6 mg).

Fractions 53—67 were combined and evaporated under reduced pressure to give a residue (2.20 g) which was separated by repeated silica gel chromatography (solvents: Et_2O, $CHCl_3$–Me_2CO) to give a new compound, named rabdolongin A (**1**) (90.8 mg).

Among the isolated compounds, trichokaurin (**8**), odonicin (**9**), and rabdosianin B (**10**) were identified on the basis of comparisons of the spectral data with those reported.[7-9]

The physical properties of rabdolongins A (**1**) and B (=maoecrystal D) (**6**)[5,6] are as follows:

Rabdolongin A (**1**): mp 134—137 °C, $[\alpha]_D^{23}$ −75.5° (c=1.02, MeOH). IR ν_{max}^{KBr}: 3360, 1730, 1365, 1250, 1040 cm^{-1}. ^{1}H-NMR δ (C_5D_5N): 1.20 and 1.25 (each 3H, s, *tert*-Me_2), 2.13 and 2.19 (each 3H, s, OAc_2), 2.58 (1H, br d, J=9 Hz, 13-H; H_j), 2.65 (1H, d, J=7 Hz, 5-H; H_i), 3.21 (1H, dd, J=12, 6 Hz, 9-H), 3.74 (2H, m, δ 3.72, t, J=3 Hz, 1-H; H_g and 3.77, t, J=3 Hz, 3-H; H_f on addition of D_2O), 4.11 (2H, s, 20-H_2; H_e), 5.09 (1H, br s, 17-H_1; H_d), 5.21 (1H, br s, 17-H_1; H_c), 5.90 (1H, d, J=7 Hz, 6-H; H_b), 6.20 (1H, t, J=2 Hz, 15-H; H_a), 6.27 (1H, br d, J=8 Hz, OH), 7.07 (1H, br d, J=6 Hz, OH), 7.78 (1H, m, OH); δ ($CDCl_3$): 0.97 and 1.14 (each 3H, s, *tert.* Me_2), 2.08 and 2.19 (each 3H, s, OAc_2), 2.24 (1H, d, J=7 Hz), 2.56—2.75 (2H, m), 2.97 (1H, m, OH), 3.56 (1H, m, changed to br t, J=3 Hz, on addition of D_2O), 3.70 (1H, m, changed to br t, J=3 Hz, on addition of D_2O), 3.72 (1H, s, OH), 3.90 (1H, dd, J=9.5, 1.5 Hz), 3.96 (1H, dd, J=9.5, 1 Hz), 4.91 (1H, br s), 5.05 (1H, dd, J=2.5, 1 Hz), 5.25 (1H, d, J=7 Hz), 5.65 (1H, t, J=2 Hz). ^{13}C-NMR δ (C_5D_5N): 15.6 (t), 21.7 (q), 22.3 (q), 23.6 (q), 28.1 (t), 28.7 (q), 31.6 (t), 32.1 (t), 37.3 (d), 39.2 (s), 39.6 (d), 41.7 (s), 45.9 (d), 51.6 (s), 66.5 (t), 68.1 (d), 75.1 (d), 75.7 (d), 77.2 (d), 96.1 (s), 109.1 (t), 160.1 (s), 171.5 (s), 171.7 (s). MS m/z: Found 450.2249 $(M)^+$. Calcd for $C_{24}H_{34}O_8$: 450.2254. *Anal.* Calcd for $C_{24}H_{34}O_8 \cdot 1/2H_2O$: C, 62.73; H, 7.68. Found: C, 62.98; H, 7.83.

Rabdolongin B (maoecrystal D) (**6**): mp 185—187 °C, $[\alpha]_D^{19}$ +14.3° (c=0.91, MeOH). IR ν_{max}^{KBr}: 3380, 1740, 1695, 1655, 1380, 1245, 1060 cm^{-1}. ^{1}H-NMR δ (C_5D_5N): 0.90 and 0.95 (each 3H, s, *tert.* Me_2), 2.14 and 2.33 (each 3H, s, OAc_2), 2.57 (1H, br dd, J=9, 4 Hz, 13-H; H_j), 2.74 (1H, dd, J=11, 6.5 Hz, 9-H; H_i), 2.82 (1H, br d, J=9.5 Hz, 5-H; H_g), 4.17 (1H, dd, J=10, 1.5 Hz, 20-H_1; H_f), 4.63 (1H, dd, J=10, 1 Hz, 20-H_1; H_e), 5.16 (2H, m, 17-H_2; H_c and H_d), 5.69 (1H, d, J=9.5 Hz, 6-H; H_b), 6.17 (1H, t, J=2.5 Hz, 15-H; H_a), 8.57 (1H, s, OH); δ ($CDCl_3$): 0.92 and 0.98 (each 3H, s, *tert*-Me_2), 2.08 and 2.24 (each 3H, s, OAc_2), 3.46 (1H, s, OH), 3.96 (1H, dd, J=10.5, 2 Hz), 4.37 (1H, dd, J=10.5, 1 Hz), 4.89 (1H, br t, J=2 Hz), 5.09 (1H, br t, J=2 Hz), 5.12 (1H, d, J=9.5 Hz), 5.67 (1H, t, J=2.5 Hz). ^{13}C-NMR δ (C_5D_5N): 17.8 (t), 21.1 (q), 21.9 (q), 23.0 (q), 27.0 (t), 29.5 (q), 32.2 (t), 32.7 (s), 35.6 (t), 35.9 (d), 38.5 (t), 42.7 (d), 49.0 (s), 52.1 (s), 54.2 (d), 64.8 (t), 73.9 (d), 75.2 (d), 96.2 (s), 109.6 (t), 158.6 (s), 170.5 (s), 170.7 (s), 212.2 (s). MS m/z: Found 432.2164 $(M)^+$. Calcd for $C_{24}H_{32}O_7$: 432.2149. *Anal.* Calcd for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.76; H, 7.61. This compound was identical with an authentic sample of maoecrystal D[5] on the basis of mixed melting point determination and comparisons of IR and ^{1}H-NMR spectra.

Rabdolongin A Diacetate (2)——Rabdolongin A (**1**) (6.0 mg) was dissolved in a mixture of acetic anhydride (0.3 ml) and anhydrous pyridine (0.3 ml) and the solution was warmed at 50 °C for 50 h. After addition of excess MeOH, the mixture was concentrated under reduced pressure to give a residue (5.8 mg), which was purified by preparative layer chromatography (solvent: $CHCl_3$–Me_2CO 19:1; developed three times) to give the diacetate (**2**) (2.8 mg) as colorless needles, mp 206—209 °C (from MeOH). IR $\nu_{max}^{CHCl_3}$: 3550—3400, 1730, 1660, 1380, 1260—1200, 1060, 1020 cm^{-1}. ^{1}H-NMR δ ($CDCl_3$): 0.87 and 1.22 (each 3H, s, *tert*-Me_2), 2.06 (6H, s, OAc_2), 2.08 and 2.21 (each 3H, s, OAc_2), 2.33 (1H, d, J=7 Hz), 2.62 (2H, m), 3.73 (1H, s, OH), 3.98 (2H), 4.61 (1H, t, J=3 Hz), 4.76 (1H, t, J=2.5 Hz), 4.96 (1H, br t, J=1.5 Hz), 5.06 (1H, dd, J=2.5, 0.5 Hz), 5.21 (1H, d, J=7 Hz), 5.65 (1H, t, J=2 Hz). MS m/z: Found 534.2455 $(M)^+$. Calcd for $C_{28}H_{38}O_{10}$: 534.2465.

Reductive Deacetylation of Rabdolongin A (1)——A solution of rabdolongin A (**1**) (43.5 mg) dissolved in anhydrous tetrahydrofuran (10 ml) was added dropwise to a suspension of lithium aluminum hydride (45 mg) in anhydrous tetrahydrofuran (5 ml) under stirring. After refluxing for 3 h, the mixture was cooled and treated with AcOEt (10 ml) and water (5 ml), successively. The resulting precipitates were removed by filtration and washed with AcOEt (10 ml × 2). The filtrate and washings were combined and washed with 1 N hydrochloric acid (50 ml) and saturated sodium chloride aqueous solution (50 ml × 3), successively. The organic phase was dried and evaporated under reduced pressure to give a residue (21.2 mg), which was recrystallized from MeOH to give dideacetylrabdolongin A (**4**) as colorless needles, mp 252—254 °C. IR ν_{max}^{KBr}: 3500—3150, 1650, 1445, 1290, 1130, 1065, 900 cm^{-1}. ^{1}H-NMR δ (C_5D_5N): 1.19 and 1.52 (each 3H, s, *tert*-Me_2), 2.65 (1H, d, J=5.5 Hz, 5-H), 2.70 (1H, m, 13-H), 3.28 (1H, dd, J=12, 5.5 Hz, 9-H), 3.80 [2H, m, changed to δ 3.76 (1H, t, J=3 Hz) and 3.83 (1H, t, J=3 Hz) on addition of D_2O], 4.09 (1H, dd, J=9.5, 2 Hz, 20-H_1), 4.23 (1H, dd, J=9.5, 1 Hz, 20-H_1), 4.42 (1H, t, J=5.5 Hz, changed to d, J=5.5 Hz on addition of D_2O, 6-H), 5.20 (1H, br s, 17-H_1), 5.26 (1H, m, 15-H), 5.50 (1H, br s, 17-H_1), 6.19 (1H, d, J=7.5 Hz, OH), 7.07 (1H, d, J=6 Hz, OH), 7.29 (1H, d, J=3.5 Hz, OH), 7.94 (1H, br s, OH), 8.07 (1H, d, J=6.5 Hz,

OH). MS *m/z*: Found 366.2026 $(M)^+$. Calcd for $C_{20}H_{30}O_6$: 366.2043.

Acid Treatment of Dideacetylrabdolongin A (4)——Dideacetylrabdolongin A (**4**) (14.1 mg) was dissolved in MeOH (3 ml). Concentrated hydrochloric acid (10 drops) was added to the solution and the mixture was stirred for 7 d at room temperature. After addition of water (30 ml), the reaction mixture was neutralized with a small amount of sodium hydrogen carbonate and extracted with AcOEt (30 ml × 3). After being washed with saturated sodium chloride aqueous solution, the AcOEt extract was dried and evaporated under reduced pressure to give a residue (12.5 mg), which crystallized on addition of $CHCl_3$. After being washed with $CHCl_3$, the dihydroketone (**5**) (11.9 mg) was collected by filtration. mp 239—242 °C, $[\alpha]_D^{27}$ −83.8° (*c*=0.37, MeOH). IR ν_{max}^{KBr}: 3550—3150, 1710, 1455, 1075 cm^{-1}. ^{1}H-NMR δ (C_5D_5N): 1.02 (1.65H, d, *J*=6.5 Hz), 1.105 (1.35H, d, *J*=7.5 Hz), 1.114 (3H, s), 1.51 (1.65H, s), 1.53 (1.35H, s), 3.67 (1H, m, changed to t, *J*=2 Hz, on addition of D_2O), 3.82 (1H, m, changed to t, *J*=3 Hz, on addition of D_2O), 4.01 (0.55H, dd, *J*=10, 1.5 Hz), 4.02 (0.45H, dd, *J*=10, 2 Hz), 4.12 (0.55H, dd, *J*=10, 1 Hz), 4.13 (0.45H, dd, *J*=10, 1 Hz), 4.32 (0.55H, t, *J*=5 Hz, changed to d, *J*=5 Hz, on addition of D_2O), 4.38 (0.45H, t, *J*=5 Hz, changed to d, *J*=5 Hz, on addition of D_2O), 6.05 (1H, m, OH), 6.87 (0.55H, d, *J*=11 Hz, OH), 7.03 (0.45H, d, *J*=10.5 Hz, OH), 7.26 (1H, m, OH). ORD λ_{max} (MeOH) nm (ϕ): 316 (−4199), 283 (1228). MS *m/z*: Found 366.2050 $(M)^+$. Calcd for $C_{20}H_{30}O_6$: 366.2043. This sample was found to be a mixture of 16*R* and 16*S* isomers in a 55 : 45 ratio as judged from the ^{1}H-NMR spectrum.

Rabdolongin A Acetonide (3)——Rabdolongin A (**1**) (12.0 mg) was dissolved in anhydrous *N,N*-dimethylformamide (1 ml). 2,2-Dimethoxypropane (1 ml) and *p*-toluenesulfonic acid (1 mg) were added to the solution and the mixture was heated at 80 °C for 3 h. The reaction mixture was concentrated under reduced pressure to give a residue which was dissolved in AcOEt (30 ml). The solution was washed with 5% sodium hydrogen carbonate aqueous solution and then with water. The dried AcOEt extract was concentrated under reduced pressure to give a residue (25.2 mg), which was purified by preparative layer chromatography (solvent: $CHCl_3$–Me_2CO 19 : 1) to give the acetonide (**3**) (8.9 mg) as an amorphous powder. IR $\nu_{max}^{CHCl_3}$: 3530, 1730, 1660, 1380, 1260—1190, 1115, 1045 cm^{-1}. ^{1}H-NMR δ ($CDCl_3$): 0.99 and 1.05 (each 3H, s, *tert*-Me_2), 1.44 and 1.57 (each 3H, s, acetonide Me_2), 2.08 and 2.19 (each 3H, s, OAc_2), 2.43 (1H, d, *J*=8.5 Hz), 3.57 (1H, s, OH), 3.69 (1H, br d, *J*=5 Hz), 3.77 (1H, m, $W_{1/2}$=8 Hz), 3.90 (2H, s), 4.91 (1H, br t, *J*=1 Hz), 5.06 (1H, dd, *J*=2.5, 1 Hz), 5.25 (1H, d, *J*=8.5 Hz), 5.63 (1H, t, *J*=2.5 Hz). MS *m/z*: Found 490.2584 $(M)^+$. Calcd for $C_{27}H_{38}O_8$: 490.2567.

Jones Oxidation of Trichokaurin (8)——Trichokaurin (**8**) (43.2 mg) was dissolved in Me_2CO (10 ml). The solution was stirred with Jones reagent (0.3 ml) for 5 min under ice cooling. After being neutralized with 5% sodium hydrogen carbonate aqueous solution, the reaction mixture was concentrated under reduced pressure. The residue was suspended in H_2O (30 ml) and the mixture was extracted with AcOEt (30 ml × 2). After being washed with saturated sodium chloride aqueous solution, the AcOEt extract was dried and evaporated under reduced pressure to give rabdolongin B (**6**) (42 mg) as colorless prisms, mp 179—182 °C. This compound was identical with the compound of natural origin on the basis of mixed melting point determination and comparisons of IR and ^{1}H-NMR spectra.

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