Rabdokaurins C and D, Two New Diterpenes from *Rabdosia longituba*

Yoshio TAKEDA,*[,a] Yukako FUTATSUISHI,[b] Teruyoshi ICHIHARA,[b] Takashi MATSUMOTO,[a] Hiromitsu TERAO,[a] Hiroshi TERADA,[b] and Hideaki OTSUKA[c]

Faculty of Integrated Arts and Sciences, The University of Tokushima,[a] Tokushima 770, Japan, Faculty of Pharmaceutical Sciences, The University of Tokushima,[b] Tokushima 770, Japan, and Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine,[c] Minami-ku, Hiroshima 734, Japan. Received October 12, 1992

From the dried aerial parts of *Rabdosia longituba* (MIQ.) HARA, two new diterpenes, named rabdokaurin C (1) and rabdokaurin D (8), were isolated together with the known compounds oridonin, lasiokaurin, effusanin B, rabdophyllin G, and rabdokaurin B. The structures of the two new compounds were determined on the basis of spectroscopic and chemical evidence.

Keywords *Rabdosia longituba*; *ent*-kaurenoid; rabdokaurin C; rabdokaurin D; Labiatae; 6,7-seco-*ent*-kaurenoid

Many diterpenes, such as oridonin-type compounds having an *ent*-7β,20-epoxykaurene skeleton, and isolongirabdiol and enmein types featuring cleavage of the bond between C-6 and C-7 of the former carbon skeleton, have been isolated[1] from the aerial parts of *Rabdosia longituba* (MIQ.) HARA.[2] Many of them show a variety of biological activities, such as antibacterial and antitumor activities.[3] In a continuation of our studies on the diterpenoid constituents of plants belonged to the genus *Rabdosia* (Labiatae), we examined the constituents of the title plant collected in Okayama Prefecture, Japan and isolated two new diterpenes, rabdokaurins C (**1**) and D (**8**), together with the known compounds oridonin (**3**),[4] lasiokaurin (**4**),[5] effusanin B (**5**),[6] rabdophyllin G (**9**),[7] and rabdokaurin B (**10**).[8] This paper deals with the structure determination of the new compounds.

Rabdokaurin C (**1**) was obtained as colorless needless, mp 232—234 °C, $[\alpha]_D$ −17.5° (c=1.16, C_5H_5N) and its molecular formula was determined as $C_{24}H_{34}O_8$ on the basis of the high-resolution MS. From an inspection of the ^{1}H- and ^{13}C-NMR spectra, rabdokaurin C (**1**) was suggested to contain two tertiary methyl groups [δ_H 0.86 and 1.17 (each 3H, s); δ_C 21.4 and 31.3 (each q)], two acetoxyl groups [δ_H 2.01 and 2.19 (each 3H, s); δ_C 21.3 (q), 21.4 (q), 169.2 (s) and 169.9 (s)], three hydroxyl groups [δ_H 4.35 (1H, s) (H_h), 8.09 (1H, m), 8.23 (1H, m)], a ketalic group [δ_C 98.3 (s)], an *exo*-methylene group [δ_H 5.34 (H_d) and 5.63 (H_b) (each 1H, br s)], a methylene group bearing an oxygen atom [δ_H 4.43 (H_i) and 4.54 (H_g) (each 1H, d, J=9.6 Hz), δ_C 63.2 (t)] and four secondary carbinyl groups [δ_H 4.90 (1H, dd, J=11.6, 6 Hz) (H_f), 5.02 (1H, s) (H_e), 5.48 (1H, br s) (H_c), and 5.79 (1H, d, J=6.6 Hz) (H_a), δ_C 72.9, 74.3, 75.9, 76.0 (each d)]. The ^{13}C-NMR spectrum (Table I) showed, besides the signals mentioned above, the presence of four methylene groups, three methine groups and four quaternary carbon atoms. These spectral data, coupled with a consideration of the structures of diterpenes so far isolated from the genus *Rabdosia*,[9] suggested that rabdokaurin C (**1**) might have a structure in which two secondary acetoxyl groups and two secondary hydroxyl groups are introduced into an *ent*-7β,20-epoxykaur-16-ene 7α-ol skeleton. The protons H_c and H_e were assigned to protons on carbon bearing a hydroxyl group, based on the facts that H_c showed a cross peak in the ^{1}H-shift correlation spectroscopy (COSY) spectrum with H_h, which disappeared on addition of D_2O, and H_e was shifted downfield in the monoacetate (**2**) obtained by usual acetylation with acetic anhydride and pyridine. The protons H_b and H_d were assigned to the protons of an *exo*-methylene group based on the ^{1}H–^{13}C-COSY spectrum. Accordingly, the protons H_a and H_f were assigned to carbon bearing an acetoxyl group. The locations of the two hydroxyl and two acetoxyl groups were elucidated mainly by interpretation of the ^{1}H-COSY spectrum. Proton H_a showed a cross peak with H_o [δ 1.76 (1H, d, J=6.6 Hz)] which showed a cross peak with H_g (20-*pro*-*R*-H) due to the W-coupling interaction. Taking into account the coupling pattern of H_a, a secondary acetoxyl group was assigned to the C-6β axial position. Another proton (H_f) on a carbon bearing a secondary acetoxyl group showed cross peaks with protons (H_n and H_q) of a methylene group which further showed cross peaks with protons (H_{r2}) of another methylene group. This fact, together with a consideration

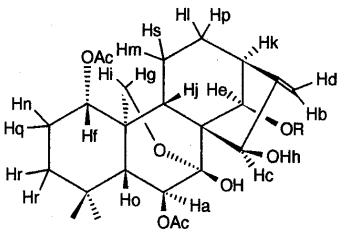
TABLE I. ^{13}C-NMR Data[a] (δ, ppm) for Rabdokaurins C (**1**) and D (**8**) in C_5D_5N

Carbon	1	8
1	76.0	77.1
2	25.3	24.1
3	37.9	34.5
4	33.6	38.7
5	55.2	46.7
6	74.3	58.5
7	98.3	171.0
8	53.3	58.8
9	44.5	42.3
10	39.8	44.3
11	16.7	17.9
12	32.2	30.2
13	45.7	35.3
14	75.9	29.3
15	72.9	202.5
16	160.7	151.4
17	110.0	118.3
18	31.3	70.6
19	21.7	20.0
20	63.2	69.4
OAc	21.3, 21.4, 169.2, 169.9	21.5, 170.2

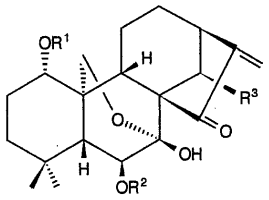
a) The assignments were based on analysis of a combination of proton noise decoupling, insensitive nuclei enhanced by polarization transfer and ^{1}H–^{13}C-COSY data, and a comparison with data for related compounds.

of the coupling pattern of H_f, suggested that an acetoxyl group might be located between a methylene group and a quaternary carbon atom, *i.e.*, C-1α or C-3α. The location was elucidated to be C-1α based on the fact that C-4 (δ 33.6) and C-10 (δ 39.8) resonated at almost the same fields as those (C-4, δ 33.9; C-10, δ 40.1) of effusanin B (**5**).[6] A proton (H_b) of an *exo*-methylene group showed a cross peak with a methine proton, H_k [δ 2.81 (1H, br d, J=9.2 Hz, 13-H)], which further showed a cross peak with H_e. Considering the coupling pattern, H_e was deduced to be located at C-14α, having a dihedral angle of *ca.* 90° to 13-H (H_k). Thus, a hydroxyl group is located at C-14β. Another hydroxyl group was elucidated to be at C-15 based on the fact that protons (H_b and H_d) of an *exo*-methylene group showed cross peaks with H_c. Thus, rabdokaurin C (**1**) was presumed to have an *ent*-7β,20-epoxy-1β,6α,7α,14α,15α-pentahydroxykaur-16-ene 1,6-diacetate structure (**1**), or its epimer at C-15. In order to confirm this and to determine the stereochemistry at C-15, chemical correlation of rabdokaurin C (**1**) and oridonin (**3**) of known absolute stereochemistry was performed. Oridonin 1,14-*O*-diacetate (**6**)[4] was reduced with $NaBH_4$ in the presence of $CeCl_3 \cdot 7H_2O$[9] to give an allylic alcohol (**7**), in which the newly formed hydroxyl group should have a β-orientation as the result of hydride attack from the less hindered α-side.[4] Acetylation of the allylic alcohol (**7**) gave the monoacetate (**2**), which was identical with the monoacetate (**2**) of rabdokaurin C (**1**). Thus, the structure of rabdokaurin C was established as *ent*-7β,20-epoxy-1β,6α,7α,14α,15α-pentahydroxykaur-16-ene 1,6-diacetate (**1**).

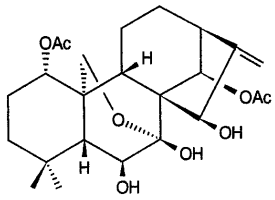
Rabdokaurin D (**8**) was obtained as colorless needles, mp 227—230 °C, $[\alpha]_D$ +34.1° (c=0.62, MeOH) and the molecular formula was determined as $C_{22}H_{30}O_7$ based on its high-resolution MS. Rabdokaurin D (**8**) was suggested to contain a tertiary methyl group [δ_H 0.90 (3H, s); δ_C 20.0 (q)], a secondary acetoxyl group [δ_H 2.19 (3H, s), 5.12 (1H, dd, J=10, 5 Hz); δ_C 21.5 (q), 77.1 (d), 170.2 (s)], two hydroxyl groups [δ_H 6.48 (2H, m)], a δ-lactone [IR ν_{max}: 1710 cm^{-1}; δ_C 171.0 (s)], three methylene groups of which two have hydroxyl groups and one has an oxygen atom of a lactone moiety [δ_H 3.37 and 3.79 (each 1H, d, J=11.0 Hz), 4.00 (2H, m), and 5.00 and 5.23 (each 1H, d, J=12.5 Hz); δ_C 58.5, 69.4 and 70.6 (each t)], and a five-membered ketone group conjugated with an *exo*-methylene group [UV λ_{max}^{MeOH} nm (ε): 232 (7910); ν_{max}: 1710 cm^{-1}; δ_H 5.35 and 5.98 (each 1H, br s); δ_C 118.3 (t), 151.4 (s), and 202.5 (s)] as partial structures. The ^{13}C-NMR spectrum (Table I) showed the presence of five methylene groups, three methine groups and three quaternary carbon atoms in addition to the signals mentioned above. These spectral data, coupled with the fact that the dihydrocompound (**12**) obtained by catalytic hydrogenation showed a negative Cotton effect in the circular dichroism (CD) spectrum,[10] like that of rabdokaurin B (**10**)[1] except for the fact that the number of acetoxyl groups was decreased from 2 to 1 and the signal due to 6-H_2 suffered an upfield shift by *ca.* 0.5 ppm in the ^{1}H-NMR spectrum compared to that of rabdokaurin B (**10**). Thus, rabdokaurin D was presumed to have a structure which corresponds to 6-*O*-deacetylrabdokaurin B (**8**). This presumption was confirmed by the finding that the diacetate (**11**) obtained by usual acetylation with acetic anhydride and pyridine is identical with the monoacetate of rabdokaurin B (**10**).



1 : R=H
2 : R=Ac



3 : R^1=R^2=H ; R^3=OH
4 : R^1=Ac ; R^2=H ; R^3=OH
5 : R^1=Ac ; R^2=R^3=H
6 : R^1=Ac ; R^2=H ; R^3=OAc



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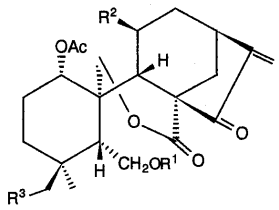
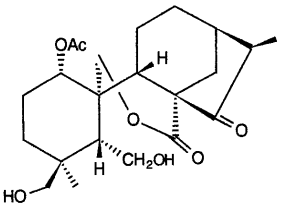


8 : R^1=R^2=H ; R^3=OH
9 : R^1=R^3=H ; R^2=OH
10 : R^1=Ac ; R^2=H ; R^3=OH
11 : R^1=Ac ; R^2=H ; R^3=OAc



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Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. UV spectra were measured on a Shimadzu UV-160 spectrometer. Optical rotations were measured on a Union-Giken PM 201 polarimeter or JASCO DIP-360 digital polarimeter. IR spectra were measured on a Hitachi 215, a Shimadzu IR-400, or a Perkin–Elmer model 1720 FTIR spectrometer. CD spectra were measured on a JASCO J-600 spectropolarimeter. ^{1}H- and ^{13}C-NMR spectra were measured on a JEOL JNM FX-200 (^{1}H, 200 MHz; ^{13}C, 50 MHz) or a JEOL JNM GSX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer. The chemical shifts are given in δ (ppm) values using tetramethylsilane as an internal standard. MS were determined on a JEOL D-300 spectrometer. Precoated silica gel plates F_{254} (0.25 and 0.5 mm in thickness, Merck) were used for TLC and preparative layer chromatography.

Plant Material The plant material used was collected in Shingou Town, Atetsu-gun, Okayama Prefecture, on 23rd September, 1989 and identified by one (H. O.) of the authors. A voucher specimen (89-RL-24-Okayama) is being kept in the laboratory of one (H. O.) of the authors.

Isolation of Diterpenoids The aerial parts (598 g) of *Rabdosia longituba* were extracted twice with refluxing MeOH (10.5 l×2) for 15 min. The combined extract was evaporated *in vacuo* and the residue was dissolved in 90% MeOH (400 ml). The solution was partitioned with *n*-hexane (400 ml×3). The 90% MeOH layer was concentrated *in vacuo*. The residue was suspended in H_2O (400 ml) and the suspension was partitioned with EtOAc (400 ml×3). The EtOAc extract was washed with H_2O, dried and evaporated *in vacuo* to give a residue (12.508 g), an

aliquot (12.070 g) of which was chromatographed over silica gel (500 g) with mixtures of $CHCl_3$ and Me_2CO containing increasing Me_2CO content. $CHCl_3$ (3 l) was used as the first eluent, then $CHCl_3$–Me_2CO (19:1) (3 l), $CHCl_3$–Me_2CO (9:1) (3 l), $CHCl_3$–Me_2CO (17:3) (3 l), $CHCl_3$–Me_2CO (4:1) (3 l), $CHCl_3$–Me_2CO (7:3) (3 l), $CHCl_3$–Me_2CO (1:1) (1.8 l) and finally Me_2CO (2 l), collecting 300 ml fractions.

Fraction nos. 18—24 gave a residue (0.690 g), which was chromatographed over silica gel (50 g) with Et_2O, collecting 4 ml fractions. Fraction nos. 26—33 gave a residue (0.076 g), which was purified by preparative layer chromatography (solvent, *n*-hexane–EtOAc 1:1) to give effusanin B (**5**) (0.059 g).

Fraction nos. 25—30 gave a residue (0.896 g), which was chromatographed over silica gel (80 g) with Et_2O, collecting 10 ml fractions. Fraction nos. 31—44 gave a residue (0.088 g), which was purified by preparative layer chromatography (solvent, *n*-hexane–EtOAc 1:2, developed twice) to give rabdokaurin C (**1**) (17.4 mg). Fraction nos. 53—85 gave a residue (0.186 g), an aliquot (50 mg) of which was purified by preparative layer chromatography (solvent, $CHCl_3$–MeOH 97:3, developed three times) to give rabdophyllin G (**9**) (20.7 mg). Fraction nos. 95—98 gave a residue (0.332 g), an aliquot (50 mg) of which was purified by preparative layer chromatography (solvent, $CHCl_3$–Me_2CO 17:3, developed twice) to give rabdokaurin B (**10**) (28.6 mg).

Fraction nos. 36—45 gave a residue (0.925 g), which was recrystallized from MeOH to give lasiokaurin (**4**) (0.197 g).

Fraction nos. 46—62 gave a residue (1.090 g), which was chromatographed over silica gel (80 g) with mixtures of $CHCl_3$ and MeOH. $CHCl_3$ (600 ml) was used as the first eluent, and then $CHCl_3$–MeOH 99:1 (600 ml), $CHCl_3$–MeOH 97:3 (600 ml) and $CHCl_3$–MeOH 19:1 (600 ml) were passed successively, collecting 100 ml fractions. Fraction nos. 17—19 gave a residue (0.346 g), an aliquot (95 mg) of which was purified by preparative layer chromatography (solvent, Et_2O, developed five times) to give rabdokaurin D (**8**) (26.3 mg).

Fraction nos. 63—69 gave a residue (0.446 g), which was chromatographed over silica gel (40 g) with mixtures of $CHCl_3$ and MeOH. $CHCl_3$–MeOH 19:1 (300 ml), $CHCl_3$–MeOH 97:3 (300 ml), $CHCl_3$–MeOH 19:1 (300 ml), and $CHCl_3$–MeOH 93:7 (300 ml) were passed successively through the column, collecting 50 ml fractions. Fraction nos. 16—18 gave a residue (0.108 g), which was purified by preparative layer chromatography (solvent, $CHCl_3$–Me_2CO 7:3, developed three times, and then $CHCl_3$–MeOH 19:1, developed five times) to give oridonin (**3**) (10.2 mg). The physical properties of the new compounds are as follows.

Rabdokaurin C (**1**): Colorless needles (MeOH), mp 232—234 °C, $[\alpha]_D^{22}$ −17.5° (c=1.16, C_5H_5N). UV λ_{max}^{MeOH}: no absorption maxima above 220 nm. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3570, 3370, 1730, 1690, 1230. ^{1}H-NMR (C_5D_5N) δ: 0.86, 1.17 (each 3H, s, *tert*-Me×2), 1.22 (1H, m, 11-H$_1$), 1.26 (2H, m, 3-H$_2$), 1.50 (1H, m, 2-H$_1$), 1.62 (1H, m, 12-H$_1$), 1.76 (1H, d, J=6.6 Hz, 5-H), 1.83 (1H, m, 2-H$_1$), 1.89 (1H, m, 11-H$_1$), 2.01 and 2.19 (each 3H, s, OAc×2), 2.31 (1H, m, 12-H$_1$), 2.81 (1H, br d, J=9.2 Hz, 13-H), 2.93 (1H, dd, J=12.8, 6.4 Hz, 9-H), 4.34 and 4.54 (each 1H, d, J=9.6 Hz, 20-H$_2$), 4.35 (1H, s, OH), 4.90 (1H, dd, J=11.6, 6.0 Hz, 1-H), 5.02 (1H, s, 14-H), 5.34 (1H, br s, 17-H$_1$), 5.48 (1H, br s, 15-H), 5.63 (1H, br s, 17-H$_1$), 5.79 (1H, d, J=6.6 Hz, 6-H), 8.09 and 8.23 (each 1H, m, OH×2). ^{13}C-NMR: see Table I. MS m/z: 450.2215 (M)$^+$. Calcd for $C_{24}H_{34}O_8$: 450.2253.

Rabdokaurin D (**8**): Colorless needles (MeOH), mp 227—230 °C, $[\alpha]_D^{21}$ +34.1° (c=0.62, MeOH). UV λ_{max}^{MeOH} nm (ε): 232 (7910). IR ν_{max}^{KBr} cm^{-1}: 3300, 1735, 1710, 1645, 1270, 1230. ^{1}H-NMR (C_5D_5N) δ: 0.90 (3H, s, *tert*-Me), 2.19 (3H, s, OAc), 3.37 and 3.79 (each 1H, d, J=11.0 Hz, 18-H$_2$), 4.00 (2H, 6-H$_2$), 5.00 (1H, d, J=12.5 Hz, 20-H$_1$), 5.12 (1H, dd, J=10, 5 Hz, 1-H), 5.23 (1H, d, J=12.5 Hz, 20-H$_1$), 5.35 and 5.98 (each 1H, br s, 17-H$_2$), 6.48 (2H, m, OH×2). ^{13}C-NMR: see Table I. MS m/z: 406.1956 (M)$^+$. Calcd for $C_{22}H_{30}O_7$: 406.1991.

Rabdokaurin C Monoacetate (2) Rabdokaurin C (**1**) (10.0 mg) was dissolved in a mixture of acetic anhydride (0.1 ml) and pyridine (0.1 ml) and the solution was left at room temperature for 12 h. After addition of excess MeOH, the solvent was removed *in vacuo*. The residue was purified by preparative layer chromatography (solvent, Et_2O) to give the monoacetate (**2**) (7.0 mg) as colorless needles, mp 175—176 °C (MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3525, 1750, 1700, 1225. ^{1}H-NMR (C_5D_5N) δ: 0.84 and 1.19 (each 3H, s), 1.51 (1H, d, J=6.4 Hz), 1.99, 2.04 and 2.17 (each 3H, s), 2.71 (1H, d, J=9.6 Hz), 4.18, 4.28 (each 1H, d, J=10.6 Hz), 4.72 (1H, dd, J=11.2, 5.8 Hz), 4.86 (1H, d, J=2.0 Hz), 5.18 and 5.23 (each 1H, br s), 5.35 (1H, d, J=6.0 Hz), 5.37 (1H, s). MS m/z: 492.2370 (M)$^+$. Calcd for $C_{26}H_{36}O_9$: 492.2359.

Conversion of Oridonin (3) into Rabdokaurin C Monoacetate (2) Oridonin diacetate (**6**)[4] (44.0 mg) was dissolved in MeOH (1 ml) and a methanolic solution of $CeCl_3 \cdot H_2O$ (0.4 M, 0.25 ml) was added to the solution. The reaction mixture was stirred for 10 min at room temperature, then $NaBH_4$ (4 mg) was added portionwise to the solution and the whole was stirred at room temperature for 5 min.[9] After addition of 2 drops of AcOH and H_2O (30 ml), the mixture was extracted with EtOAc (30 ml×3). The EtOAc extract was washed with saturated NaCl aqueous solution, dried and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (4 g) with Et_2O to give an allylic alcohol (**7**) (29 mg) as an amorphous powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3525, 1750, 1740, 1710, 1240. ^{1}H-NMR (C_5D_5N) δ: 1.02 and 1.12 (each 3H, s, *tert*-Me×2), 1.98 and 2.09 (each 3H, s, OAc×2), 3.82 (1H, d, J=8.8 Hz), 4.16 and 4.27 (each 1H, d, J=11 Hz), 4.92 (1H, br s), 5.16 and 5.29 (each 1H, br s), 5.35 (1H, br s). An aliquot (18 mg) of **7** was acetylated with a mixture of acetic anhydride (0.5 ml) and pyridine (0.5 ml) for 12 h at room temperature. The product was purified by preparative layer chromatography (solvent, *n*-hexane–Et_2O 1:9) to give rabdokaurin C monoacetate (**2**) (13.6 mg), mp 176.5—177.5 °C (MeOH). MS m/z: 492.2387 (M)$^+$. Calcd for $C_{26}H_{36}O_9$: 492.2359. This compound was identical with authentic rabdokaurin C monoacetate (**2**) on the basis of mixed melting point determination and direct comparisons of the spectral data.

Dihydrorabdokaurin D (12) Rabdokaurin D (**8**) (4.5 mg) was dissolved in MeOH (5 ml) and 5% Pd–C (10 mg) was added to the solution. The mixture was stirred under an atmosphere of hydrogen for 2 h. After removal of the catalyst by filtration, the filtrate was concentrated *in vacuo* to give a residue, which was purified by preparative layer chromatography (solvent, $CHCl_3$–MeOH 9:1) to give dihydrorabdokaurin D (**12**) (3.6 mg), mp 229—232 °C (MeOH). IR ν_{max}^{KBr} cm^{-1}: 3430, 1736, 1235, 1165, 1116, 1045. ^{1}H-NMR (C_5D_5N) δ: 0.87 (3H, s, *tert*-Me), 1.12 (3H, d, J=7 Hz), 2.19 (3H, s, OAc), 2.50 (1H, m), 2.57 (1H, dd, J=12.5, 4 Hz), 3.14 (1H, m), 3.37 (1H, d, J=10.5 Hz), 3.79 (1H, d, J=10.5 Hz), 4.01 (2H), 5.14 (1H, br t, J=6 Hz), 5.20 (1H, d, J=12 Hz), 6.35 (2H, m, OH×2). MS m/z: 408.2099 (M$^+$). Calcd for $C_{22}H_{32}O_7$: 408.2147. CD (MeOH) $\Delta\varepsilon_{304.4}$: −0.61.

Rabdokaurin D Diacetate (11) Rabdokaurin D (**8**) (4.4 mg) was acetylated with a mixture of acetic anhydride (0.3 ml) and pyridine (0.3 ml) for 30 h at room temperature. The product was purified by preparative layer chromatography ($CHCl_3$–Me_2CO 4:1) to give the diacetate (**11**) (4.4 mg), mp 196—198 °C (MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1715, 1640, 1365, 1290, 1240—1200, 1125, 1280, 1050, 1035. ^{1}H-NMR ($CDCl_3$) δ: 0.99 (3H, s, *tert*-Me), 1.96 (3H, s, OAc), 2.06 (6H, s, OAc×2), 3.09 (1H, dd, J=9, 5 Hz), 3.66 (1H, d, J=11.5 Hz), 3.97 (1H, d, J=11.5 Hz), 4.12 (2H, d, J=4 Hz), 4.36 (1H, d, J=12 Hz), 4.75 (1H, br t, J=7 Hz), 4.89 (1H, d, J=12 Hz), 5.55, 6.08 (each 1H, br s). MS m/z: 490.2206 (M)$^+$. Calcd for $C_{26}H_{36}O_9$: 490.2203. This compound was identical with an authentic sample of rabdokaurin B monoacetate on the basis of mixed melting point determination and direct comparisons of the spectral data.

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