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Studies on the Diterpenoid Constituents of *Rabdosia ternifolia*: Structural Elucidation of New Diterpenoids, Rabdoternins A, B and C

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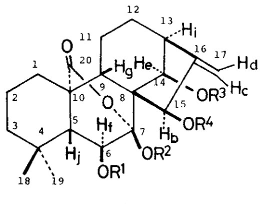
Three new diterpenoids, rabdoternins A (1), B (2) and C (3) have been isolated from the dried leaves of *Rabdosia ternifolia* (D. DON) HARA. Their structures have been elucidated on the basis of spectroscopic and chemical evidence.

Keywords *Rabdosia ternifolia*; Labiatae; rabdoternin A; rabdoternin B; rabdoternin C; diterpenoid; *ent*-7β,20-epoxy-kaur-16-en-7α-ol; structure elucidation

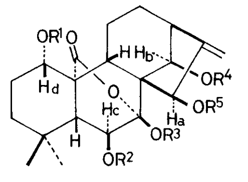
During the course of our studies on biologically active diterpenoids from the plants of the genus *Rabdosia*[2)] (Labiatae), we have isolated over forty new diterpenoids, some of which showed antibacterial and antitumor activities.[3)] From *R. ternifolia* (D. DON) HARA, we have already isolated a new diterpenoid, isodonoic acid (**12**), together with known compounds, longikaurin A (**7**), longikaurin E (**8**) and isodonal (**11**).[4)] In this study, we examined the diterpenoid constituents of the dried leaves of the title plant collected in Yunnan, China and isolated three new diterpenoids, rabdoternins A (**1**), B(**2**) and C (**3**),[5)] together with two known compounds, oridonin (**9**)[6)] and ponicidin (**13**).[7)] This paper describes the structural elucidation of the new compounds.

The new compounds, rabdoternins A (**1**), B (**2**) and C (**3**), were isolated from the methanolic extract of the dried leaves of *R. ternifolia* according to the procedures described in the experimental section in yields of 0.0020, 0.0014 and 0.0018%, respectively.

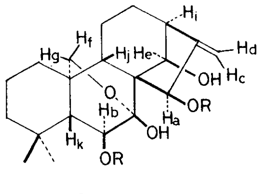
Rabdoternin A (**1**), mp 250—252 °C, $[\alpha]_D$ −45.6° (MeOH), was obtained as colorless needles and was assigned the molecular formula $C_{20}H_{28}O_6$ on the basis of its high resolution mass spectrum (high-MS) and elemental analysis. Rabdoternin A (**1**) did not show any absorption maximum above 220 nm in the ultraviolet (UV) spectrum. It contained an *exo*-methylene group [δ_H 5.32 (H_d) and 5.65 (H_c); δ_C 110.4 (t) and 159.1 (s)] and a lactone group [ν_{max} 1725 cm^{-1}; δ_C 175.4 (s)] as partial structures, as judged from its infrared (IR) spectrum, and proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra (Tables I and II). The presence of hydroxyl groups in the structure of **1** was suggested from the fact that strong absorption bands (ν_{max} 3425 and 3225 cm^{-1}) were observed in the IR spectrum and the three proton signals due to three secondary carbinyl protons were observed at δ_H 4.26 (1H, dd, J=4 and 4 Hz, changed to d, J=4 Hz on addition of D_2O; H_f), 4.84 (1H, s; H_e), and 5.65 (2H, s; H_b, H_c) in the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum showed the presence of three secondary carbinyl carbon atoms (δ_C 71.7, 72.4 and 74.7) and a ketalic carbon atom (δ_C 107.8), suggesting that there are four hydroxyl groups in the structure of **1** and that three of them are secondary and one is tertiary. In addition to the signals described above, the ^{13}C-NMR spectrum showed signals due to two methyl groups, five methylene groups, three methine groups and three quaternary carbon atoms. Acetylation of **1** with a mixture of acetic anhydride and pyridine gave the tetraacetate (**4**). The ^{1}H-NMR spectrum of **1** showed two singlets at δ_H 0.94 and 1.12 (each 3H, s) due to tertiary methyl groups. The spectral features mentioned above are like



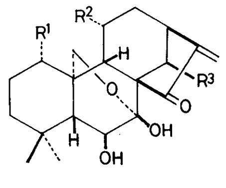
1 : $R^1=H_a$, $R^2=R^3=R^4=H$
4 : $R^1=R^2=R^3=R^4=COMe$
5 : $R^1=R^4=H$, $\left.{R^2 \atop R^3}\right\}\!>\!CMe_2$
6 : $\left.{R^1 \atop R^4}\right\} = \left.{R^2 \atop R^3}\right\}\!>\!CMe_2$



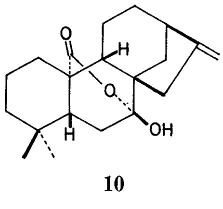
2 : $R^1=R^2=R^3=R^4=R^5=H$
15 : $R^1=R^2=R^3=R^4=R^5=COMe$
16 : $R^1=R^2=R^5=H$, $\left.{R^3 \atop R^4}\right\}\!>\!CMe_2$



3 : R=COMe
17 : R=R=H



7 : $R^1=R^2=H$, $R^3=OH$
8 : $R^1=R^3=H$, $R^2=OCOMe$
9 : $R^1=R^3=OH$, $R^2=H$



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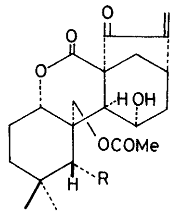
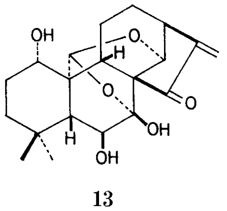


11 : R=CHO
12 : R=COOH



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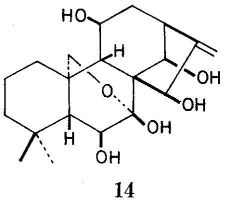

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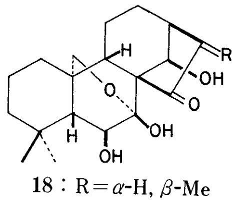
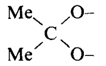


18 : R=α-H, β-Me
19 : R=α-Me, β-H

Table I. ^{1}H-NMR Spectral Data$^{a)}$ for Rabdoternins A (**1**), B (**2**), C (**3**), Longikaurin A (**7**), and Their Derivatives

Proton	**1**	**2**	**3**	**4**	**5**$^{b)}$	**6**$^{b)}$	**7**	**15**$^{b)}$	**16**	**17**
1-H		3.52 (m)$^{c)}$						4.76 (dd, 5.5, 11.5)	3.60 (m)$^{c)}$	
4-Me_2	0.94 (s)	0.98 (s)	0.96 (s)	0.85 (s)	0.86 (s)	0.84 (s)	1.06 (s)	0.78 (s)	0.96 (s)	1.12 (s)
	1.12 (s)	1.14 (s)	1.17 (s)	1.04 (s)	0.99 (s)	1.04 (s)	1.26 (s)	1.04 (s)	1.20 (s)	1.20 (s)
5-H	1.74 (d, 4)	1.78 (d, 4)	1.75 (dd, 1.5, 7.5)	1.85 (d, 6)					1.75 (d, 5.5)	1.56 (d, 6)
6-H	4.26$^{d)}$	4.24$^{d)}$	5.87 (d, 7.5)	6.18 (d, 6)	3.87$^{d)}$	3.98 (d, 6)	4.20$^{d)}$	6.23 (d, 5.5)	4.19$^{d)}$	4.20 (m)$^{d)}$
	(dd, 4, 4)	(dd, 4, 4)			(dd, 6, 3)		(dd, 6.5, 11)		(dd, 5.5, 5)	
9-H	2.88	3.12	2.50	2.89	2.48			2.96 (dd, 7, 12)	3.03	
	(dd, 6, 13)	(dd, 6, 12)	(dd, 5.5, 12.5)	(dd, 6, 13)	(dd, 6, 14)				(dd, 6.5, 13)	
13-H	2.80 (d, 8)	2.82 (d, 8)	2.79 (br d, 10)	2.73 (d, 10)	2.68 (d, 8)		3.18 (br d, 9.5)	2.63 (br d, 10.5)	2.76 (br d, 9)	2.84 (br d, 8)
14-H	4.84 (s)	4.94 (s)	5.00 (s)	5.32 (s)	4.34 (s)	4.24 (s)	5.13 (br s)	5.33 (s)	4.61 (s)	4.92 (s)
15-H	5.65 (s)	5.66 (br s)	6.70 (t, 2)	6.51 (t, 2)	4.98 (m)	5.22 (m)		6.08 (br s)	5.49 (t, 2.5)	5.65 (s)
17-H_2	5.32 (s)	5.33 (br s)	5.27 (d, 2)	5.26 (br s)	5.24 (m)	5.13 (m)	5.51 (br s)	5.09 (d, 1)	5.31 (m)	5.32 (br s)
	5.65 (s)	5.66 (br s)	5.43 (br s)	5.44 (br s)	5.30 (m)	5.22 (m)	6.28 (br s)	5.24 (br s)	5.62 (br s)	5.65 (s)
20-H_2			3.92 (dd, 1.5, 9.5)				3.95 (dd, 1.5, 10)			3.98 (d, 10)
			4.23 (dd, 1, 9.5)				4.16 (br d, 10)			4.17 (dd, 2, 10)
OH	6.42 (s)	4.70 (d, 10)			3.18 (d, 3)		6.89 (d, 10)		5.82 (d, 3)	6.56 (m)
	8.70 (br s)	6.35 (s)			4.28 (d, 3)		7.37 (m)		9.09 (d, 5)	7.84 (2 × OH, m)
	9.14 (d, 4)	8.90 (br s)					9.02 (m)			8.38 (m)
		9.30 (d, 4)								
MeCO–			2.15 (s)	1.99, 2.02				2.01, 2.03, 2.04,		
			2.33 (s)	2.21, 2.35 (s)				2.10, 2.21 (s)		
					1.48 (s)	1.56 (6H, s)			1.45 (s)	
					1.72 (s)	1.63 (s)			1.79 (s)	
						1.73 (s)				

a) Unless otherwise noted, spectra were measured in C_5D_5N. Multiplicity and *J* values (in Hz) are parentheses. Abbreviations: s, singlet; br s, broad singlet; d, doublet; br d, broad doublet; t, triplet; dd, doublet of doublets; m, multiplet. *b*) Measured for $CDCl_3$ solution. *c*) The signals changed to dd on addition of D_2O: **2**, $J=8$ and 8 Hz; **16**, $J=6$ and 11.5 Hz. *d*) The signals changed to d on addition of D_2O: **1**, $J=4$ Hz; **2**, $J=4$ Hz; **5**, $J=6$ Hz; **7**, $J=6.5$ Hz; **16**, $J=5.5$ Hz; **17**, $J=6$ Hz.

Table II. Carbon-13 Chemical Shifts (δ)$^{a)}$ of Rabdoternins A (**1**), B (**2**) and C (**3**)

Carbon	**1**	**2**	**3**
1	32.3 (t)$^{b)}$	73.4 (d)	31.9 (t)$^{d)}$
2	17.2 (t)	32.8 (t)$^{c)}$	15.2 (t)
3	40.9 (t)	39.2 (t)	41.7 (t)
4	34.3 (s)	34.1 (s)	33.7 (s)
5	54.7 (d)	55.0 (d)	54.1 (d)
6	71.7 (d)	72.0 (d)	74.1 (d)$^{e)}$
7	107.8 (s)	108.4 (s)	97.9 (s)
8	53.6 (s)	53.4 (s)	52.3 (s)
9	42.7 (d)	44.5 (d)	46.9 (d)
10	44.8 (s)	48.4 (s)	36.1 (s)
11	19.2 (t)	20.9 (t)	18.9 (t)
12	29.6 (t)$^{b)}$	31.0 (t)$^{c)}$	31.7 (t)$^{d)}$
13	45.4 (d)	45.5 (d)	45.5 (d)
14	74.7 (d)	74.7 (d)	75.5 (d)
15	72.4 (d)	72.5 (d)	73.8 (d)$^{e)}$
16	159.1 (s)	159.3 (s)	158.8 (s)
17	110.4 (t)	110.1 (t)	111.1 (t)
18	31.4 (q)	31.1 (q)	33.1 (q)
19	21.1 (q)	20.9 (q)	22.5 (q)
20	175.4 (s)	176.1 (s)	66.7 (t)
$\underline{C}H_3CO$			21.3, 22.0 (q)
$CH_3\underline{C}O$			170.6, 170.9 (s)

a) The spectra were measured for C_5D_5N solutions. The assignments were based on proton noise decoupling, off resonance decoupling and single frequency selective decoupling experiments, and comparison of the data with those of closely related compounds. Multiplicity is given in parentheses: s, singlet; d, doublet; t, triplet; q, quartet. *b—e*) The assignments with the same superscript might be reversed.

those observed for longikaurin A (**7**)[9] except for the appearance of the signals due to a lactone carbonyl group and a secondary carbinyl carbon atom in **1** instead of those due to a methylene group having an oxygen atom on it (C-20) and a ketone group (C-15) in the ^{1}H- and ^{13}C-NMR spectra. This suggested that rabdoternin A (**1**) has *ent*-7β,20-epoxy-kaur-16-en-7α-ol-20-one (**10**) or its enantiomer as its basic skeleton. The location of one of three secondary hydroxyl groups and the stereochemistry around this group were deduced as follows. In the ^{1}H-NMR spectrum of **1**, irradiation at the frequency of H_f collapsed the signals due to H_j at δ_H 1.74 and H_a at δ_H 9.14 to singlets. On irradiation at the frequency of H_j or H_a, H_f collapsed to a doublet ($J=4$ Hz) in each case. On the other hand, nuclear Overhauser enhancement(NOE)s for H_f (9.5%) and H_j (10%), and for H_f (13.6%) were observed on irradiation at δ_H 1.12 and 0.94, separately. On irradiation at the frequency of H_j, NOE (11.1%) for H_g at δ_H 2.88 was also observed. Thus, an axial hydroxyl group located at C-6β in ring B, which takes a boat conformation. Additionally, a methine proton, H_j takes β-axial configuration at C-5 and a methine proton, H_g, showing NOE from H_j, is located at the 1,3-β-diaxial position at C-9. The locations of the remaining two secondary hydroxyl groups were deduced from the following results. In the ^{1}H-NMR spectrum of **1**, the chemical shifts and coupling pattern of H_b and H_e are analogous to the signals due to 15α-H and 14α-H of rubescensin C (**14**) [δ_H 5.34 (15α-H) and 4.50 (14α-H)],[8] leading to the presumption that two hydroxyl groups might be located at C-15β and C-14β. This presumption was confirmed as follows. In the ^{1}H-NMR spectrum of the tetraacetate (**4**), H_c at δ_H 5.44 and H_d at δ_H 5.26 collapsed to doublets ($J=2$ Hz) and H_e at δ_H 5.32 became sharp on irradiation at the frequency of H_i at δ_H 2.73. On the other hand, H_d collapsed to a doublet ($J=1$ Hz) and H_c became sharp when the frequency of H_b at δ_H 6.51 was irradiated. Thus, H_b was assigned to 15-H, which is allylic to the *exo*-methylene group, and H_e was assigned to 14α-H which has a dihedral angle of *ca.* 90° to 13-H (H_i). Treatment of **1** with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid in *N*,*N*-dimethylformamide (DMF) gave the 7;14-acetonide (**5**) and 6;15, 7;14-diacetonide (**6**). In the ^{1}H-NMR spectrum of **5**, NOEs for H_b at δ_H 4.98 (8.6%) and H_e at δ_H 4.34 (9.1%) were observed on irradiation at δ 1.48 and 1.72, respectively. The configurations of the hydroxyl groups at C-14 and C-15 were thus determined as β. On the basis of these findings, the structure of rabdoternin A should be represented as *ent*-7β,20-epoxy-kaur-16-en-6α,7α,14α-tetraol-20-one (**1**) or its enantiomer. The absolute stereochemistry will be described later.

Rabdoternin B (**2**), mp 262—265 °C, $[\alpha]_D$ −72.5° (MeOH), was obtained as colorless needles. The molecular formula, $C_{20}H_{28}O_7$, determined on the basis of its elemental analysis and high-MS, has one more oxygen atom compared with that of **1**. Rabdoternin B (**2**) contained a lactone group [^{13}C-NMR δ_C 176.1 (s)], an *exo*-methylene group [^{1}H-NMR δ_H 5.33 and 5.66; ^{13}C-NMR δ_C 110.1 (t) and 159.3 (s)] and hydroxyl groups (IR 3570, 3420 and 3260 cm^{-1}) as partial structures as in the case of **1**. The ^{13}C-NMR spectrum further showed signals due to four secondary carbinyl carbon atoms (δ_C 72.0, 72.5, 73.4 and 74.7) and a ketalic carbon atom (δ_C 108.4) in addition to the signals due to two methyl groups, four methylene groups, three methine groups and three quaternary carbon atoms. Besides singlets [δ_H 0.98 and 1.14 (each 3H, s)] due to two tertiary methyl groups, the ^{1}H-NMR spectrum of **2** showed signals due to four secondary carbinyl protons [δ_H 3.52 (m, changed to dd, $J=8$ and 8 Hz on addition of D_2O); H_d, 4.24 (dd, $J=4$ and 4 Hz, changed to d, $J=4$ Hz on addition of D_2O); H_c, 4.94 (s); H_b, and 5.66 (s), H_a]. The spectral features mentioned above are like those of **1** except for the appearance of a new signal at δ_H 3.52 (H_d) due to a proton on carbon having a secondary hydroxyl group in the ^{1}H-NMR spectrum, and an increment of the number of secondary carbinyl carbon atoms by 1 and a decrease in that of methylene group by 1 were observed in the ^{13}C-NMR spectrum. Acetylation of **2** with a mixture of acetic anhydride and pyridine gave the pentaacetate (**15**) and the treatment of **2** with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid in DMF gave the 7;14-acetonide (**16**). These data suggested that rabdoternin B might have a structure in which a secondary hydroxyl group was introduced into the structure of rabdoternin A (**1**). The location of the secondaryl hydroxyl group was presumed to be located at C-1α from the analogy of the chemical shift and the coupling pattern with those of oridonin (**9**) [δ_H 3.64 (1H, dd, $J=8$ and 8 Hz), 1-H].$^{6)}$ This presumption was further supported by the fact that the ^{13}C-NMR signals due to C-2 and C-10 resonated 15.6 and 3.6 ppm downfield compared to those of **1** and finally confirmed by the finding that NOE (4%) was observed for the signal at δ_H 3.52 on irradiation at δ_H 1.78 in the ^{1}H-NMR spectrum of **2** and a NOE (7.6%) for the signal at δ_H 3.03 was observed on irradiation at δ 3.60 (1-H) in the ^{1}H-NMR spectrum of **16**. The stereochemistry of the hydroxyl groups at C-14 and C-15 was supported by the fact that NOEs for H_a at δ_H 5.49 (5.9%) and H_b at δ_H 4.61 (12.8%) were observed on irradiation at δ_H 1.45 and 1.79, respectively, in the ^{1}H-NMR spectrum of **16**. Thus, the structure of rabdoternin B should be represented as *ent*-7β,20-epoxy-kaur-16-en-1β,6α,7α,14α,15α-pentaol-20-one (**2**) or its enantiomer. The absolute stereochemistry will be described later.

Rabdoternin C$^{5)}$ (**3**), mp 222—224 °C, $[\alpha]_D$ −112.5° (MeOH), was obtained as colorless granules. The molecular formula was determined as $C_{24}H_{34}O_7$ on the basis of elemental analysis and high MS. Besides singlets due to two tertiary methyl groups (δ_H 0.96 and 1.17) and two acetyl groups (δ_H 2.15 and 2.33), the ^{1}H-NMR spectrum showed signals due to an *exo*-methylene group [δ_H 5.27 (1H, d, $J=$ 2 Hz); H_d and 5.43 (1H, br s); H_c], a methylene group having an oxygen functional group [δ_H 3.92 (1H, dd, $J=9.5$ and 1.5 Hz; H_f and 4.23 (1H, dd, $J=9.5$ and 1 Hz); H_g], and three secondary carbinyl protons on carbons having a hydroxyl group or an acetoxy group [δ_H 5.00 (1H, s); H_e, 5.87 (1H, d, $J=7.5$ Hz); H_b and 6.70 (1H, t, $J=2$ Hz); H_a]. The ^{13}C-NMR spectrum showed the presence of a methylene carbon atom having an oxygen function (δ_C 66.7), three secondary carbinyl carbon atoms (δ_C 73.8, 74.1 and 75.5), and a ketatic carbon atom (δ_C 97.9) in addition to the signals due to an *exo*-methylene group [δ_C 111.1 (t) and 158.8 (s)], four methyl groups, five methylene groups, three methine groups and three quaternary carbon atoms. These spectral data are very like those of longikaurin A (**7**) except for the disappearance of the signal due to a ketone group (C-15) and the appearance of the signals due to a methine group having an oxygen functional group and two acetyl groups in the ^{1}H- and ^{13}C-NMR spectra. This suggested that rabdoternin C has a structure in which the ketone group at C-15 in **7** is reduced to an allylic alcohol and then two of the three secondary hydroxyl groups are acetylated. Lithium aluminum hydride reduction of **3** gave deacetylrabdoternin C (**17**), which was treated under the conditions of the garryfoline-cuauchichicine rearrangement$^{10)}$ to give 16*R*- and 16*S*-dihydrolongikaurin A (**18** and **19**).$^{9)}$ This fact confirmed the locations of the secondary carbinyl groups, β-orientation of the carbinyl group at C-15 and the absolute stereochemistry in the structure of rabdoternin C. Finally, the locations of two acetyl groups were determined as follows. One acetyl group was located on OH-6β since the corresponding carbinyl proton signal (H_b) in **3** showed a downfield shift (δ_H 5.87) compared with those of **1**, **7** and **17** in the ^{1}H-NMR spectra. On the other hand, another acetyl group was determined to be located on OH-15β on the basis of the fact that the corresponding signal (δ_H 6.70) in **3** showed a similar chemical shift to that of **4** and a downfield shift compared with that of **17**. Thus, the structure of rabdoternin C is represented as *ent*-7β,20-epoxy-kaur-16-en-6α,7α,14α,15α-tetraol 6,15-diacetate (**3**).

The absolute stereochemistry of rabdoternins A (**1**) and B (**2**), which had remained obscure, was elucidated to be as pictured on the basis of the fact that **1** and **2** showed negative plane curves, as in the case of rabdoternin C (**3**), in the optical rotatory dispersion (ORD) spectra.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on Hitachi EPI-S 2 spectrometer or Hitachi 215 spectrometer. ^{1}H-NMR spectra were taken with a JEOL PS 100, JEOL JNM FX 100 or JEOL JNM FX 200 spectrometer. ^{13}C-NMR spectra were taken with either of the latter two Fourie transform (FT) instruments for solutions in C_5D_5N. Tetramethylsilane was used as an internal standard and chemical shifts are given in δ (ppm) values. MS were determined with a JEOL JMS D-300 spectrometer. UV spectra were recorded with a Hitachi 330 spectrophotometer. Optical rotations and ORD spectra were taken with a JASCO ORD/UV-5 spectrometer. Kiesel gel 60 (0.063—0.200 mm, Merck) was used for column chromatography and precoated Silica gel 60 F_{254} plates (0.25 and 0.5 mm in thickness) were used for thin layer chromatography

(TLC) and preparative layer chromatography. Extracts were dried over anhydrous sodium sulfate or magnesium sulfate.

Isolation of Diterpenoids Dried leaves (9.1 kg) of *Rabdosia ternifolia* (D. DON) HARA, collected in Yunnan, China, were extracted with MeOH (36 l) at room temperature for 10 d. The MeOH extract was concentrated *in vacuo* to about 1.8 l. H_2O (0.2 l) was added to the concentrated solution and the resulting 90% MeOH solution was partitioned with *n*-hexane (2 l × 3). The 90% MeOH layer was concentrated *in vacuo*. The residue was partitioned between EtOAc (total 3 l) and H_2O (1.5 l). The dried EtOAc extract was evaporated *in vacuo* to give a residue (338.7 g), whcih was chromatographed over silica gel (3 kg) with a mixture of $CHCl_3$ and Me_2CO as the eluant, with increasing Me_2CO content. The slower eluate (15 g) at 15% acetone content was rechromatographed on a silica gel (500 g) column with $CHCl_3$–MeOH (19 : 1). The earlier eluate (3.1 g) was repeatedly purified by chromatography on silica gel [solvent: $CHCl_3$–Me_2CO; Et_2O] and finally recrystallized from MeOH to give rabdoternin C (**3**) (165 mg). The slower eluate (5.1 g) was further separated by chromatography over silica gel (250 g) with $CHCl_3$–Me_2CO as the eluant, with increasing Me_2CO content, and the product was recrystallized from MeOH to give rabdoternin A (**1**) (182 mg) and rabdoternin B (**2**) (123 mg). The earlier eluate (5 g) at 20% Me_2CO content was further chromatographed twice with $CHCl_3$–Me_2CO as the eluant and the product was recrystallized from MeOH to give ponicidin (**13**) (365 mg). The eluate at 30% Me_2CO content gave a residue (40.8 g), an aliquot (3 g) of which was further purified by chromatography on silica gel and by recrystallization of the product to give oridonin (**9**) (1.07 g). The properties of the isolated diterpenoids are as follows.

Rabdoternin A (**1**), mp 250—252 °C, $[\alpha]^{24}$ (nm) $-40.4°$ (620), $-45.6°$ (590), $-56.0°$ (550), $-69.0°$ (500), $-115.9°$ (400) ($c=0.19$, MeOH). UV λ_{max}^{MeOH}: no absorption maxima above 220 nm. IR ν_{max}^{KBr} cm^{-1}: 3425, 3225, 1725, 1660, 1640. ^{1}H-NMR: see Table I. ^{13}C-NMR: see Table II. MS *m/z*: 364.1896 $(M)^+$. Calcd for $C_{20}H_{28}O_6$: 364.1886. *Anal.* Calcd for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 65.54; H, 7.80.

Rabdoternin B (**2**), mp 262—265 °C. $[\alpha]^{20}$ (nm) $-62.1°$ (620), $-72.5°$ (590), $-77.7°$ (550), $-93.3°$ (500), $-155.4°$ (400) ($c=0.19$, MeOH). UV λ_{max}^{MeOH}: no absorption maxima above 220 nm. IR ν_{max}^{KBr} cm^{-1}: 3570, 3420, 3260, 1745, 1665, 1650. ^{1}H-NMR: see Table I. ^{13}C-NMR: see Table II. MS *m/z*: 380.1849 $(M)^+$. Calcd for $C_{20}H_{28}O_7$: 380.1834. *Anal.* Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.20; H, 7.49.

Rabdoternin C (**18**), mp 222—224 °C $[\alpha]^{26}$ (nm) $-107.1°$ (620), $-112.5°$ (590), $-133.9°$ (550), $-166.1°$ (500), $-294.6°$ (400) ($c=0.56$, MeOH). UV λ_{max}^{MeOH}; no absorption maxima above 220 nm. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600—3150, 1730, 1260. ^{1}H-NMR: see Table I. ^{13}C-NMR: see Table II. MS *m/z*: 434.2279 $(M)^+$. Calcd for $C_{24}H_{34}O_7$: 434.2304. *Anal.* Calcd for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 66.54; H, 8.19.

Oridonin (**9**), mp 243—249 °C, $[\alpha]_D^{20}$ $-68.0°$ ($c=0.20$, MeOH) and ponicidin (**13**), mp 241—242 °C, $[\alpha]_D^{20}$ $-130°$ ($c=0.12$, MeOH) were identical with authentic samples on the basis of mixed melting point determination and comparisons of IR and ^{1}H-NMR spectra.

Rabdoternin A Tetraacetate (4) Rabdoternin A (**1**) (20 mg) was acetylated with a mixture of acetic anhydride (0.2 ml) and pyridine (0.2 ml) at room temperature for 24 h. Excess MeOH was added to the reaction mixture and the solvent was removed *in vacuo*. The residue (34.5 mg) was purified by preparative layer chromatography (solvent: Et_2O) to give the tetraacetate (**4**) as an amorphous powder. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1740, 1660, 1600, 1380. ^{1}H-NMR: see Table I. MS *m/z*: 532.2279 $(M)^+$. Calcd for $C_{28}H_{36}O_{10}$: 532.2252.

7;14-Monoacetonide (5) and 6;15,7;14-Diacetonide (6) of Rabdoternin A (1) Rabdoternin A (**1**) (20.8 mg) was dissolved in DMF (0.5 ml) and 2,2-dimethoxypropane (0.5 ml) and *p*-toluenesulfonic acid (0.5 mg) were added. The mixture was heated at 82 °C for 6.5 h. The solvent was removed *in vacuo* and the residue was partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ extract was washed successively with saturated $NaHCO_3$ aqueous solution and H_2O, dried, and evaporated *in vacuo* to give a residue (26.0 mg), which was separated by preparative layer chromatography (solvent: Et_2O). The band showing an *Rf* value of 0.6 gave **5** (19.5 mg) and the band showing an *Rf* value of 0.7 gave **6** (3.6 mg).

7;14-Monoacetonide (**5**): IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 3460, 1750, 1660, ^{1}H-NMR ($CDCl_3$): see Table I. MS *m/z*: 404.2241. Calcd for $C_{23}H_{32}O_6$: 404.2199.

6;15,7;14-Diacetonide (**6**): IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1665. ^{1}H-NMR: see Table I. MS *m/z*: 444.2491. Calcd for $C_{26}H_{36}O_6$: 444.2473.

Rabdoternin B Pentaacetate (15) Rabdoternin B (**2**) (19.0 mg) was acetylated with a mixture of acetic anhydride (0.5 ml) and pyridine (0.5 ml) at room temperature for 24 h. The reaction mixture was treated and purified as above to give the pentaacetate (**15**) (17.1 mg). IR $\nu_{max}^{CHCl}{}_3$ cm^{-1}: 1780, 1750, 1730, 1660, 1230, 1205. ^{1}H-NMR: see Table I. MS *m/z*: 590.2365 $(M)^+$. Calcd for $C_{30}H_{38}O_{12}$: 590.2363.

Rabdoternin B 7;14-Monoacetonide (16) A mixture of rabdoternin B (**2**) (17.6 mg), 2,2-dimethoxypropane (0.5 ml) and *p*-toluenesulfonic acid (1 mg) was heated at 84 °C for 6 h. Work-up as before gave a residue, which was purified by preparative layer chromatography ($CHCl_3$–Me_2CO, 93 : 7) to give the 7;14-monoacetonide (**16**) (14.2 mg) as an amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 3475, 3425, 3200, 1720, 1660, 1370, 1225. ^{1}H-NMR see Table I. MS *m/z*: 420.2153 $(M)^+$. Calcd for $C_{23}H_{32}O_7$: 420.2148.

Conversion of Rabdoternin C (3) to Dihydrolongikaurin A (18 and 19) A suspension of $LiAlH_4$ (150 mg) in anhydrous Et_2O (15 ml) was added dropwise to a solution of rabdoternin C (72 mg) in anhydrous Et_2O (20 ml). The mixture was refluxed for 2 h. To the cooled mixture, EtOAc (25 ml) was added. The separated organic layer was washed successively with 2 N HCl and H_2O, dried and evaporated *in vacuo* to give a residue (50 mg), which was purified on a silica gel (10 g) column with $CHCl_3$–Me_2CO as the eluant with increasing Me_2CO content. The eluate at 20% Me_2CO content gave the deacetyl derivative (**17**) (19 mg) (^{1}H-NMR: see Table I). The deacetyl derivative (**17**) (19 mg) was dissolved in MeOH (2 ml), then 20% HCl aqueous solution (6 ml) was added and the mixture was stirred at room temperature for 39 h. Excess H_2O was added and the mixture was extracted with EtOAc. The EtOAc extract was washed successively with saturated $NaHCO_3$ aqueous solution and H_2O, dried and evaporated *in vacuo*. The residue was separated by preparative layer chromatography [solvent: $CHCl_3$–Me_2CO 9 : 1, developed three times] to give 16*S*-dihydrolongikaurin A (**19**) (3.9 mg) and 16*R*-dihydrolongikaurin A (**18**) (8.7 mg) as syrups. Both compounds were identical with authentic samples on the basis of comparisons of the IR, ORD and ^{1}H-NMR spectra.

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