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牛尾草中一新的对映－贝壳杉烷型二萜

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摘要：从牛尾草［*Isodon ternifolius*（D. Don）Kudo］的地上部分分离得到一个新的对映－贝壳杉烷型二萜，命名为牛尾草素 H（1），通过波谱方法鉴定了它的结构。此外，还分离得到 5 个已知的对映－贝壳杉烷型二萜化合物：香茶菜醛（2），长管香茶菜素 A，E 和 G（3－5），开展香茶菜素 E（6），以及木樨草素（7），芹菜素（8），α－香树脂醇（9），乌索酸（10）和 2α－羟基乌索酸（11）。

关键词：牛尾草；唇形科；对映－贝壳杉烷型二萜；牛尾草素 H
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A New *ent*-Kauranoid from *Isodon ternifolius*

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Abstract： A new *ent*-kauranoid named rabdoternin H **(1)** was isolated from the aerial part of *Isodon ternifolius* and its structure was determined by the spectroscopic methods. Five known *ent*-kaurane diterpenoids，isodonal **(2)**，longikaurin A，E，G **(3－5)** and effusanin E **(6)**，together with luteolin **(7)**，apigenin **(8)**，α-amyrin **(9)**，ursolic acid **(10)** and 2α-hydroxy-ursolic acid **(11)** were also reported in this paper.

Key words： *Isodon ternifolius*；Labiatae；*ent*-Kauranoid；Rabdoternin H

Isodon ternifolius（D. Don）Kudo，a perennial herb or shrub mainly distributed in Yunnan，Guizhou，Guangdong and Guangxi Province，has been used to treat dysenteric enteritis，pharyngitis，tonsillitis etc（Wu *et al*，1977）. A series of *ent*-kaurane diterpenoids from this plant have been reported previously（Sun *et al*，1982；Takede *et al*，1990；Takeda *et al*，1994）. Our re-investigation on this plant led to the isolation of a new *ent*-kaurane diterpenoid，rabdoternin H **(1)** and ten known compounds，isodonal **(2)**（Sun *et al*，1982），longikaurin A **(3)**（Takeda *et al*，1988a），longikaurin E **(4)**（Sun *et al*，1982），longikaurin G **(5)**（Takeda *et al*，1988b），effusanin E **(6)**（Wang *et al*，

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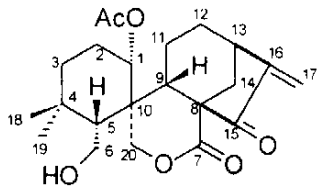

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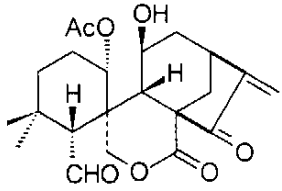

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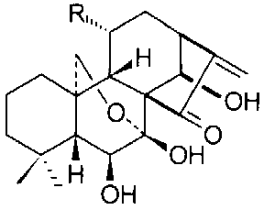

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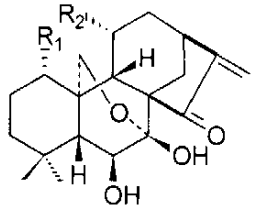
5 R=OH



4 R_1=H R_2=OAc
6 R_1=OH R_2=OH

1989), luteolin (**7**) (Markham *et al*, 1978), apigenin (**8**) (Markham *et al*, 1978), α-amyrin (**9**) (Mahato *et al*, 1994), ursolic acid (**10**) and 2α-hydroxy-ursolic acid (**11**).

Rabdoternin H (**1**), colorless needles, showed an EIMS molecular ion peak at *m/z* 390 in accordance with the formula $C_{22}H_{30}O_6$, which was confirmed by analysis of its ^{13}C NMR (DEPT) spectra. It possessed an *exo*-methylene group conjugated with a carbonyl group on a five-membered ring from the following spectral data: UV λ_{max}^{MeOH}nm: 232.0; IR $\nu_{max}^{KBr}cm^{-1}$: 1712 and 1648; ^1H NMR: δ 5.95 and 5.33 (each 1H, brs); ^{13}C NMR: δ 118.3 (CH_2), 151.4 (C) and 202.5 (C). In addition to the above-mentioned signals, the ^{13}C NMR spectrum also showed the presence of an acetoxyl group, two methyl, seven methylenes (including two oxygenated ones), four methines (including one oxygen-bearing one), three quaternary carbons and a lactone carbonyl group. With consideration of the types of diterpenoids in the *Isodon* genus, these facts indicated that **1** was an *ent*-kauranoid.

There were no correlations between H-5, H-6 and C-7; H-1 and C-7 in HMBC spectrum, which indicated the basic skeleton of **1** was 6, 7-*seco*-spiro-lacton-*ent*-kauranoid. The NOE effects (H-20a with Me-19, H-5β with H-9β) also confirmed the presumption. On the basis of $^1H-^1H$ COSY spectrum, a hydroxyl was assigned to C-6. The acetoxyl was assigned to C-1, because the methine at δ 77.1 (C-1) and the correlation between H-1 and the ester carbonyl at δ 170.2 in HMBC spectrum were observed. The acetoxyl group was judged to be α-orientated due to the observation of NOE effects between H-1 and H-5β, H-11. In conclusion, rabdoternin H (**1**) was elucidated as 1α-acetoxy-6-hydroxy-6, 7-*seco*-*ent*-kaur-16-en-15-one-7, 20-olide.

Compounds **2-9** were identified as isodonal (**2**), longikaurin A, E, G (**3-5**), effusanin E (**6**), luteolin (**7**), apigenin (**8**), α-amyrin (**9**), ursolic acid (**10**) and 2α-hydroxy-ursolic acid (**11**), respectively, by comparing their physical and spectral data with those reported in the literature.

Experimental

General　Melting point was measured on an XRC－1 micro melting point apparatus and uncorrected. Optical rotation was taken on a SEPA－300 polarimeter. IR spectral data was measured on a Bio-Rad FTS－135 spectrometer with KBr pellets. UV spectra was obtained on a UV 210A spectrometer. MS spectra were recorded on a VG Auto Spec-3000 spectrometer. NMR spectra were run on a Bruker AM－400 and a DRX－500 instrument with TMS as internal standard.

Extraction and Isolation　Plant material was collected in Malipo County of Yunnan Province in October, 1994, and identified as *Isodon ternifolius* (D. Don) Kudo by Prof. Zhong-Wen Lin. A voucher specimen was deposited in the Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences.

The air-dried and powdered plants (8.0 kg) were extracted with 70% acetone at room temperature for 3 days each time. The extract was concentrated and filtered, and the filtrate was partitioned with petroleum-ether and EtOAc successively. The EtOAc extract (109 g) was subjected to column chromatography on a Si gel column and eluted with $CHCl_3$ containing increasing amounts of Me_2CO system to give six fractions (I-VI). Fractions I-V were further purified by repeated column chromatography on Si gel and recrystallization to yield compounds **1** (23 mg), **2** (21 mg), **3** (37 mg), **4** (35 mg), **5** (43 mg), **6** (1.2 g), **7** (21 mg), **8** (11 mg), **9** (23 mg), **10** (5 g) and **11** (137 mg).

Table 1　^1H, ^{13}C NMR, $^1H-^1H$ COSY and HMBC data of **1** in C_5D_5N

C	^{13}C NMR (125 MHz) δ (mult)	H	^1H NMR (500 Hz) δ (mult, J in Hz)	COSY	HMBC (H to C)
1	77.1 (d)	1β	5.01 (m)	2	20, OAc
2	24.4 (t)	2α, β	1.88 (m)	1, 3	1, 3
3	40.0 (t)	3α, β	1.38 (m)	2	1, 2, 4
4	33.9 (s)	5β	1.72 (br s)	6a, 6b	4, 6
5	53.6 (d)	6a	3.83 (overlap)	5, 6b	4, 5, 10
6	58.9 (t)	6b	3.80 (overlap)	5, 6a	4, 5, 10
7	170.9 (s)	9β	3.21 (d, 13.1)	11α	1, 5, 7, 8, 9, 10, 11, 12, 14, 15
8	58.7 (s)	11α	1.40 (m)	9, 11β	8, 9, 12
9	42.3 (d)	11β	1.85 (m)	11α	8, 9, 10, 12, 13
10	44.4 (s)	12α	1.99 (m)	12β, 13α	9, 11, 13, 14, 16
11	17.9 (t)	12β	1.34 (m)	12α	14, 16
12	30.2 (t)	13α	2.91 (m)	12α, 14β	8, 11, 15, 16, 17
13	35.3 (d)	14α	2.15 (overlap)	14β	7, 8, 9, 12, 13, 15
14	29.3 (t)	14β	2.58 (dd, 4.4, 12.3)	13α, 14α	8, 9, 12, 13, 15, 16, 17
15	202.5 (s)	17a	5.95 (br s)	17b	13, 15, 16
16	151.4 (s)	17b	5.33 (br s)	17a	13, 15
17	118.3 (t)	Me－18	0.99 (s)		3, 4, 5, 19
18	33.6 (q)	Me－19	0.78 (s)		3, 4, 5, 18
19	23.6 (q)	20a	5.12 (ABd, 12.2)	20b	1, 7, 9
20	68.9 (t)	20b	4. 84 (ABd, 12.2)	20a	1, 9
OAc	170.2 (s), 21.5 (q)	OAc	2.17 (s)		1

Rabdoternin H (**1**), $C_{22}H_{30}O_6$; colorless needles (MeOH); mp 246－248℃; $[\alpha]_D^{24.9}$ + 36.3° (*c* 0.903, MeOH); UV λ_{max}^{MeOH} nm (logε): 232.0 (3.87); IR ν_{max}^{KBr} cm^{-1}: 3415, 2948, 1740, 1712, 1648, 1447, 1407, 1366, 1293, 1267, 1233, 1188, 1046; EI-MS (70eV) *m/z* (%): 390 $[M]^+$ (78), 362 (18), 348 (15), 330 $[M-AcOH]^+$ (23), 312 (20), 284 (21),

257 (30), 239 (26), 227 (31), 192 (16), 178 (31), 133 (48), 119 (40), 105 (69), 91 (100), 81 (65); ^{1}H and ^{13}C NMR data see Table 1.

Isodonal (**2**), $C_{22}H_{28}O_7$; colorless needles (MeOH); EI-MS (70eV) *m/z* (%): 404 [M]$^+$ (25), 386 [M-H_2O]$^+$ (9), 344 [M-AcOH]$^+$ (100), 326 [M-AcOH-H_2O]$^+$ (12), 316 (28), 298 (23), 270 (20), 245 (87), 227 (57) 217 (52), 149 (67), 81 (70); ^{1}H NMR (500 MHz, C_5D_5N) δ: 10.01 (1H, d, J = 1.8 Hz, CHO), 6.03 and 5.40 (each 1H, s, H_2 – 17), 5.51 (1H, m, H – 1β), 5.44 and 5.22 (each 1H, ABd, J = 12.4 Hz, H_2 – 20), 4.41 (1H, m, H – 11α), 2.93 (1H, d, J = 4.5 Hz, H – 5β), 2.15 (3H, s, OAc), 0.98 and 0.95 (each 3H, s, 2 × Me); ^{13}C NMR (125 MHz, C_5D_5N) δ: 204.9 (d, C – 6), 200.8 (s, C – 15), 170.3 (s, C – 7), 150.6 (s, C – 16), 119.3 (t, C – 17), 76.0 (d, C – 1), 67.1 (t, C – 20), 65.2 (d, C – 11), 61.2 (d, C – 5), 58.5 (s, C – 8), 46.8 (d, C – 9), 44.6 (s, C – 10), 41.4 (t, C – 12), 40.2 (t, C – 3), 34.6 (d, C – 13), 34.5 (s, C – 4), 33.2 (q, C – 18), 29.9 (t, C – 14), 24.5 (q, C – 19), 24.4 (t, C – 2), OAc: 170.3, s, 21.4, q.

Longikaurin A (**3**), $C_{20}H_{28}O_5$; colorless needles (MeOH); EI-MS (70eV) *m/z* (%): 348 [M]$^+$ (83), 330 [M-H_2O]$^+$ (35), 319 (16), 302 (45), 284 (22), 269 (20), 217 (39), 177 (36), 167 (60), 151 (83), 133 (43), 109 (58), 85 (68); ^{1}H NMR (500 MHz, C_5D_5N) δ: 6.86 (1H, d, J = 10.0 Hz, OH – 6β), 6.26 and 5.50 (each 1H, s, H_2 – 17), 5.11 (1H, s, H – 14α), 4.16 (1H, dd, J = 10.0, 6.3 Hz, H – 6α), 4.13 and 3.93 (each 1H, ABd, J = 10.0 Hz, H_2 – 20), 3.15 (1H, d, J = 9.5 Hz, H – 13α), 1.23 and 1.04 (each 3H, s, 2 × Me); ^{13}C NMR (125 MHz, C_5D_5N) δ: 208.8 (s, C – 15), 153.0 (s, C – 16), 119.6 (t, C – 17), 98.4 (s, C – 7), 74.2 (d, C – 6), 73.6 (d, C – 14), 66.3 (t, C – 20), 62.7 (s, C – 8), 60.8 (d, C – 9), 52.5 (d, C – 5), 43.9 (d, C – 13), 41.5 (t, C – 3), 36.5 (s, C – 10), 34.0 (s, C – 4), 33.7 (q, C – 18), 30.7 (t, C – 1), 30.2 (t, C – 12), 22.4 (q, C – 19), 19.0 (t, C – 11), 16.7 (t, C – 2).

Longikaurin E (**4**), $C_{22}H_{30}O_6$; colorless needles (MeOH); EI-MS (70eV) *m/z* (%): 390 [M]$^+$ (100), 372 [M-H_2O]$^+$ (4), 330 [M-AcOH]$^+$ (35), 312 [M-AcOH-H_2O]$^+$ (30), 284 (27), 269 (18), 255 (13), 227 (10), 213 (14), 200 (16), 179 (16), 151 (35), 120 (24); ^{1}H NMR (500 MHz, C_5D_5N) δ: 6.61 (1H, d, J = 11.0 Hz, OH – 6β), 5.99 and 5.30 (each 1H, s, H_2 – 17), 5.43 (1H, t, J = 4.5 Hz, H – 11β), 4.40 and 4.22 (each 1H, ABd, J = 9.2 Hz, H_2 – 20), 4.30 (1H, dd, J = 11.0, 7.5 Hz, H – 6α), 2.07 (3H, s, OAc), 1.28 and 1.06 (each 3H, s, 2 × Me); ^{13}C NMR (125 MHz, C_5D_5N) δ: 209.7 (s, C – 15), 153.1 (s, C – 16), 117.2 (t, C – 17), 96.2 (s, C – 7), 75.0 (d, C – 6), 68.8 (d, C – 11), 68.7 (t, C – 20), 60.1 (d, C – 9), 59.2 (s, C – 8), 53.4 (d, C – 5), 41.7 (t, C – 3), 38.0 (t, C – 12), 37.2 (s, C – 10), 34.5 (t, C – 1), 34.2 (q, C – 18), 33.9 (s, C – 4), 31.2 (d, C – 13), 27.7 (t, C – 14), 22.8 (q, C – 19), 18.8 (t, C – 2), OAc: 169.8, s, 21.6, q.

Longikaurin G (**5**), $C_{20}H_{28}O_6$; colorless needles (MeOH); EI-MS (70eV) *m/z* (%): 364

[M]$^+$ (68), 346 [M-H_2O]$^+$ (51), 328 (12), 315 (31), 300 (17), 269 (10), 215 (17), 175 (24), 167 (42), 151 (69), 136 (36), 123 (43), 109 (57), 85 (100), 69 (74); ^{1}H NMR (500 MHz, C_5D_5N) δ: 6.79 (1H, d, J = 11.0 Hz, OH－6β), 6.39 (1H, s, H－14α), 6.27 and 5.50 (each 1H, s, H_2－17), 5.16 and 4.29 (1H, ABd, J = 8.6 Hz, H_2－20), 4.40 (1H, m, H－11β), 4.31 (1H, dd, J = 7.5, 11.0 Hz, H－6α), 1.40 (1H, d, J = 7.5 Hz, H－5β), 1.32 and 1.11 (each 3H, s, 2 × Me); ^{13}C NMR (125 MHz, C_5D_5N) δ: 209.4 (s, C－15), 153.5 (s, C－16), 118.7 (t, C－17), 98.9 (s, C－7), 75.1 (d, C－14), 72.5 (d, C－6), 69.2 (t, C－20), 65.2 (d, C－11), 63.0 (s, C－8), 60.0 (d, C－9), 56.4 (d, C－5), 43.5 (d, C－13), 42.7 (t, C－12), 41.5 (t, C－3), 37.6 (s, C－10), 34.6 (q, C－18), 34.0 (s, C－4), 31.2 (t, C－1), 23.0 (q, C－19), 19.0 (t, C－2).

Effusanin E (**6**), $C_{20}H_{28}O_6$; colorless needles (MeOH); EI-MS (70eV) *m/z* (%): 364 [M]$^+$ (76), 346 [M-H_2O]$^+$ (8), 300 (8), 285 (10), 267 (9), 259 (10), 229 (12), 192 (16), 179 (18), 161 (31), 149 (24), 135 (30), 121 (42), 107 (45), 95 (50), 85 (75); ^{1}H NMR (500 MHz, C_5D_5N) δ: 6.88 (1H, d, J = 11.0 Hz, OH－6β), 5.95 and 5.28 (each 1H, s, H_2－17), 5.18 and 4.37 (each 1H, ABd, J = 9.4 Hz, H_2－20), 4.57 (1H, br s, H－11β), 4.33 (1H, dd, J = 11.0, 7.0 Hz, H－6α), 3.87 (1H, dd, J = 10.0, 6.2 Hz, H－1β), 3.68 (1H, d, J = 11.6 Hz, H－14α), 1.31 and 1.12 (each 3H, s, 2 × Me); ^{13}C NMR (125 MHz, C_5D_5N) δ: 211.4 (s, C－15), 154.5 (s, C－16), 115.3 (t, C－17), 96.3 (s, C－7), 75.4 (d, C－1), 73.5 (d, C－6), 67.0 (d, C－11), 65.7 (t, C－20), 60.9 (d, C－5), 60.0 (s, C－8), 55.1 (d, C－9), 43.1 (s, C－10), 39.4 (t, C－3 and 12), 34.9 (q, C－18), 34.0 (s, C－4), 33.8 (d, C－13), 29.4 (t, C－2), 27.1 (t, C－14), 22.5 (q, C－19).

Luteolin (**7**), $C_{15}H_{10}O_6$; yellow powder; EI-MS (70eV) *m/z* (%): 286 [M]$^+$ (100), 258 (20), 229 (10), 153 [A_1 + 1]$^+$ (31), 134 [B_1]$^+$ (16), 69 (15). Its ^{1}H and ^{13}C NMR data are consistent with those of luteolin reported in the literature (Markham *et al*, 1978).

Apigenin (**8**), $C_{15}H_{10}O_5$; yellow powder; EI-MS (70eV) *m/z* (%): 270 [M]$^+$ (100), 242 (31), 213 (7), 153 [A_1 + 1]$^+$ (31), 121 [B_1]$^+$ (35), 96 (11), 69 (26). Its ^{1}H and ^{13}C NMR data are consistent with those of apigenin reported in the literature (Markham *et al*, 1978).

α-Amyrin (**9**), $C_{30}H_{50}O$; white powder; EI-MS (70eV) *m/z* (%): 426 [M]$^+$ (18), 411 (4), 218 (100), 203 (27), 189 (16), 161 (9), 149 (20), 135 (21), 81 (24), 69 (33), 55 (37). Its ^{1}H and ^{13}C NMR data are consistent with those of α-amyrin reported in the literature (Mahato *et al*, 1994).

Ursolic acid (**10**), $C_{30}H_{48}O_3$; white powder; EI-MS (70eV) *m/z* data and Rf value on TLC are consistent with those of authentic sample.

2α-Hydroxy-ursolic acid (**11**), $C_{30}H_{48}O_4$; white powder; EI-MS (70eV) *m/z* data and Rf value on TLC are consistent with those of authentic sample.

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