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DITERPENOIDS FROM *ISODON CALCICOLA* VAR. *SUBCULVA*

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Key Word Index—index; *Isodon calcicola* var. *subculva*; Labiatae; *ent*-kaurenoids; calcicolins B–E.

Abstract—Four new diterpenoids, calcicolins B–E, together with five known diterpenoids, calcicolin A, weisiensin A, adenanthin, forrestin C and nervosanin, have been isolated from the leaves of *Isodon calcicola* var. *subculva*. The new compounds were determined as 1α, 3β-dihydroxy-7β, 11β-diacetoxy-*ent*-kaur-16-en-6,15-dione; 1α, 11β-diacetoxy-3β, 6β-dihydroxy-*ent*-kaur-16-en-15-one; 1α, 6α, 7β, 11β-tetraacetoxy-3β, 15β-dihydroxy-*ent*-kaur-16-ene, and 1α, 6α, 11β, 15β-tetra-acetoxy-3β, 7β-dihydroxy-*ent*-kaur-16-ene by means of spectrometry, including 2D NMR techniques.

INTRODUCTION

Isodon calcicola [(Hand.-Mazz.) Hara] var. *subculva* [(Hand.-Mazz) C. Y. Wu et H. W. Li], which is distributed in the northeast area of Yunnan Province and Sichuan Province, P.R. China [1], is used in Chinese traditional folk medicine to treat sore throats and inflammation. A previous phytochemical investigation [2] has shown the presence of two *ent*-kaurenoids, calcicolin A and weisiensin A [3], in this plant. The reinvestigation of this plant has led to the isolation of four new diterpenoids, calcicolin B–E (**1–5**), together with five known diterpenoids, calcicolin A, weisiensin A [2], adenanthin (**5**) [4], forrestin C (**7**) [5] and nervosanin [6]. In this paper, we report on the isolation and structure elucidation of these new compounds by spectral analysis.

RESULTS AND DISCUSSION

Calcicolin B (**1**) was assigned the molecular formula $C_{24}H_{32}O_8$ (448.2093, calc 448.2097) by HREIMS analysis. Its UV and IR spectra showed the characteristic absorption bands for a five-membered ring α, β-unsaturated *exo*-methylene conjugated with a ketone at 238 nm and 1720 cm^{-1}, respectively. The ^1H NMR spectrum showed the presence of three tertiary methyls (δ 1.25, *s*, CH_3-19; δ 1.09, *s*, CH_3-20, and δ 0.80, *s*, CH_3-18) and two acetyl methyls (δ 2.19, *s*, and δ 1.90, *s*, 2 × OAc). The ^{13}C and DEPT NMR spectra indicated that **1** possessed 3 × CH_3, 3 × CH_2, 7 × CH, and three quaternary carbons, two ketone carbons (δ 206.2, C-6 and δ 202.2, C-15), one double bond, and two acetoxy functions (δ 171.8, 21.4 and 169.6, 21.0), and was therefore, a tetracyclic diterpene with four substituents. By comparison of the spectroscopic data with those reported for related compounds of this species [7, 8], **1** was identified as an *ent*-kaurenoid. The ^1H, ^{13}C and DEPT NMR spectra of **1** were very similar to those of adenanthin (**5**) [4], a known kaurenoid also isolated from *I. calcicola* var. *subculva*, the only difference being the absence of a signal at δ 1.82 and δc 169.2 in the spectra of 1. The mass spectrum of **1** showed the molecular ion (*m/z* 448) to be 42 amu less than that of adenanthin. These data indicated that **1** had one less acetoxy and one more hydroxyl function than adenanthin. In the ^1H–^1H COSY, ^{13}C–^1H COSY and COLOC NMR spectra of **1**, apart from the indicated partial structures, such as rings A–B, and

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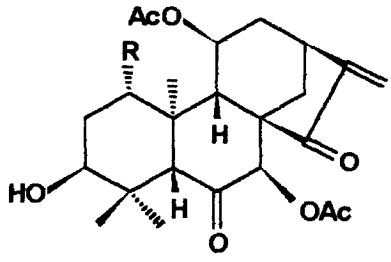
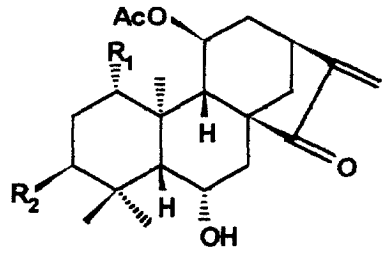
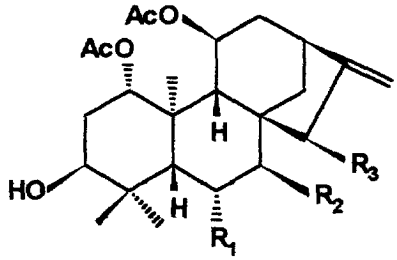


1. R = OH,
5. R = OAc,



2. R_1 = OAc, R_2 = OH,
6. R_1 = OH, R_2 = OAc



3. R_1 = OAc, R_2 = OAc, R_3 = OH
4. R_1 = OAc, R_2 = OH, R_3 = OAc
7. R_1 = OH, R_2 = OAc, R_3 = OH

Table 1. ^{13}C NMR data of calcicolins **B**–**E**(**1**–**4**) in $CDCl_3$

	1	2[a]	3	4
1	75.2(*d*)	80.1(*d*)	79.6(*d*)	79.8(*d*)
2	34.9(*t*)	31.8(*t*)	32.4(*t*)	32.2(*t*)
3	76.1(*d*)	76.3(*d*)	76.2(*d*)	76.4(*d*)
4	36.3(*s*)	38.2(*s*)	37.8(*s*)	37.8(*s*)
5	50.7(*d*)	46.6(*d*)	40.3(*d*)	38.8(*d*)
6	206.2(*s*)	66.9(*d*)	70.7(*d*)*	73.7(*d*)
7	80.0(*d*)	41.9(*t*)	75.5(*d*)	75.6(*d*)
8	53.2(*s*)	48.9(*s*)	45.7(*s*)	46.5(*s*)
9	56.1(*d*)	58.7(*d*)	48.3(*d*)	48.6(*d*)
10	50.9(*s*)	43.2(*s*)	42.3(*s*)	42.4(*s*)
11	70.2(*d*)	70.2(*d*)	70.6(*d*)*	69.2(*d*)
12	37.4(*t*)	38.3(*t*)	39.4(*t*)	39.8(*t*)
13	35.9(*d*)	37.2(*d*)	38.2(*d*)	38.6(*d*)
14	33.8(*t*)	38.3(*t*)	34.9(*t*)	35.5(*t*)
15	202.2(*s*)	209.2(*s*)	81.0(*d*)	80.6(*d*)
16	149.3(*s*)	149.8(*s*)	156.0(*s*)	151.4(*s*)
17	114.3(*t*)	112.6(*t*)	105.9(*t*)	106.2(*t*)
18	26.3(*q*)	28.4(*q*)	28.2(*q*)	28.2(*q*)
19	22.4(*q*)	23.8(*q*)	23.4(*q*)	23.8(*q*)
20	13.9(*q*)	15.1(*q*)	14.8(*q*)	15.0(*q*)
OAc	171.8	171.0	170.5	172.2
	169.6	169.6	169.9	170.6
	21.4	21.8	169.0	170.0
	21.0	21.1	168.6	169.7
			21.6	21.7
			21.4	21.7
			21.3	21.5
			21.3	21.5

[a] The data were recorded in $CDCl_3$ CD_3OD (9:1).
* Assignment may be exchanged.

$-CHCHCH_2CHCH_2-$ (C-9, C-11 to C-13 and C-14), there were cross peaks of two acetyls (δ 171.8, 169.6) with H-7 (δ 4.76) and H-11 (δ 5.75), respectively. Therefore, the acetyl groups had to be attached to C-7 and C-11, and two hydroxyl groups to C-1 and C-3. Thus, unambiguous assignments of all carbons were completed and are listed in Table 1. According to the results of the ^1H–^1H and ^{13}C–^1H COSY experiments, the relative configurations of C-1–OH and C-11–OAc were α and β, respectively, on the basis of the coupling constants for H-1 with H-2α (J = 11.7 Hz) and H-2β (J = 4.4 Hz); and H-11 with H-12β (J = 4.5 Hz). The the broad singlet signal at 3.34 for H-3 indicated that it had α-orientation. The C-7–OAc had β-orientation on the basis of the γ-effect of the acetyl group to C-5 and C-9, and comparison of these ^1H and ^{13}C data with those of adenanthin. Therefore, **1** was identified as 1α, 3β-dihydroxy-7β, 11β-diacetoxy-*ent*-kaur-16-en-6,15-dione.

The molecular formula of Calcicolin C (**2**) was determined as $C_{24}H_{34}O_7$ by positive HR FABMS [m/z 435.2320 (M + 1), Δ 6.2 amu]. Its UV and IR spectra showed the characteristic absorption bands for a five-membered ring with an α, β-unsaturated *exo*-methylene conjugated with a ketone at 236 nm

and 1710 cm^{-1}, respectively. The ^1H NMR spectrum showed the presence of three tertiary methyls (δ 1.54, *s*, CH_3-20; δ 1.18, *s*, CH_3-19, and δ 0.98, *s*, CH_3-18) and two acetyl methyls (δ 2.11, *s*, and δ 1.73, *s*, 2 × OAc). The ^{13}C and DEPT NMR spectra indicated that **2** possessed 3 × CH_3, 4 × CH_2, 7 × CH, and three quaternary carbons, one ketone carbon (δ 202.2, C-15), one double bond and two acetyl functions, and was therefore, a tetracyclic diterpene with four substituents. By comparison of the spectroscopic data with those reported for related compounds of this species [7, 8], **2** was identified as an *ent*-kaurenoid. Its mass spectrum showed the same $[M]^+$ (*m/z* 434) as that of inflexinol (**6**) [9]. The ^1H NMR data for **2** were very similar to those for inflexinol (for which ^{13}C NMR data have not been reported) except for two signals, i.e., the value of H-1 was down field shifted from δ 3.69 (*dd*, J = 12, 5 Hz) in inflexinol to δ 4.86 (*brd*, J = 8.9 Hz) in **2** and the value of H-3 was upfield shifted from δ 4.71 (*t*, J = 3 Hz) in inflexinol to δ 3.36 (*brs.*) in **2**. Therefore, the difference between **2** and inflexinol was the substituents attached at C-1 and C-3. The ^1H–^1H COSY, ^{13}C–^1H COSY and COLOC NMR spectra, were consistent with rings A–B, and –$CHCHCH_2CHCH_2$– (C-9, C-11 to C-13 and C-14), 1-Hβ (δ 4.86) and H-11α (δ 5.58) were correlated with δ 171.0 and 169.6 respectively, and established that the two acetyl groups were attached at C-1 and C-11. Thus, all carbon atoms were assigned, as listed in Table 1.

The relative configuration of the substituents were established from the following evidence: C-1–OAc and C-3–OH were α and β, respectively, on the basis of the coupling constants H-1 with H-2α (*brd*, J = 8.9 Hz); and a broad singlet signal at δ 3.36 for H-3. A broad multiplet signal at δ 4.38 for H-6β, and a broad singlet signal at δ 5.58 for H-11α indicated that an α-OH and a β-OAc were attached to C-6 and C-11, respectively. Therefore, **2** is 1α, 11β-diacetoxy-3β, 6α-dihydroxy-*ent*-kaur-16-en-15-one.

Calcicolin D (**3**) gave a quasi-molecular ion at *m/z* 537.2767 [HRFABMS (positive)] which indicated that the molecular formula was $C_{28}H_{40}O_{10}$. Unlike **1** and **2**, **3** did not give rise to the characteristic UV and IR absorption bands for a five-membered ring α, β-unsaturated *exo*-methylene conjugated with a ketone. The ^1H, ^{13}C and DEPT NMR spectra of **3** were similar to those of forrestin C (**7**) [5], a known diterpenoid also isolated from *I. calcicola* var. *subculva*. The only difference between **3** and forrestin C was that **3** had one less hydroxyl group than forrestin C but an extra acetyl group. Inspection of the ^1H–^1H COSY, ^{13}C–^1H COSY and COLOC NMR spectra of **3** indicated that the acetyl was attached to C-6 in **3** instead of a hydroxyl group in forrestin **C**. Thus, H-6 (δ 5.08) was correlated with an acetyl group (δ 169.0) in the COLOC NMR spectrum of **3**. The assignments of all carbon atoms are shown in Table 1.

The relative configurations of the substituents were assigned on the basis of the coupling constants for H-1β with H-2α (J = 11.4 Hz) and H-2β (J = 4.3 Hz), and for H-3α with H-2α (J = 2.6 Hz) and H-2β (J = 2.6 Hz) which indicated that C-1–OAc and C-3–OH were α and β, respectively. The acetyl functions attachment to C-6 and C-7 were α and β, respectively, on the basis of the coupling constants for H-6β with H-5β (J = 1.6 Hz) and H-7α (J = 3.5 Hz), and for H-7α with H-6β (J = 3.5 Hz). The coupling constants for H-11α with H-12β (J = 4.6 Hz) showed that the C-11–OAc was in the β-orientation. The C-15–OH was assigned to the β-orientation because of the γ-effect of hydroxyl group to C-9 and comparison of its ^{13}C NMR data with that of forrestin C (δ 48.8). Therefore, **3** is 1α, 6α, 7β, 11β-tetraacetoxy-3β, 15β-dihydroxy-*ent*-kaur-16-ene.

The molecular formula of calcicolin E (**4**) was found to be $C_{28}H_{40}O_{10}$ from the positive high resolution FAB mass spectrum [537.2752 (M + 1) calc 537.2700]. Its mass spectrum showed the same $[M]^+$ as that of **3** and its other spectral data were very similar to those of **3**. Thus, **4** is an isomer of **3** which differs from **3** in the position of its substituents. Comparison of the ^1H, ^{13}C, and ^{13}C–^1H COSY NMR spectra of **4** and **3** indicated that the two signals at δ 4.87 (1H, *d*, J = 3.5 Hz, H-7α, ^{13}C δ 75.5) and 4.15 (1H, *brs*, H-15α, ^{13}C δ 81.0) in **3** were shifted to δ 3.56 (1H, *d*, J = 3.4 Hz, H-7α, ^{13}C δ 75.6) and 5.50 (1H, *brs*, H-15α, ^{13}C δ 80.6) in **4**, respectively. From this evidence, a hydroxyl group and an acetyl group were attached at C-7β and C-15, respectively. The change in substituent at C-7β from an acetyl group to a hydroxyl function results in a chemical shift of C-6 from δ 70.6 in **3** to δ 73.7 in **4** ie about 3 ppm. The relative configurations of C-7–OH and C-15–OAc were assigned β-orientation based on the coupling constant for H-7 with H-6β (*d*, J = 3.4 Hz) and the γ-effect of the acetyl group to C-9 and comparison of the ^{13}C NMR data with that of **3** (δ 48.3) and that of forrestin C (δ 48.8). Therefore, the structure of **4** is 1α, 6α, 11β, 15β-tetraacetoxy-3β, 7β-dihydroxy-*ent*-kaur-16-ene. The ^{13}C NMR data for **4** are listed in Table 1.

EXPERIMENTAL

General

Mps: uncorr.; UV: MeOH; ^1H NMR, ^1H–^1H COSY, NOESY: 400.13 MHz; ^{13}C NMR and DEPT: 100.6 MHz; ^1H–^{13}C COSY and COLOC: 400.13 MHz/100.6 MHz. $CDCl_3$ or CD_3OD with TMS as int. standard. EI-, FAB- and HR–MS: VG Auto Spec 3000 instrument.

Plant material

Leaves of *Isodon calcicola* [(Hand.-Mazz. Hara] var. *subculva* [(Hand.-Mazz) C. Y. Wu et H. W. Li] (Labiatae) was collected from Huize county, Yunnan Province, P. R. China, in July, 1996, and identified by Prof. H.-W. Li. A voucher specimen (KIB 96-07-01, Lin) is deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica, Kunming, R. P. China.

Extraction and isolation

Dried and powdered leaves (3 kg) were extracted with EtOH (×3) under reflux for 2 hr., and the solvent was removed *in vacuo*. The residue was partitioned between H_2O and petrol (×3) and EtOAc (×3). After removal of the solvent *in vacuo*, the EtOAc extract (120 g) was subjected to CC on silica gel, eluted with a $CHCl_3$–Me_2CO gradient ($CHCl_3 \rightarrow Me_2CO$). The Frs. were combined by monitoring with TLC and decolourized on MCI with MeOH–H_2O (4:1). Then, Frs. 2–7 were further purified by repeated CC on silica gel with petrol–Me_2CO (7:1, 7:2, 7:3), cyclohexane–C_6H_6–*iso*-PrOH (10:2:1, 6:3:1) and $CHCl_3$–Me_2CO (15:1, 10:1, 7:1) to yield calcicolin B (**1**, 15 mg), calcicolin C (**2**, 40 mg), calcicolin D (**3**, 80 mg), calcicolin E (**4**, 8 mg), adenanthin (**5**), forrestin C (**7**), nervosanin [6], calcicolin A, weisiensin A, and oleanic acid.

*Calcicolin B (**1**)*

$C_{24}H_{32}O_8$, colourless crystals, mp 114–116°, $[\alpha]_D^{20.8}$ −34.36° (MeOH, *c* 0.29). UV λ_{max}^{MeOH} nm (log ϵ): 238(3.63); IR ν_{max}^{KBr} cm^{-1}: 3450(br.), 2920, 1720, 1630, 1430, 1370, 1230, 1030, 950, 815; HRMS: 448.2093 calc. 448.2097, EIMS (70 eV) *m/z* (rel. int): 448$[M]^+$(10), 388$[M-HOAc]^+$(5), 376(55), 346(30), 328(40), 310(55), 295(20), 284(30), 274(35), 256(65), 231(50), 58(100); ^1H NMR($CDCl_3$) δ: 5.82(1H 5.82 (1H, *brs*, H-17a), 5.75(1H, *d*, *J* = 4.5 Hz, H-11α), 5.25(1H, *brs*, H-17b), 4.76(1H, *s*, H-7α), 4.18(1H, *dd*, *J* = 11.7, 4.4 Hz, H-1β), 3.47(1H, *s*, H-5β), 3.34 (1H, *brs*, H-3α), 3.05(1H, *brd*, *J* = 3.3 Hz, H-13α), 2.36(1H, *brs*, H-9β), 2.19, 1.90(each 3H, *s*, 2 × OAc), 2.16(1H, overlapped, H-12α), 2.07(1H, *d*, *J* = 12.5 Hz, H-14α), 2.00(1H, *m*, H-2α), 1.90(1H, overlapped, H-12β), 1.76(1H, *ddd*, *J* = 14.5, 4.4, 3.6 Hz, H-2β), 1.63(1H, *dd*, *J* = 12.5, 4.2 Hz, H-14β), 1.25(3H, *s*, Me-19), 1.09(3H, *s*, Me-20), 0.80(3H, *s*, Me-18).

*Calcicolin C (**2**)*

$C_{24}H_{34}O_7$, colourless crystals, mp 248.5–250.0°, $[\alpha]_D^{21.9}$ −39.94° (MeOH, *c* 0.31). UV λ_{max}^{MeOH} nm (log ϵ): 236(3.58); IR ν_{max}^{KBr} cm^{-1}: 3350, 2920, 2860, 1710, 1635, 1420, 1360, 1250, 1060, 940; HRMS (positive FAB): 435.2320 calc. 435.2382. EIMS (70 eV) *m/z* (rel. int): 434$[M]^+$(1), 374$[M-HOAc]^+$(100), 331(60), 314(40), 296(70), 278(35), 260(53); H^1 H NMR ($CDCl_3$–CD_3OD: 9:1) δ: 5.79(1H, *brs*, H-17a), 5.58(1H, *brs*, H-11α), 5.17(1H, *brs*, H-17b), 4.86(1H, *brd*, *J* = 8.9 Hz, H-1β), 4.38(1H, *m*, H-6β), 3.36(1H, *brs*, H-3α), 2.99(1H, *m*, H-13α), 2.78(1H, *d*, *J* = 12.5 Hz, H-14α), 2.13(2H, overlapped, H-7α and H-12α), 2.11, 1.74 (each 3H, *s*, 2 × OAc), 1.93(1H, overlapped, H-2α), 1.80(1H, overlapped, H-12β), 1.77(1H, overlapped, H-2β), 1.70(1H, overlapped, H-9β), 1.54(3H, *s*, Me-20), 1.53(2H, overlapped, H-5β and H-14β), 1.38(1H, *brd*, *J* = 13.6 Hz, H-7β), 1.18(3H, *s*, Me-19), 0.98(3H, *s*, Me-18).

*Calcicolin D (**3**)*

$C_{28}H_{40}O_{10}$, colourless crystals, mp 196–197.5°, $[\alpha]_D^{20.6}$ −43.62° (MeOH, c 0.30). UV no absorption; IR ν_{max}^{KBr} cm^{-1}: 3520, 3480, 2920, 2860, 1740–1700(br.), 1650, 1420, 1360, 1250, 1060, 940, 910; HRMS (positive FAB): 537.2767 calc. 537.2700, EIMS (70 eV) *m/z* (rel. int.): 536$[M]^+$ (5), 476$[M-HOAc]^+$(10), 416$[M-2 \times HOAc]^+$(30), 374(55), 356(95), 338(15), 314(80), 296(100), 281(80), 278(35), 263(63); ^1H NMR($CDCl_3$) δ: 5.61(1H, *d*, *J* = 4.6 Hz, H-11α), 5.20(1H, *dd*, *J* = 11.4, 4.3 Hz, H-1β), 5.08(1H, *dd*, *J* = 3.5, 1.6 Hz, H-6β), 5.03(1H, *brs*, H-17a), 4.89(1H, *brs*, H-17b), 4.87(1H, *d*, *J* = 3.5 Hz, H-7α), 4.15(1H, *brs*, H-15α), 3.42(1H, *t*, *J* = 2.6 Hz, H-3α), 2.56(1H, *brd*, *J* = 3.6 Hz, H-13α), 2.29(1H, *brs*, H-9β), 2.16(1H, *d J* = 1.6 Hz, H-5β), 2.13(1H, overlapped, H-14α), 2.11, 2.05, 1.99, 1.84 (each 3H, *s*, 4 × OAc), 2.00(2H, overlapped, H-2α and H-12α), 1.84(1H, overlapped, H-12β), 1.80(1H, m, H-2β), 1.50(3H, *s*, Me-20). 1.25(1H, *dd*, *J* = 12.2, 4.4 Hz, H-14β), 0.96(3H, *s*, Me-19), 0.90(3H, *s*, Me-18).

*Calcicolin E (**4**)*

$C_{28}H_{40}O_{10}$, colourless crystals, mp 117–119.5°, $[\alpha]_D^{22.6}$ −46.25° (MeOH, *c* 0.40). UV no absorption; IR ν_{max}^{KBr} cm^{-1}: 3500–3480(br.), 2920, 1860, 1740 ~ 1710 (br.), 1360, 1260–1220(br.), 1120, 1050, 950, 910; HRMS (positive FAB): 537.2752 calc. 537.2700, EIMS (70 eV) *m/z* (rel. int.): 536$[M]^+$ (1), 476$[M-HOAc]^+$ (5), 416$[M-2 \times HOAc]^+$(15), 374(20), 356(55), 314(37), 171(60), 57(100); ^1H NMR($CDCl_3$) δ: 5.55 (1H, *d*, *J* = 4.5 Hz, *brs*, H-11α), 5.50(1H, *brs*, H-15α), 5.14 (1H, *dd*, *J* = 12.3, 4.4 Hz, H-1β), 5.12(1H, *brs*, H-17a), 4.89(1H, *brs*, H-17b), 4.76(1H, *brd*, *J* = 3.4 Hz, H-6β), 3.56(1H, *d*, *J* = 3.4 Hz, H-7α), 3.44(1H, *brt*, *J* = 2.5 Hz, H-3α), 2.61(1H, *brd*, *J* = 3.5 Hz, H-13α), 2.39(1H, *brs*, H-5β), 2.32(1H, *brs*, H-9β), 2.13, 2.05, 2.01, 1.83 (each 3H, *s*, 4 × OAc), 1.47(3H, *s*, Me-20). 1.00(3H, *s*, Me-19), 0.98(3H, *s*, Me-18).

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