

Two New Diterpenoids from *Isodon Lungshengensis*

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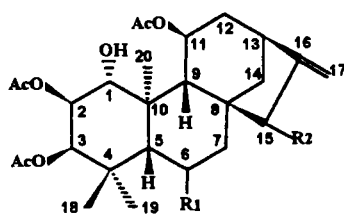
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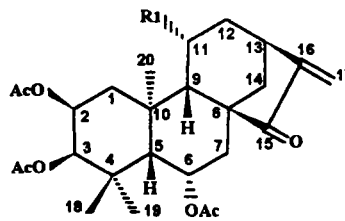
Abstract Two new diterpenoids, lungshengenin B and C (1-2), were isolated from *Isodon lungshengensis*. The structures were determined as 1 α -hydroxy-2 β ,3 β ,11 β ,15 β -tetraacetoxyl-ent-kaur-16-en-6-one; 11 α -hydroxy-2 β ,3 β ,6 α -triacetoxyl-ent-kaur-16-en-15-one by 1D and 2D NMR techniques (COSY, HETCOR, COLOC).

In a previous paper, we had reported on a new diterpenoid, lungshengenin A^[1] (3), the first *ent*-kaurene diterpenoid in which there are three oxy-groups on the A-ring, isolated from *Isodon lungshengensis* C. Y. Wu et H. W. Li, a perennial herb of the Labiatae family, which is distributed in Longsheng county of the Guangxi Zhuang Autonomous Region, and is used as an agent for the treatment of hepatitis in local folk medicine. Further investigation of this plant led to the isolation of two new diterpenoids named as lungshengenin B-C (1-2). This paper deals with their structural elucidation.



1. $R_1 = \text{OH}$, $R_2 = \beta\text{-OAc}$

3. $R_1 = \alpha\text{-OH}$, $R_2 = \text{O}$



2. $R_1 = \text{OH}$

4. $R_1 = \text{OAc}$

Lungshengenin B (1), colorless cubes crystallized from cyclohexane, mp 166.3-167.8°C; $[\alpha]_D^{22.5} -65.47^\circ$ (c 0.57, CHCl_3); HREIMS (found 534.2453, calc. 534.2464) suggested the molecular formula $\text{C}_{28}\text{H}_{38}\text{O}_{10}$. EIMS (70 eV) m/z (rel. int. %): 534 $[\text{M}]^+$ (17), 516(35), 474(61), 456(10), 432(32), 414(100), 372(35), 354(51), 312(85), 294(88). It was shown the presence of three methyl carbons, three methylenes, eight methines, three quaternary carbons, one ketonic carbon, one *exo*-methylene group and four acetoxyl groups in the IR, MS, ^1H , ^{13}C NMR and DEPT spectra (see Table 1). Due to the absence of the characteristic absorption in UV and IR at about 240 nm and 1700 and 1640 cm^{-1} for an α , β -unsaturated *exo*-methylene ketone, it was obvious that the *exo*-methylene group (δ 151.5, 106.9) and the ketone (δ 209.4) were unconjugated. The ^1H - ^1H COSY and ^{13}C - ^1H COSY spectra of 1 revealed the following partial structure -CHCHCH- (C-1 to C-3) and -CHCHCH₂CHCH₂- (C-9, C-11 to C-14). The HETCOR experiment indicated there were relations between the C-4 and H-3, H-5, Me-18 and Me-19, between C-8 and H-7, H-9, H-11 and H-15, and between C-10 and H-5, H-9 and Me-20, therefore 1 was deduced as polysubstituted *ent*-kaurene diterpenoid. The location of

the four acetoxyl groups and the carbonyl function were determined by the COLOC spectrum simultaneously (Figure 1.). On the other hand, the relative configuration of substituents was also confirmed from the following evidence: the coupling constants H-1 β with H-2 α ($J=10.0$ Hz), H-2 α with H-3 α ($J=3.0$ Hz) and H-11 α with H-9 β ($J=4.5$ Hz). In addition, the δ_c of Me-18 and Me-20 were up-field, and there were the NOE correlations between H-7 α with H-15 α and H-14 β with H-15 α , all of which could only be explained as the results of the substituents with the orientation of C-1 α , C-2 β , C-3 β , C-11 β and C-15 β . Therefore, the structure of **1** deduced as 1 α -hydroxy-2 β ,3 β ,11 β ,15 β -tetraacetoxo-*ent*-kaur-16-en-6-one.

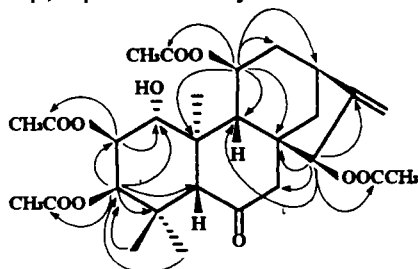


Figure 1. The ^1H - ^{13}C long-range COSY of **1**

Lungshengenin **C** (**2**) was obtained as colorless needles (from acetone), had a molecular formula of $\text{C}_{26}\text{H}_{36}\text{O}_8$ deduced from HREIMS (found 476.2405, calc. 476.2410), mp 199.3–201.1°C. $[\alpha]_D^{25} -53.71^\circ$ (c 0.39, CHCl_3); UV (CHCl_3) λ_{max} 241.5 nm ($\log \epsilon$ 3.77); IR (KBr) ν_{max} 3480 (br.), 1713 and 1631 cm^{-1} ; EIMS (70 eV) m/z (rel. int. %): 476[M] $^+$ (5), 458(1), 416(5), 356(6), 296(70), 257(100). The NMR spectra of **2**, compared with that of lushanrubescensin **C** (**4**) $^{[1,2]}$ which was also isolated from this plant, differed only in the C-ring signals: the acetoxyl group at C-11 α of **4** was replaced by a hydroxy group in **2**, which was also verified by COSY, HETCOR and COLOC experiments. Thus, **2** was elucidated as 11 α -hydroxy-2 β ,3 β ,6 α -triacetoxo-*ent*-kaur-16-en-15-one.

Table 1. ^{13}C NMR data for lungshengenin **B**, **C** (**1**, **2**) in $\text{C}_5\text{D}_5\text{N}$ (100.6 MHz, δ in ppm)

C	1	2	C	1	2
1	76.4 (d)	40.6 (t)	15	81.4 (d)	207.9 (s)
2	72.9 (d)	67.8 (d)	16	151.5 (s)	150.8 (s)
3	78.0 (d)	77.7 (d)	17	106.9 (t)	111.7 (t)
4	37.0 (s)	39.9 (s)	18	26.7 (q)	28.0 (q)
5	58.3 (d)	49.2 (d)	19	21.9 (q)	22.7 (q)
6	209.4 (s)	68.8 (d)	20	16.8 (q)	20.0 (q)
7	54.1 (t)	41.3 (t)	OAc	171.1	170.5
8	49.5 (s)	48.7 (s)		170.7	170.3
9	54.5 (d)	63.5 (d)		170.4	170.0
10	49.5 (s)	38.5 (s)		170.3	21.5
11	70.0 (d)	65.0 (d)		21.9	21.0
12	38.9 (t)	38.7 (t)		21.7	20.6
13	39.1 (d)	38.0 (d)		20.8	
14	36.8 (t)	37.9 (t)		20.4	

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