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THE STRUCTURES OF LUNGSHENGENIN D AND F

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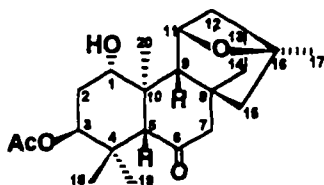
(Received 22nd January 1998)

Abstract:-Two novel *ent*-kaurane diterpenoids, lungshengenin D(1) and F(2), were isolated from *Isodon lungshengensis*. Their structures were elucidated on the basis of spectral evidence as 1 α -hydroxy-3 β -acetoxy-11 β ,16 β -epoxy-*ent*-kauran-6-one and 1 α -hydroxy-2 β ,3 β ,11 β -triacetoxy-*ent*-kaur-16-ene-15-one, respectively.

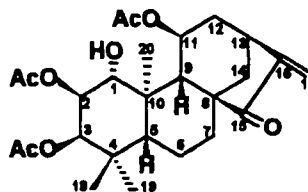
Key words:-*Isodon lungshengensis*; Labiatae; *ent*-kaurenoids; lungshengenin D and F.

INTRODUCTION

The genus *Isodon* (Labiatae) is rich in *ent*-kaurane diterpenoids which have been identified as the main biologically active constituents. As part of a program directed toward the isolation of biologically active metabolites from plants of the *Isodon* genus, we have recently investigated the constituents of *Isodon lungshengensis* C. Y. Wu et H. W. Li which has been used as a medicinal herb in local folk to treat hepatitis for a long time, and have isolated a series of new *ent*-kaurane diterpenoids. Among them, the structures of two compounds, named lungshengenin D(1) and F(2) respectively, have some peculiarities. Besides having four rings as usual, lungshengenin D has an extra ring formed by an ether link between C-11 and C-16. Lungshengenin F is one of only a few diterpenoids to be found in the nature in which there are three oxy-groups on the A-ring¹. This paper deals with their structural elucidation.



1



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RESULTS AND DISCUSSION

Lungshengenin D (1), colorless prisms crystallized from cyclohexane, was shown to have a molecular formula $C_{22}H_{32}O_5$ by HREIMS spectrometry⁵ (found 376.2236, calc. 376.2250), suggesting seven degrees of unsaturation. The ^{13}C -NMR and DEPT spectra of 1 indicated carbon signals of five Me groups, five CH_2 units, six methines, four quaternary carbons and two ketonic carbons (δ 210.2 and 170.3). It gave IR absorption bands for a hydroxy group (3365 cm^{-1}), one ketonic and one acetoxy carbonyl bonds ($1725, 1690\text{ cm}^{-1}$) and an ether bond ($1105, 1045\text{ cm}^{-1}$). The 1H - 1H COSY and ^{13}C - 1H COSY spectra of 1 revealed the following partial structures: $-CHCH_2CH-$ (C-1 to C-3) and $-CHCHCH_2CHCH_2-$ (C-9, C-11 to C-14). According to the HETCOR experiment, compound 1 possessed an *ent*-kaurane diterpenoid skeleton with a ketonic oxygen at position C-6, and unsaturated functionalities of ring D ($=CH_2$ and $C=O$) were reduced. From the spectra of MS, IR, 1H and ^{13}C -NMR, the presence of one acetoxy group and one hydroxy group was shown clearly. However, the extra degree of unsaturation required by the molecular formula indicated the presence of an additional ring. The δ 70-90 region of the ^{13}C -NMR spectrum of 1 exhibited four oxygenated carbons signals at δ 85.1 (s), 79.4 (d), 79.3 (d), 74.3 (d), respectively (three oxygenated methine carbons and one oxygenated quaternary carbon), suggesting that one oxygen atom which is one of the three oxygenated substituents in 1 was connected with two carbons to form an epoxy unit. The linkage of this additional ring through an ether bridge from C-11 to C-16 was established unambiguously by analysis of the 2J and 3J heteronuclear couplings visualized through a COLOC experiment, i.e. H-11 α (δ 5.71, t, $J=3.4\text{ Hz}$) was correlated to C-16 (δ 85.1) in its COLOC spectrum. Meanwhile, the location of the other substituents was also determined by the same experiment (Figure 1.) and the 1H - 1H COSY.

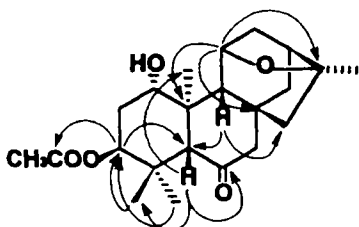


Figure 1. The 1H - ^{13}C long-range COSY of 1

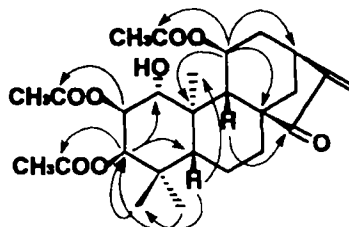


Figure 2. The HMBC spectrum of 2

The relative configurations of substituents with an orientation of C-1 α , C-3 β , C-11 β and C-16 β were achieved by the NOESY experiment. The correlation between H-1 β and H-5 β , H-1 β and H-9 β , H-3 α and H-19 and H-11 α and H-20 protons were clearly revealed from the across peaks of the NOESY spectrum. Therefore, the structure of 1 was deduced as 1 α -hydroxy-3 β -acetoxy-11 β ,16 β -epoxy-*ent*-kauran-6-one⁶. This conclusion was also supported

by comparing 1 with similar compounds to have been reported such as euphoranginol C², isodoglutinosin B³ and liangshanin G⁴.

Lungshengenin F (2), obtained as colorless cubes from acetone, had a molecular formula of C₂₆H₃₆O₈, suggested by HREIMS (found 476.2410, calc. 476.2393). Compound 2 exhibited signals for three methyl carbons, four methylenes, seven methines, three quaternary carbons, one ketonic carbon, one *exo*-methylene group (δ 151.3 and 111.9), three acetoxy groups and one hydroxy group from the IR, MS, ¹H, ¹³C-NMR and DEPT spectra. ¹H-¹H COSY, HMQC and HMBC experiments revealed that 2 was an *ent*-kaurene diterpenoid. Due to the UV absorption at 240 nm and the IR bands at 1734, 1647 cm⁻¹, the ketonic bond and the *exo*-methylene group were obviously conjugated. ¹H-¹H COSY and HMBC experiments also showed that the oxygen substituents were at C-1, C-2, C-3 and C-11 (Figure 2). On the other hand, the observation of the NOESY correlation such as between H-1 β and H-5 β , H-1 β and H-9 β , H-2 α and H-19, H-2 α and H-20, H-3 α and H-19 and H-11 α and H-20 protons confirmed that the substituents unambiguously possessed an orientation of C-1 α , C-2 β , C-3 β and C-11 β . Thus, 2 was elucidated as 1 α -hydroxy-2 β ,3 β ,11 β -triacetoxy-*ent*-kaur-16-ene-15-one⁷.

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4. F.L. Zhang, Y.L. Xu and H.D. Sun (1989) Diterpenoid constituents of *Rabdosia liangshanica*. *Phytochemistry*, **28**, 1671-1674.
5. **General Experimental Procedures.** All the mps were obtained on a Koffler apparatus which was uncorrected. IR spectral data were measured on a Perkin-Elmer 577 or Bio-Rad FTS-135 spectrometer with KBr pellets. NMR spectra were recorded on a Bruker AM-400 or DRX-500 instrument with TMS as internal standard and pyridine-*d*₅ as solvent. ¹H-NMR, ¹H-¹H COSY spectra were recorded at 400.13 or 500.13 MHz; ¹³C-NMR and DEPT spectra were recorded at 100.6 or 125.8 MHz. ¹³C-NMR assignments were determined by ¹³C-¹H COSY and HMQC spectra. The HREIMS and EIMS data were carried out on a VG Auto Spec-3000 spectrometer.

6. Properties of 1: $C_{22}H_{32}O_5$ (HREIMS found 376.2236, calc. 376.2250); colorless prisms, m.p. 199.2–200.6 °C; $[\alpha]_D^{22}$: +26.42° ($CHCl_3$, $c=0.27$); UV ($CHCl_3$) λ_{max} : no absorption; IR ν_{max} : 3365 (s), 2945 (s), 2920 (s), 2860 (s), 1725 (s), 1690 (s), 1430 (m), 1380 (s), 1230 (s), 1175 (s), 1105 (s), 1045 (s), 980 (s), 825 (m) cm^{-1} ; EIMS m/z (rel. int. %): 376 $[M]^+$ (49), 333 (32), 316 (56), 298 (26), 288 (9), 273 (28), 219 (100), 201 (31); 1H -NMR δ : 6.35 (1H, d, $J=5.8$ Hz, H-1 α -OH), 4.32 (1H, dd, $J=5.8$ and 3.0 Hz, H-1 β), 2.22 (2H, t, $J=3.0$ Hz, H₂-2 α and 2 β), 4.83 (1H, t, $J=3.0$ Hz, H-3 α), 2.96 (1H, s, H-5 β), 1.83 (1H, d, $J=11.0$ Hz, H-7 β), 1.38 (1H, d, $J=11.0$ Hz, H-7 α), 2.55 (1H, br d, $J=3.4$ Hz, H-9 β), 5.71 (1H, t, $J=3.4$ Hz, H-11 α), 1.94 (1H, dt, $J=11.8$ and 3.4 Hz, H-12 α), 1.27 (1H, m, H-12 β), 2.13 (1H, overlapped, H-13 α), 2.15 (1H, overlapped, H-14 β), 2.09 (1H, overlapped, H-14 α), 2.75 (1H, d, $J=13.3$ Hz, H-15 α), 2.10 (1H, d, $J=13.3$ Hz, H-15 β), 1.38 (3H, s, Me-17), 1.08 (3H, s, Me-18), 1.50 (3H, s, Me-19), 1.34 (3H, s, Me-20), 2.00 (3H, s, Ac). ^{13}C -NMR δ : 14.5 (C-20), 20.9 (AcO), 22.4 (C-19), 23.4 (C-17), 27.0 (C-18), 33.0 (C-2), 35.9 (C-4), 40.3 (C-14), 44.6 (C-12), 46.1 (C-13), 48.3 (C-8), 48.7 (C-10), 53.5 (C-15), 57.7 (C-7), 59.8 (C-9), 60.6 (C-5), 74.3 (C-1), 79.3 (C-3), 79.4 (C-11), 85.1 (C-16), 170.3 (AcO), 210.2 (C-6).
7. Properties of 2: $C_{26}H_{36}O_8$ (HREIMS found 476.2410, calc. 476.2393); colorless cubes, m.p. 94.7–96.1 °C; $[\alpha]_D^{22}$: -94.88° ($CHCl_3$, $c=0.47$); UV ($CHCl_3$) λ_{max} : 240 nm (log ϵ 3.91); IR ν_{max} : 3473 (br m), 2945 (m), 2881 (m), 1734 (s), 1647 (m), 1456 (m), 1435 (m), 1372 (s), 1258 (s), 1240 (s), 1035 (s), 963 (m) cm^{-1} ; EIMS m/z (rel. int. %): 476 $[M]^+$ (14), 433 (52), 416 (61), 373 (9), 356 (42), 331 (23), 313 (78), 296 (100), 278 (24), 253 (20), 241 (26), 200 (60); 1H -NMR δ : 4.31 (1H, d, $J=10.0$ Hz, H-1 β), 5.68 (1H, dd, $J=10.0$ and 2.4 Hz, H-2 α), 5.37 (1H, d, $J=2.4$ Hz, H-3 α), 1.61 (1H, dd, $J=11.7$ and 2.8 Hz, H-5 β), 1.49 (1H, br d, $J=11.7$ Hz, H-6 β), 1.33 (1H, overlapped, H-6 α), 2.20 (1H, overlapped, H-7 β), 1.39 (1H, overlapped, H-7 α), 2.11 (1H, br s, H-9 β), 6.94 (1H, t, $J=2.7$ Hz, H-11 α), 2.07 (2H, overlapped, H₂-12 β and 12 α), 2.91 (1H, br d, $J=3.0$ Hz, H-13 α), 2.38 (1H, d, $J=12.1$ Hz, H-14 β), 1.34 (1H, overlapped, H-14 α), 5.97 (1H, s, H-17a), 5.18 (1H, s, H-17b), 0.84 (3H, s, Me-18), 0.95 (3H, s, Me-19), 1.36 (3H, s, Me-20), 2.04, 1.86, 1.73 (each 3H, 3 \times Ac). ^{13}C -NMR δ : 15.7 (C-20), 18.2 (C-6), 20.6 (AcO), 20.9 (AcO), 21.3 (AcO), 21.4 (C-19), 28.1 (C-18), 34.6 (C-7), 37.1 (C-14), 37.3 (C-13), 37.6 (C-4), 38.1 (C-12), 45.3 (C-10), 49.0 (C-5), 51.1 (C-8), 60.4 (C-9), 71.5 (C-11), 72.7 (C-2), 76.7 (C-1), 77.9 (C-3), 111.9 (C-17), 151.3 (C-16), 169.5 (AcO), 170.7 (AcO), 170.8 (AcO), 208.4 (C-15).