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Two New Acyclic Diterpene-γ-lactones from the Leaves of *Salix matsudana*

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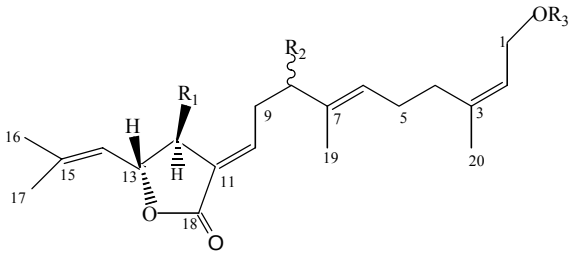
Abstract: Two new acyclic diterpene-γ-lactones named hanliuine III (**1**) and hanliuine IV (**2**) were isolated from leaves of *Salix matsudana* (Chinese name "hanliu"). Their structures were deduced from spectral data.

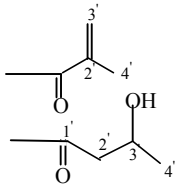
Keywords: *Salix matsudana*, acyclic diterpene - γ-lactone.

Salix matsudana Koidz., a species of *Salicaceae*, is mostly distributed in northern and western in China[1], especially in eastern Gansu. Its leaves are reported to be useful for treating jaundice, hepatitis, rheumatism, arthritis and eczema[2, 3]. But its chemical constituents were scarcely known. Continuing our previous work on the constituents of this herb two new acyclic diterpenoids **1** and **2** were obtained.



1 R_1 = OAc R_2 = H R_3 =

2 R_1 = OH R_2 = H R_3 =



Compound **1** was a yellow gum with $[\alpha]_D^{20}$ -130.5 ($CHCl_3$, *c* 0.25). Its HR-EIMS gave a peak at *m/z* 445 $[M+1]^+$ corresponding to the molecular formula $C_{26}H_{36}O_6$ (*m/z* 444.5676; calc.444.5682). The IR spectrum displayed absorption bands for α, β - un-saturated-γ-lactone (1751, 1685 cm^{-1}), acetyl carbonyl (1740 cm^{-1}) methacrylate and carbonyl (1705 cm^{-1}). The ^{13}C NMR and DEPT spectra (**Table 2**) of **1** clearly exhibited

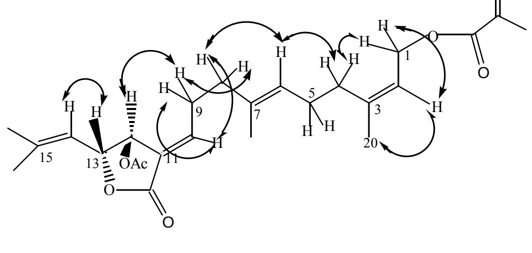
26 carbon signals (6×CH_3, 6×CH_2, 6×CH, 5×C, 3×CO). Meanwhile, the ^{1}H- ^{1}H COSY and HMQC spectra indicated the presence of an acyclic diterpene-γ-lactone skeleton[4, 5] with an acetyl group located at C-12, a methacrylate group at C-1, and without a hydroxyl group at C-8. Close similarity in chemical shifts, coupling patterns and coupling constants led us to assume the similarity of the structures of hanliuine I and hanliuine II[4]. Only the difference was found at C-8. The HMQC spectrum showed that the non-equivalent methylene protons at δ 2.18 (ddd, J=10.0, 6.0, 2.0 Hz, H-8a) and δ 2.03 (brt, J=11.0 Hz, H-8b) correlated with C-8 (t, δ 26.3). And the ^{1}H-^{1}H COSY spectrum obviously displayed that the signals at δ 2.18 and 2.03 were coupled with the non-equivalent methylene protons at δ 2.26 (dddd , J=12.4, 12.4, 10.4, 2.0 Hz, H-9a) and 2.10 (dddd, J=12.0, 8.0, 6.0, 2.0 Hz, H-9b) , which in turn correlated with a vinyl proton at δ 6.94 (H-10). In the HMBC spectrum, C-8 /H-6, H-9a, H-9b, H-19 and C-9/H-8a, H-8b, H-10, confirmed the structural fragment =CH(10)-CH_2(9) -CH_2(8)-C(7). In addition , its ^{1}HNMR spectrum gave the proton signals: δ 6.03 (brs , H-3'a), 5.58 (t, H-3'b) and 1.90 (brs, CH_3-4'). Meanwhile, according to the signals of ^{13}C NMR spectrum at δ 166.0 (CO), 135.4 (C), 126.8 (CH_2), 18.3 (CH_3) and cross signals: C-1'/ H-1, H-3'a, H-3'b, H-4' and C-4'/ H-3'a, H-3'b in HMBC spectrum, the presence of a methacrylate at C-1 was strongly confirmed. Since the HMBC spectrum showed cross peak of an acetyl carbonyl signal (δ 170.0) with H-12 (δ 4.88), the acetyl group must be attached to C-12.

The relative stereochemistry of compound **1** was determined on the basis of the NOESY information (**Figure 1**). Comparison of its NOESY spectrum with those of structurally related natural products[4], their relative stereochemistry was the same. But the absolute configuration at C-12 and C-13 were not determined, the coupling constant $J_{12, 13}$ =2 Hz was in agreement with a dihedral angle of *ca* 70 or 115° which revealed a *trans*-relationship of H-12 and H-13 [5].

Therefore, the structure of compound **1** was deduced as an acyclic diterpene-γ-lactone named hanliuine III.

Compound **2** was a pale yellow gum with $[\alpha]_D^{20}$ –126.9 ($CHCl_3$, *c* 0.25). Its HR-EIMS revealed a molecular formula of $C_{24}H_{36}O_6$ (*m/z* 420.5470, calc. 420.5462).

Figure 1 The key correlations of **1** in NOESY



The ^{13}C NMR and DEPT spectra (**Table 2**) of **2** displayed 24 carbon signals(5×CH_3, 6×CH_2, 7×CH, 4×C, 2×CO). Its IR spectrum gave absorption bands for hydroxyl (3350

cm^{-1}) and α, β-unsaturated-γ-lactone (1748, 1680 cm^{-1}) and ester carbonyl (1718 cm^{-1}). The ^{1}H, ^{13}C NMR and DEPT (**Table 1** and **2)**, IR, MS and NOESY spectral data of **2** were very similar to those of **1** (**Figure 1**). Comparing the ^{13}C NMR and ^{1}H NMR spectra of **2** with those of **1** led to the conclusion that the main difference was the substitution of 3-hydroxy-butyrate group [^{13}C NMR: δ 22.1(q), 45.5 (t), 63.8 (d), 171.0 (s); ^{1}H NMR: as shown in the **Table 1**] at C-1 in **2.** Furthermore, in the HMBC spectrum the correlation peak between H-1 and CO of 3-hydroxy-butyrate group was clearly observed. So this group must be attached to C-1. Besides, a hydroxy at C-12 rather than an acetoxy group was confirmed by the HMBC spectrum. From the above information, hanliuine IV was determined to have the structure as shown in **2**.

Table 1 ^{1}H NMR Data of Compound **1** and **2** ($CDCl_3$, TMS, δ ppm) ∗

No.	**1** δ_H	**2** δ_H
1a, 1b	6.50 d (7.2)	6.22 d (7.0)
2	5.68 tq (7.5, 1.6)	5.60 tq (7.2,1.8)
4	2.07 m	2.10 m
5	1.89 m	1.90 m
6	5.26 brt (6.9)	5.26 brt (6.8)
8a	2.18 ddd (10.0,6.0,2.0)	2.16 ddd (10.2,6.0,2.1)
8b	2.03 brt (11.0)	1.98 brt (11.2)
9a	2.26 dddd (12.4,12.4,10.4,2.0)	2.23 dddd (12.2,12.3, 10.6,2.0)
9b	2.10 dddd (12.0,8.0,6.0,2.0)	2.10 dddd (12.1, 7.9, 6.0, 2.0)
10	6.94 ddd (10.6, 6.6, 1.9)	6.81 ddd (10.6,6.5,2.0)
12	4.88 brs	4.57 brs
13	5.40 brs	5.36 brs
14	5.06 brs	5.06 brs
16	1.79 s	1.78 s
17	1.72 s	1.72 s
19	1.48 s	1.51 s
20	1.58 s	1.56 s
OH		3.95 brs
OAc	2.03 s	
2′a		2.63 dd (8.9, 15.0)
2′b		2.75 dd (4.2, 15.0)
3′a	6.03 brs	4.38 m
3′b	5.58 t (1.6)	
4	1.90 s	1.21 d (7.3)

∗Assignment from ^{1}H-^{1}H COSY, HMQC, HMBC and NOESY

Table 2 ^{13}C NMR Data of Compound **1**and **2** (CDC_{l3}, TMS, δ ppm)*

Carbon No.	**1** δ_C	DEPT	HMBC	**2** δ_C	DEPT	HMBC
1	70.4	CH_2	H-2	70.2	CH_2	H-2
2	126.4	CH	H-1a, H-1b, H-20	126.0	CH	H-1a, H-1b, H-20
3	138.0	C	H-2, H-4, H-20	138.1	C	H-2, H-4, H-20
4	31.4	CH_2	H-2, H-20	30.8	CH_2	H-2, H-20
5	24.9	CH_2	H-4, H-6	24.9	CH_2	H-4, H-6
6	124.3	CH	H-8, H-19	124.8	CH	H-8, H-19
7	126.2	C	H-5, H-8, H-19	126.1	C	H-5, H-8, H-19
8	26.8	CH_2	H-6, H-9a, H-9b, H-19	26.3	CH_2	H-6, H-9a, H-9b, H-19
9	32.4	CH_2	H-8a, H-8b, H-10	31.8	CH_2	H-8a, H-8b, H-10
10	142.0	CH	H-8a, H-8b, H-9a, H-9b, H-12	141.9	CH	H-8a,H-8b,H-9a,H-9b, H-12
11	133.1	C	H-9a, H-9b, H-10, H-12, H-13	133.4	C	H-9a,H-9b,H-10,H-12,H-13
12	73.9	CH	H-10, H-13, H-14	71.1	CH	H-10, H-13, H-14
13	82.9	CH	H-12, H-17	82.7	CH	H-12, H-17
14	121.0	CH	H-12, H-13, H-16, H-17	120.7	CH	H-12, H-13, H-16, H-17
15	140.0	C	H-13, H-16, H-17	140.0	C	H-13, H-16, H-17
16	25.7	CH_3	H-14, H-17	25.7	CH_3	H-14, H-17
17	18.5	CH_3	H-14, H-16	18.5	CH_3	H-14, H-16
18	170.0	CO	H-10, H-12, H-13	170.1	CO	H-10, H-12, H-13
19	11.1	CH_3	H-6, H-8a, H-8b	11.2	CH_3	H-6, H-8a, H-8b
20	23.8	CH_3	H-2, H-4	23.8	CH_3	H-2, H-4
OAc	170.0	CO	H-12			
	20.9	CH_3				
1′	166.0	CO	H-1, H-3′a, H-3′b, H-4′	171.0	CO	H-1, H-2′a, H-2′b,H-3′
2′	135.4	C	H-3′a, H-3′b, H-4′	45.5	CH_2	H-3′, H-4′
3′	126.8	CH_2	H-4′	63.8	CH	H-2′a, H-2′b, H-4′
4′	18.3	CH_3	H-3′a, H-3′b	22.1	CH_3	H-2′a, H-2′b, H-3′

*Assignment from ^1H-^1H COSY, HMQC and HMBC

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