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Three New Cucurbitacins from *Hemsleya lijiangensis*

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Abstract: Three new cucurbitacins were isolated from the BuOH extract of the rhizomes of *Hemsleya lijiangensis.* Their structures were elucidated as 23, 24 -dihydro cucurbitacin F-16, 25-diacetate(**1**), 23, 24-dihydro cucurbitacin F-16, 25-diacetate-2-O- β -D –glucopyranoside (**2**), 23, 24-dihydro-cucurbitacin F-16-acetate(**3**), respectively; by spectral analyses.

Key words: *Hemsleya lijiangensis*, Cucurbitaceae, Hemslecins D, E, F.

The plants of the genus *Hemsleya* Cogn. are abundant in Yunnan and Sichuan provinces, China. Most of them were used as famous traditional medicines. *H.lijiangensis* is mainly distributed in Lijiang of Yunnan, and was also a useful folk medicine for treatments of bacillary dysentery, bronchitis and tuberculosis. In the research for its biologically active constituents[1], we found three new cucurbitacins from the BuOH extract of the rhizomes of *H. lijiangensis*. Based on the various spectral analyses, their structures were elucidated as 23, 24-dihydro cucurbitacin F-16, 25- diacetate(**1**)、23, 24-dihydro cucurbitacin F-16-acetate(**2**) and 23, 24 b-dihydro- cucurbitacin F-16, 25-diacetate-2-O-β-D-glucopyranoside(**3**), called as hemslecins D (**1**), E(**2**), F(**3**); respectively.

Compound **1** was isolated as a white powder, HRFAB-MS [*m/z* : 603.3500 $[M-H]^-$, (100)(calcd. for $C_{34}H_{51}O_9$ 603.3533)], ^{13}C NMR and DEPT spectra established the molecular formula of **1** as $C_{34}H_{52}O_9$. The formula of **1** showed that compound has nine unsaturations of rings and double bonds. Its IR spectrum indicated absorption bands for hydroxyl groups (3446 cm^{-1}), cabornyl groups (1736, 1679 cm^{-1}). The ^1H and ^{13}C NMR spectra exhibited methyl groups, six methylene groups, six methine groups, twelve quaternary carbons, and their characteristic signals (10xCH_3 : δ_H1.94 1.92 1.44 1.15 1.39 1.18 1.18 1.10 0.98 0.95,1.94 1.92) suggested that the compound **1** has the skeleton of cucurbitacin F. The ^{13}C NMR signals at δc 137.8 and 120.7 that was correlated in the HMBC experiment with the ^1H NMR signal at δ_H 5.67 (d,1H, J=5.8Hz) were assigned to an E-trisubstituted double bond. Compared its ^{13}C and ^1H NMR spectra with that of 23, 24-dihydro cucurbitacin F-25-O-acetate[1-2], the ^{13}C NMR and ^1H NMR spectra were closely similar to those of 23,24-dihydrocucurbitacin F-25-O-acetate, expect for the

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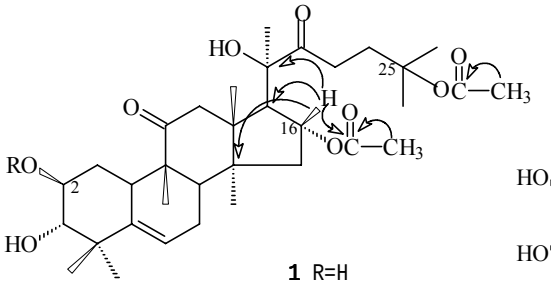
presence of an acetyl group. The shift of down-field at H-16 indicated that **1** had one acetyl group in C-16. The presence of δ_H 5.10 (t, 1H, J=7.96, 7.92 Hz) and the coupling with C-14, C-18 and 16-$COCH_3$ in ^1H NMR and HMBC spectra indicated that H-16 is in β-form. Compound **1** was determined as 23, 24-dihydro- cucurbitacin F-16,25-diacetate .

Compound **2** was assigned the molecular formula $C_{40}H_{62}O_{14}$ by FAB-MS (*m/z* 765[M-1]$^-$) and ^{13}C DEPT NMR. The IR, ^1H and ^{13}C NMR spectra of **2** revealed signals due to ten singlet methyl groups, six methylene groups, eleven methine groups , twelve quaternary carbons , a trisubstituted double bond . The ^1H and ^{13}C NMR spectra of **2** was very similar to those of **1**, expect for the signals of six secondary hydroxyl groups , indicating that **2** had one more sugar than **1**. The signals of sugar moiety at δc 101.1,77.8,76.3, 75.5,69.4, 61.4 in ^{13}C NMR spectra and aromeric proton at δ_H 5.22 (brd, J<4Hz) suggested that compound **2** was α-glucoside of **1**. Since the C-2 signal of glucoside obviously shifted down-field about Δδ 4.9 ppm from δ_H 68.3 to 73.2, it indicated that the glucoside linked with C-2. Therefore, compound **2** was determined as 23, 24-dihydro cucurbitacin F-16, 25-diacetate-2-O-α-D- glucopyranoside.

Compound **3** was assigned the molecular formula $C_{32}H_{50}O_8$ by FAB-MS (*m/z* 561[M-1]$^-$) and ^{13}C DEPT NMR spectra. The ^1H and ^{13}C NMR spectra of **3** revealed signals due to nine methyl groups , six methylene groups , six methine groups , eleven quaternary carbons, a trisubstituted double band. The ^1H and ^{13}C NMR spectra of **3** was very similar to those of **1**, except for the absence of one acetyl group. The ^1H and ^{13}C NMR also displayed the shifted up-field about Δδ 11 ppm (δc 81.0 of 1 to δc 69.8 of 3) at C-25, indicating that C-25 was lacked of one acetyl group. The correlations of C-16 with other carbons was insisted on the HMBC spectra, also showed the acetyl group linkage to C-16. Thus, compound **3** was determined as 23, 24- dihydro- cucurbitacin F-16-acetate .



1 R=H
2 R=Glu

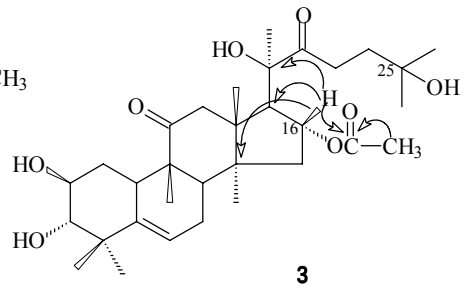


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Table 1 ^{13}C NMR Spectral data for compounds **1-3** (100.6MHz,CD_3OD,TMS)

Carbon No.	**1**	**3**	**2**
1	30.4t	30.8t	30.5t
2	68.3d	68.2d	73.2d
3	78.7d	78.8d	77.3d
4	41.6s	41.5s	41.3s
5	137.8s	137.9s	138.0s
6	120.7d	120.5d	120.0d
7	23.8t	23.7t	23.7t
8	33.7d	33.7d	33.7d
9	47.9s	47.8s	47.8s
10	42.4d	42.4d	42.5d
11	212.4s	212.5s	212.5s
12	48.6t	48.5t	48.7t
13	48.4s	48.4s	47.8s
14	50.0s	50.0s	50.0s
15	43.3t	43.3t	43.3t
16	74.2d	74.2d	74.1d
17	54.0d	53.9d	54.0d
18	20.1q	20.0q	20.1q
19	18.9q	18.9q	18.7q
20	78.5s	78.4s	78.7s
21	24.2q	24.2q	24.3q
22	212.4s	213.7s	213.5s
23	29.2t	29.0t	27.6t
24	35.2t	37.1t	35.1th
25	81.0s	69.8s	81.0s
26	26.5q	26.5q	26.5q
27	28.0q	29.2q	25.9q
28	19.5q	19.5q	19.5q
29	20.9q	20.9q	20.8q
30	25.3q	25.3q	25.5q
25-OAc	171.4s		170.1s
	22.3q		22.2q
16-OAc	171.4s	170.0s	170.0s
	20.9q	20.9q	20.8q
2-O-glu			
C-1′			101.1d
C-2′			75.5d
C-3′			77.8d
C-4′			69.4d
C-5′			76.3d
C-6′			61.4t

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