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NOTE

A New Diterpenoid From The Steam of *Hibiscus mutabilis* Linn.

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Phytochemical investigation of the stem of *Hibiscus mutabilis* Linn. led to the isolation and identification of a new diterpenoid named Hibtherin A. The structure was elucidated by analysis of spectroscopic data.

Key Words: *Schisandra lancifolia* Linn, Hibtherin A, Phytochemical investigation.

Hibiscus mutabilis Linn. is a member of *Hibiscus* family growing in P. R. China[1]. Its root, stem, leaf and flower are used as a folk medicine in China for thousand of years[1]. It has the pharmacodynamic effects for promoting blood, detoxicating, detumescence and analgesics[2-4]. The present study led to the isolation of a new diterpenoid from the stem of *Hibiscus mutabilis* Linn. Its structure was established by means of MS and extensive NMR spectra.

Optical rotation was measured in Horiba SEPA-300 High Sensitive Polarimeter. IR spectra was obtained in KBr disc on a Bio-Rad Wininfmred spectrophotometer. ESI-MS were measured on a VG Auto Spec-3000 MS spectrometer. ^{1}H, ^{13}C NMR and 2D NMR spectra were recorded on Bruker DRX-500 instruments with TMS as internal standard.

The stem of *Hibiscus mutabilis* Linn. was collected in Kunming, Yunnan Province, P.R. China, in October 2006 and was identified by Prof. S.G. Wu. A voucher specimen (No. KIB 01-06-25) was deposited in our laboratory.

Extraction and isolation: The air-dried and powdered stem of *Hibiscus mutabilis* Linn. (0.58 kg) were extracted with 70 % acetone at room temperature and the extract was partitioned successively with petroleum ether and ethyl acetate, respectively. The ethyl acetate extract (32.6 g) was subjected to column chromatography over silica gel eluting with a chloroform-acetone (1:0, 9:1, 8:2, 1:1, 0:1) gradient system to give fractions 1-5. Fraction 1 (1.48 g) was further purified by HPLC with mobile phase of methanol-water (78:22) to yield Hibtherin A (14.6 mg).

Hibtherin A (Fig. 1) was isolated as colourless oil and its molecular formula $C_{22}H_{36}O_3$ was deduced by a combination of ^{13}C NMR spectral data and HRESIMS (m/z 371.2567). The molecular formula accounted for five degrees of unsaturation,

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one of them represented by an acetoxyl group at δ 170.8 in the ^{13}C NMR spectrum, corroborated by the 1730 cm^{-1} absorption in the IR spectrum. A second unsaturation was related to a vinyl group inferred from the typical ^{13}C NMR signals at 147.4 (C-14) and 111.2 (C-15) and ^{1}H NMR signals at δ 5.84 (1H, dd, *J* = 17.5 and 10.6 Hz, H-14), 5.12 (1H, dd, *J* = 17.5 and 1.4 Hz, H-15 α) and 4.90 (1H, dd, *J* = 10.5, 1.4 Hz, H-15β). The ^{13}C NMR (CPD) spectrum showed the presence of 22 carbon signals assigned to five methyls, six methylenes, three methines, a vinyl moiety, one acetyl group, as well as to four non-hydrogenated carbon atoms after comparison with both DEPT 135 and HMQC spectra. The above data are consistent with a manoyl oxide diterpene with an acetoxy substituent. The presence of the acetylated hydroxyl group at the C-6 position was supported by the observed $^{3}J_{C\text{-}H}$ long-range correlations displayed for H-6 (δ 5.10, td, *J* = 4.2 and 11.2 Hz) and the carbon signals at δ 170.8 (C-21) and 74.6 (C-8). In the HMBC spectrum (Fig. 2) the correlation of H-14 (δ 5.84, dd, *J* = 10.6 and 17.5 Hz) with the carbon signal[5] at δ 29.0 was sufficient to assure the correct assignment of CH_3-16. The 4-axial orientation inferred to this methyl group was in agreement with the chemical shift at δ 29.0. The proposed relative stereochemistry was further supported by the NOESY experiment (Fig. 3), which clearly revealed dipolar interaction between CH_3-16/CH_3-17 and CH_3-16/H-12eq. Similarly, the α-equatorial orientation suggested to the acetyl group was defined based on nOe correlations of H-6 with the methyl groups 17, 19 and 20. Additional one effects observed for H-5/H-7ax/H-9ax; H-1ax/H-9ax and, H-9ax/H-12ax supported the stereochemistry established for Hibtherin A. Complete assignments of the NMR data of Hibtherin A were achieved by ^{1}H, ^{1}H-COSY, HMQC, HMBC and NOESY experiments. Thus, the structure of the new diterpenoid was unambiguously established.

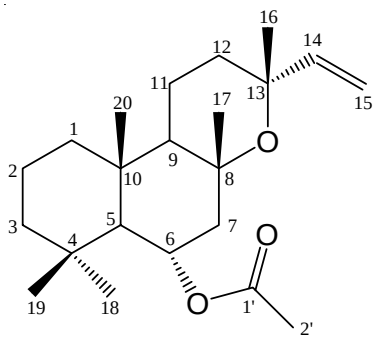

Fig. 1. Structure of Hibtherin A

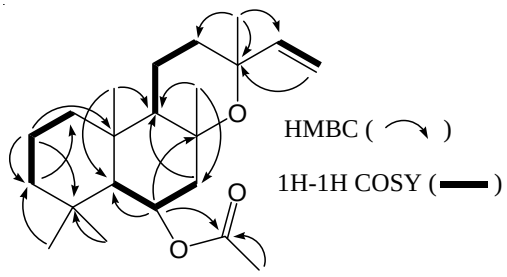

Fig. 2. Selected HMBC and ^{1}H-^{1}H COSY correlations of Hibtherin A

Hibtherin A: $C_{22}H_{36}O_3$, Colourless oil; $[\alpha]2_D^{23.2}$ + 25.5 (c 0.321, $CHCl_3$); UV ($CHCl_3$) end absorption; IR (KBr, ν_{max}, cm^{-1}): 2932, 2865, 1730, 1452, 1370, 1245, 1028; ^{1}H NMR and ^{13}C NMR data ($CDCl_3$, 500 MHz), Table-1; HRESIMS (positive ion mode) m/z 371.2567 $[M + Na]^+$ (calcd. 371.2562 for $C_{22}H_{36}O_3Na$).

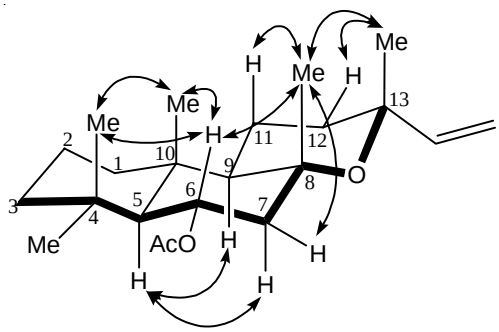

Fig. 3. Selected NOESY correlations for Hibtherin A

TABLE-1
^{1}H NMR AND ^{13}C NMR DATA FOR HIBTHERIN A IN $CDCl_3$ (δ ppm)

No.	δC (mult.)	δ_H (mult, *J*, Hz)	No.	δC (mult.)	δ_H (mult, *J*, Hz)
1	39.4, t	1.52, 0.86	12	34.5, t	1.76, 1.64
2	18.0, t	1.55, 1.41	13	73.5, s	
3	43.7, t	1.36, 1.20	14	147.4, d	5.84 (dd, 17.5, 10.6)
4	33.3, s		15	111.2, t	5.12 (dd, 17.4, 1.4)
5	59.4, d	1.29			4.90 (dd, 10.5, 1.4)
6	70.8, d	5.10 (td, 11.2, 4.2)	16	29.0, q	1.26 (s)
7	49.7, t	2.09 (dd, 11.3, 4.2)	17	27.4, q	1.40 (s)
		1.55	18	35.5, q	1.02 (s)
8	74.6, s		19	21.7, q	0.83 (s)
9	53.8, d	1.48	20	16.3, q	0.88 (s)
10	37.7, s		1’	170.8, s	
11	15.9, t	1.62, 1.48	2’	21.6, q	2.04 (s)

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