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A New Diterpene Acid from the Flowers of *Heteropappus altaicus*

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Abstract: A new compound, named heteraltaic acid was isolated from the flowers of *Heteropappus altaicus* (willd) Novopokr.. The compound was elucidated as (5R, 6S, 8aS) –5-[2-(3-furyl) ethyl-5, 6, 8a-trimethyl-4a, 5, 6, 7, 8, 8a -hexahydro-1-naphthalenecarboxylic acid] by the combination of 1D and 2D NMR techniques (HSQC, HMBC) and X-ray analysis.

Keywords: *Heteropappus altaicus*, diterpene acid, new compound.

The flowers of *Heteropappus altaicus* (willd.) Novopokr. are used as Mongolian medicine to clean heat and expel miasma, relieve inflammation, treat extravasated plague, influenza, measles, scarlatina, hot blood, "Paori" heat and so on[1]. The constituents of arial part of *H. altaicus* have been investigated and some diterpenes of *trans*-clerodane type, 5, 10-*seco*-clerodanetype and one alicyclic diterpene[2], triterpenoid saponins[3], as well as flavone derivatives[4] were isolated. In the present paper, we report the isolation and structural elucidation of a new diterpene acid **1**, named heteraltaic acid from the flowers of this plant.

Compound **1,** colorless prisms (MeOH), mp 115-116℃, $[\alpha]_D^{20}$ −70.94 (*c* 0.058, $CHCl_3$). High-resolution electron impact mass spectroscopy (HREIMS) of the compound **1** showed the molecular ion at *m/z* 314.1877, corresponding to $C_{20}H_{26}O_3$ (calcd. 314.1882). The IR spectrum indicated the presence of a carboxylic acid group (3200-2600, 1700 cm^{-1}). The ^{1}H-NMR spectra of compound **1** showed singlets of two tertiary methyls at δ 0.85, 1.29ppm, a doublet of a secondary methyl at δ 0.75ppm and signals of six prontons in desheilding area δ(6-8) ppm. Combination of ^{1}H-NMR, ^{13}C-NMR, HMQC and HMBC spectra of compound **1** allowed us to figure out the skeleton (**Figure 1**). The ^{1}H-NMR, ^{13}C-NMR data of the compound were similar to those of nidoresedic acid **2**[5-6], 10-*epi*-nidoresedic acid **3**[7-8]. However, the configuration of **1** was unknown. To confim the configuration of **1**, its X-ray diffraction analysis was carried out and the relative configuration was confirmed as [(5R, 6S, 8aS)-5-[2-(3–furyl) ethyl-5, 6, 8a-trimethyl-4a, 5, 6, 7, 8, 8a–hexahydro-1-naphthalenecar-boxylic acid],

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comparing the spectral data of the known compounds[5-8].

The crystal data were as follows: $C_{20}H_{26}O_3$.0.5 CH_3OH, M=314.42(deducting solvent); orthorhombic system, space group, $P22_12_1$; Z=4, a = 6.972(1), b=15.381(1), c=18.570(1)Å. V=1991.4(3) Å, Dc=1.11g/cm^3. All unique intensity data were collected by MAC DIP-2030K diffractmeter, R_f=0.067, Rw=0.065 ($w=1/\sigma|F|^2$) for 2438 unique reflections with $|F|^2 \geq 3\sigma|F|^2$ with graphite–monochromated MoK_αradiation. X-ray diffraction analysis gave the computer generated perspective drawing shown in **Figure 2** with an R factor of 0.067, confirming the structure of **1**. Its relative stereochemistry was unequivocally established as (±)[(5R, 6S, 8aS)-5-[2-(3-furyl)ethyl-5, 6, 8a-trimethyl-4a, 5, 6, 7, 8, 8a-hexahydro-1-naphthalenecarboxylic acid]. Its crystal structure is deposited in CCDC and its CIF was 254560[9]. The new compoud was named as heteraltaic acid. [Note: The structure of nidoresedic acid cited in literature 10 from literature 6 was wrong. The true structure of nidoresedic acid was as in literature 6. The configuration of 15-CH_3 in nidoresedic acid was not β-oriented but α-oriented. In fact, nidoresedic acid and heteraltaic acid are two different compounds].

Compound **1**, IR (KBr)cm^{-1}: 3200–2600, 1700, 1640, 880; UV λ_{max}^{MeOH} nm(logε): 206 (3.98), 2.86 (3.93). EI: (70eV) *m/z* (rel. int. %): 314.2 (17, M^+), 299 (96), 219 (13), 81 (97); HREIMS *m/z* 314.1877 (calcd.314.1882), molecular formula: $C_{20}H_{26}O_3$; ^{1}H-NMR (500MHz, pyridine-d_5, δ ppm) and ^{13}C–NMR (125MHz, pyridine-d_5, δ ppm) were shown in **Table 1**.

Figure 1 HMBC and HMQC correlation of compound **1**

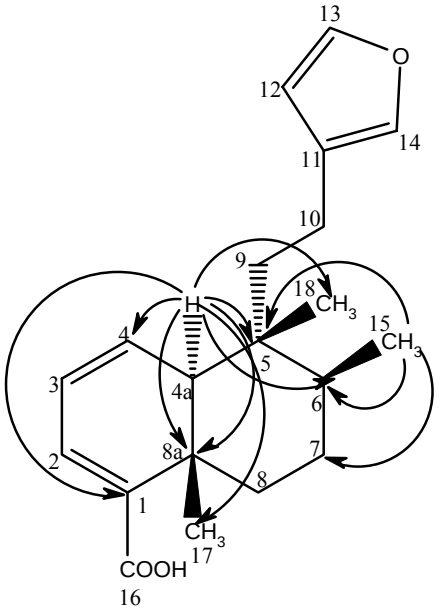

Figure 2 Crystal structure of compound **1**

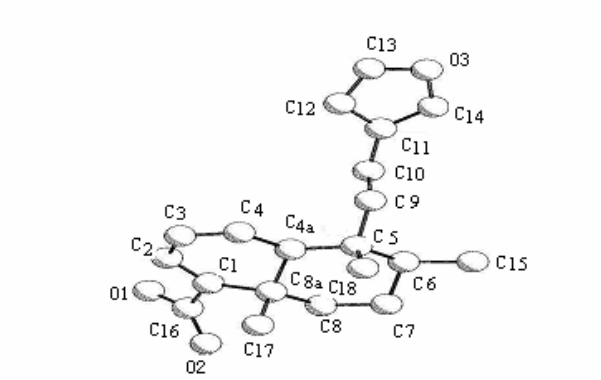

Table 1 ^{1}H- NMR(500 MHz) and ^{13}C-NMR(125 MHz) spectra data of the **1** in C_5D_5N (δ ppm; J Hz)

Position	δ^{a}_{C}	δ^{a}_{H}	Position	δ^{a}_{C}	δ^{a}_{H}
1	142.5		9	38.2	1.78 (ddd, 1H, J=4.5, 4.0, 5.0)
					1.63 (ddd, 1H, J=4.5, 4.0, 4.5)
2	130.5	7.16 (br d, 1H, J=4.5)	10	18.2	2.28 (ddd, 1H, J=4.5, 4.5, 4.5)
					2.16 (ddd, 1H, J=4.5, 4.5, 4.5)
3	133.9	6.19 (m 1H,)	11	125.9	
4	124.9	6.19 (m 1H,)	12	111.5	6.43 (br s, 1H, J =0.5)
4a	48.6	2.45 (br s)	13	143.1	7.59 (d, 1H, J =1.5)
5	38.4		14	138.9	7.49 (br s, 1H, J= 0.5)
6	35.7	1.50 (m)			
7	27.4	1.48 (m), 1.51 (m)	15	15.6	0.75 (d, 1H, J =6.0)
8	35.0	1.60 (br d)	16	169.9	
		2.91 (br d, J =13)	17	15.6	1.29 (s)
8a	38.9		18	19.4	0.85 (s)

[a]Assignment based on HMBC and HMQC.

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