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New Sesquiterpenoids from *Hedychium yunnanense gagnep*

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Abstract: Two new sesquiterpenoid trialcohol isomers named 1β, 4α 11α-trihydroxyeudesmane (**1**) and Yunnanensehedychetriol (**2**), were isolated from the fresh rhizomes of *Hedychium Yunnanense gagnep* .Their structures were elucidated by spectroscopic methods.

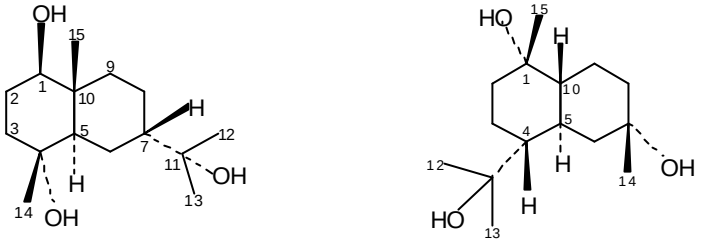
Keywords: *Hedychium yunnanene,* Zingiberaceae , sesquiterpenoid trialcohol isomers , 1*b*, 4*a*, 11*a*-trihydroxyeudesmane,Yunnanensehedychetriol .

Hedychium yunnannense Gagnep is the unique species of Zingiberaceae occurring only in Yunnan province of China and its wild resource is very abundant. Several sesquiterpenoids and diterpenoids from the petroleum ether fraction of the ethanol extract of the plant have been reported[1, 2] by Zhao Qing *et al*. Some of them show antioxidant and cytotoxic activities. In order to use the wild plant resources efficiently, we made further systematic investigations on the chemical constituents of the rhizomes of *Hedychium yunnanense gagnep* resulting in the isolation of several sesquiterpenoids and diterpenoids. We report here two new sesquiterpenoid trialcohol isomers. The structure elucidations were on the basis of the combinations of MS, IR and NMR spectroscopic methods.

Compound **1,** colorless needles from acetone, mp. 159-160℃, $[\alpha]_D^{15}$ + 0.125 (acetone, c 0.028)**.** The molecular formula $C_{15}H_{28}O_3$ was established by the positive FABMS together with ^{13}CNMR, DEPT (distortionless enhancement by polarization transfer) spectra. In its FAB mass spectrum, very weak molecular ion peak at *m/z* 256(0.5)[M^+], but strong dehydrated peak at 239(11)[M-H_2O+1], 221(100)[M-2H_2O+1], 203(41)[M-3H_2O+1] were observed. Its IR spectrum showed absorption attributed to hydroxyl groups (3410.4, 3373.7cm^{-1}). The ^{1}HNMR and ^{13}CNMR data were listed in **Table 1**. It can be seen that C-1, C-4 and C-11 were connected with a hydroxyl group respectively. The unsaturated number of the compound is 2. All the informations suggested that the compound is typically eudesmane sesquiterpenoid. According to Masayoshi Ando *et al*' s discovery[3],when the naturally occuring endesmane derivatives based on a *trans*-fused decalin system, the C-15 signal appeared around δ 18.5ppm. On the contrary, the C-15 signal of the *cis*-endesmane derivatives appeared around δ 28-31ppm. In compound **1**, C-15 signal existed at 13.79ppm, suggested that this compound

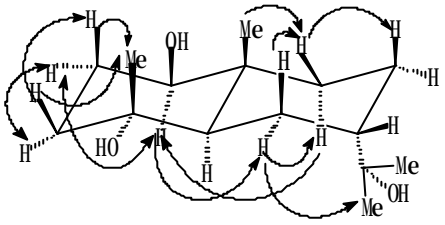
is a *trans*-endesamane derivative. All the ^{1}HNMR and ^{13}CNMR signals of **1** were assigned by 2D NMR (**Table 1**). In its ^{1}H-^{1}H COSY spectrum, the correlation of H1-H2, H2-H3, H5-H6, H6-H7, H7-H8, H8-H9, were observed. In its NOESY spectrum, the correlation of H1 between H 9***a***, H 8***a***,H 5, H 3***a***, H 2***a*** ;H 15 between H 14, H 9***b***, H 7; H 14 between H 9***b***, H 8***b***, H 7, H 6***b*** were observed (**Figure 2**). Consequently, compound **1** was named as 1***b***, 2***a***, 11***a***-trihydroxyeudesmane shown as **Figure 1.**

Figure 1. Structures of Compound **1** and **2**

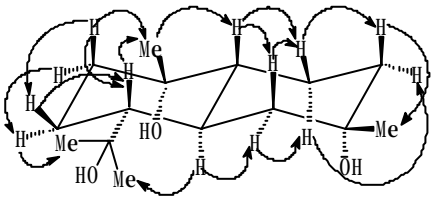


1 **2**

Figure 2. NOEs observed in Compounds **1** and **2**



1



2

Table 1 ^{1}H and ^{13}CNMR data (400MHz, MeOH)

	Compound 1			Compound 2		
	C δppm	DEPT	H δppm, JHz	C δppm	DEPT	H δppm, JHz
1	80.40	CH	3.21,t,J=7.6	75.48	C	
2	29.42	CH_2	1.53,m	26.28	CH_2	0.89,m, H-2*a* 1.14,m,H-2*b*
3	41.93	CH_2	1.64,d,J=12.5,H-3*b* 1.52,m,H-3*a*	39.82	CH_2	1.56,m
4	72.51	C		50.79	CH	1.55,m
5	54.11	CH	1.12,m	54.58	CH	1.72,m
6	23.19	CH_2	1.14,m,H-6*a* 1.53,m, H-6*b*	27.76	CH_2	0.92,m,H-6*a* 1.71,m,H-6*b*
7	50.80	CH	1.21,d,J=12.1,H-7*a*	82.56	C	
8	22.67	CH_2	1.85,m,H-8*a* 1.03,m,H-8*b*	26.67	CH_2	1.19,m,
9	42.08	CH_2	0.99,m,H-9*a* 1.82,m,H-9*b*	39.50	CH_2	1.56,m,H-9*a* 2.08,m,H-9*b*
10	40.18	C		52.65	CH	2.46,m
11	73.46	C		74.46	C	
12	26.92	CH_3	1.16,s	27.35	CH_3	1.05,s
13	27.47	CH_3	1.18,s	25.75	CH_3	1.02,s
14	22.55	CH_3	1.08,s	28.42	CH_3	1.10,s
15	13.79	CH_3	0.65,s	24.29	CH_3	1.08,s

Compound **2**, colorless crystal needles from acetone. mp. 97-98℃. $[\alpha]_D^{15}$ +0.200 (acetone, c 0.068)**.** It also has a molecular formula $C_{15}H_{28}O_3$ proposed on the basis of the combination of positive FAB mass spectrum ^{13}CNMR and DEPT spectra. In its FAB mass spectrum, no molecular ion peak, but two strong dehydrated peak at *m/z* 221 (100) [M-2H_2O+1] and 203 (97) [M-3H_2O+1] were observed respectively. Its ^{1}HNMR, ^{13}CNMR and DEPT spectra data (**Table1**) showed four methyl carbons. The three quaternary carbon signals in ^{13}C NMR indicated that all the quaternary carbon were linked with hydroxy group which have strong absorption at 3366.0 cm^{-1} in IR spectrum. The unsaturated number of the compound is 2. On the basis of these informations and compared the spectra data with those of the synthesized compound (±)[1*S*-(1*b*,4*b*,4a*b*,6*a*,8a*a*)]-1,6-Dimethyl-4-(1-methylethyl)-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,6-naphthalenediol[4], the basic molecular skeleton of **2** was depicted as Cadinane type[5]. All the ^{1}HNMR and ^{13}CNMR signals of **2** were assigned by 2D NMR (**Table 1**) . In its ^{1}H-^{1}H COSY spectrum, the correlation of H2-H3, H3-H4, H4-H5, H5-H6, H8-H9, H9-H10, H5-H10 were observed. In its NOESY spectrum, the correlation of H 5 between H 2*a*, H 6*a*, H 9*a*, H 12; H 15 between H 4*b*, H 10*b*; H 10*b* between H 6*b*, H 9*b*, H 14; H14 between H 9*b*, H 6*b* were observed(**Figure 2**). Consequently, the structure of compound **2** was described as **Figure 1**. and named as Yunnanensehedychetriol.

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