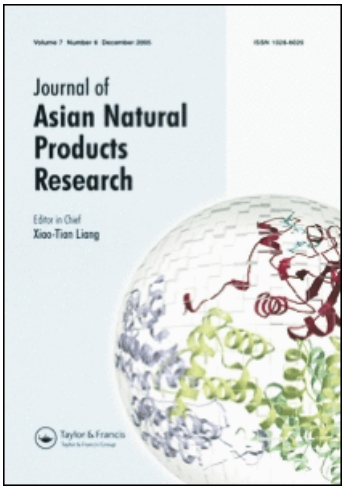

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Dihydroayapin, a New Coumarin Compound from *Dendrobium Densiflorum*

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DIHYDROAYAPIN, A NEW COUMARIN COMPOUND FROM *DENDROBIUM DENSIFLORUM*

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A new coumarin named dihydroayapin (**1**) together with seven known compounds were isolated from the stems of *Dendrobium densiflorum*. On the basis of physicochemical and spectral evidences, the structure of **1** was established as 6,7-methylenedioxy-3,4-dihydrobenzopyran-2-one.

Keywords: *Dendrobium densiflorum*; Coumarin derivative; Dihydroayapin

INTRODUCTION

The Chinese drug 'ShiHu', the stems of *Dendrobium* species (*Orchidaceae*), has been used in traditional Chinese medicine as a tonic and antipyretic from ancient days in China. Earlier work on *Dendrobium densiflorum* led to the isolation of the coumarins, fluorenones, triterpenes [1,2]. We report in this paper the isolation and structure elucidation of a new coumarin compound–dihydroayapin from *D. densiflorum*, along with seven known compounds (Fig. 1).

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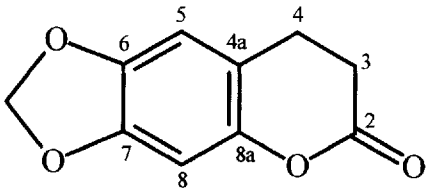

1

FIGURE 1

RESULTS AND DISCUSSION

The ethanolic extract of the stems of *D. densiflorum* gave a new coumarin and seven known compounds after separation by column chromatography on silica gel. Known compounds were identified as friedelin [3], scopolin [4], ayapin, aesculatin dimethyl ether [5], dengibsin, dendroflorin [6] and defusin [7] by comparison with reported data. Dihydroayapin was obtained as yellow plate crystals from acetone, m.p. 178–180°C, The HREI mass spectrum was consistent with the molecular formula $C_{10}H_8O_4$, [HRMS *m/z* 192.1744 (M^+). Calcd. 192.1736]. IR bands were at 1751 and 1600, 1501, 1444 cm^{-1} showing the presence of carbonyl group and aromatic group. The ^1H NMR spectrum of dihydroayapin exhibited two singlets at δ 6.62 and 6.58 corresponding to two *p*-aromatic protons, and two signals at δ 2.88 (2H, m) and 2.74 (2H, m) indicating the presence of two vicinal methylene groups. In the COLOC spectrum, the two singlets at δ 6.62 and 6.58 showed correlations with the carbon signals at δ 147.1 (C-7), 146.3 (C-8a), 144.1 (C-6) and 114.6 (C-4a) identically, the former three belonging to the oxygenated quaternary carbons, the latter one being attributed to a non-oxygenated quaternary carbon. On the other hand, the two proton signals at δ 2.88 and 2.74 showed long-range correlations with carbon signals at 168.5 (C-2), 114.6 (C-4a), 23.6 (C-4) and 168.5, 114.6, 146.3, 107.0 (C-5), 29.1 (C-3), respectively, indicating that the methylene appeared as a multiplet at δ 2.88 must be connected with the quaternary carbon at δ 114.6 and the methylene appeared as a multiplet at δ 2.74 must be connected with the carbonyl group.

The ^1H NMR spectrum of dihydroayapin also exhibited a singlet for two equivalent protons at δ 6.00, showing long-range correlations with carbon signals at δ 144.1 and 147.3, characteristic of methylenedioxy protons in an aromatic ring.

Hence, the structure of dihydroayapin was deduced to be 6,7-methylenedioxo-3,4-dihydro-benzopyran-2-one. The δ_C values of dihydroayapin were assigned by $^{13}C-^1H$ COSY and COLOC experiments (Table I).

TABLE 1 ^{1}H-NMR, ^{13}C-NMR, ^{13}C–^{1}H COSY and COLOC data of 1

Position	*^{1}H-NMR*	*^{13}C-NMR*	*^{13}C–^{1}H COSY*	*COLOC*
2		168.5		
3	2.74 (2H, m)	29.1	2.74 (29.1)	168.5, 114.6, 23.6
4	2.88 (2H, m)	23.6	2.88 (23.6)	168.5, 114.6, 146.3, 107.0, 29.1
4a		114.6		
5	6.62 (1H, s)	107.0	6.62 (107.0)	144.1, 114.6, 147.1, 146.3
6		144.1		
7		147.1		
8	6.58 (1H, s)	99.1	6.58 (99.1)	147.1, 146.3, 144.1, 114.6
8a		146.3		
OCH_2O	6.00 (2H, s)	101.6	6.00 (101.6)	144.1, 147.3

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points reported are uncorrected. Silica gel (200–300 mesh) was used for column chromatography. UV spectra were obtained with a Shimadzu 202 UV spectrometer in MeOH solutions and IR spectra were taken with a Perkin-Elmer 983 IR spectrometer in KBr disc. NMR spectra were measured with a Bruker ACF-300 spectrometer with TMS as an internal standard, and chemical shifts were recorded in δ values. MS and HR-MS were taken with a Finnigan FTMS-2000 spectrometer.

Plant Material

Dendrobium densiflorum was collected in March 1997 at Xishuangbanna, Yunnan Province, China. A voucher specimen(No. D970515) was identified by Prof. Xu Luoshan and deposited in the Herbarium of China Pharmaceutical University, Nanjing, China.

Extraction and Isolation

Fresh stems of *Dendrobium densiflorum* (8 kg) were extracted with EtOH. The EtOH extract was concentrated under reduced pressure and was soxhletted for 4 h each with petrol (60–90°C), $CHCl_3$ and EtOAc successively. The residue (11 g) from petrol extract upon extensive chromatography over silica gel yielded fridelin (15 mg) from 15% $CHCl_3$/petrol, defusin (25 mg) from 30% $CHCl_3$/petrol, and scopolin (15 mg) from 50% $CHCl_3$/petrol. The residue (23 g) from $CHCl_3$ extract was chromatographed on a silica gel

column eluting with petrol containing increasing amounts of $CHCl_3$, yielding ayapin (1.2 g) from 25% $CHCl_3$/petrol, aesculatin dimethyl ether (0.8 g) with 30% $CHCl_3$/petrol, dengibsin (35 mg) with 50% $CHCl_3$/petrol, dendroflorin (20 mg) from 70% $CHCl_3$/petrol. The EtOAc solution was concentrated and chromatographed over silica gel using EtOAc/petrol (3 : 7) solvent system, yielding dihydroayapin (10 mg).

Identification

Dihydroayapin (**1**) Yellow plate crystals, m.p. 178–180°C, HRMS: *m/z* obsd. 192.1744 (M^+). calcd.: 192.1736, UV λ_{max}^{MeOH} (nm): 296.5; IR ν_{max}^{KBr} (cm^{-1}): 2916, 1751, 1600, 1501, 1444; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.62 (1H, s, H-5), 6.58 (1H, s, H-8), δ 6.00 (2H, s, $-OCH_2O-$), δ 2.88 (2H, m, H-4), 2.74 (2H, m, H-3) ^{13}C-NMR (75 MHz, $CDCl_3$): 168.5 (2), 29.1 (3), 23.6 (4), 114.6 (4a), 107.0 (5), 144.1 (6), 147.1 (7), 99.1 (8), 146.3 (8a), 101.6 ($-OCH_2O-$).

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