A New Diol from Dimocarpus longan Seeds

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Abstract: Objective To investigate the chemical constituents of *Dimocarpus longan* seeds in Sapindaceae. Methods The chemical constituents were isolated from the ethanol extract of *D. longan* seeds by silica gel column chromatography. Their structures were identified on the basis of physical and chemical properties and spectral analysis. Results One compound was isolated and identified as 2-methyl-1,10-undecanediol, named longandiol (1). Conclusion Compound 1 is a new compound.

Key words: Dimocarpus longan; longan seeds; longandiol; new diol; Sapindaceae

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Introduction

Dimocarpus longan Lour. syn. Euphoria longana Lam. (Longan) is an evergreen tree in Sapindaceae, widely grown in Southern China, India, and Southeast Asia (Jiang et al, 2002). Longan pulps are tasty and rich in nutritious ingredients (Cai et al, 2002). Furthermore, the dried longan pulps are used as a tonic in traditional Chinese medicine to nurture heart and spleen, nourish blood, calm mind, add luster and beauty to the skin, and have therapeutic effects on heart palpitation, insomnia, amnesia, and anxiety (Jiangsu New Medicinal College, 1977). In recent years, the production of longan fruits in China is dramatically increasing due to continuous development of plantation and improvement of agricultural management (Gu et al, 2008). Currently, longan pulps are consumed as fresh and processed fruits while the seeds which account for about 17% of the fresh weight of whole fruits (Xiao et al, 2004) are discarded as waste or burned as fuel. However, in Chinese folk medicine, longan seeds are used to prevent pain, hemorrhage, hernia, and skin diseases (Jiangsu New Medicinal College, 1977). Recent studies showed that longan seeds extract had strong scavenging activities of free radicals (Rangkadilok et al, 2007), inhibition on the proliferation of human colorectal carcinoma cells (Chung et al, 2010), antifatigue effect (Zheng et al, 2010),

hypoglycemic effect (Huang, Zou, and Liu, 2006), and so on. HPLC-ESI-MS analysis confirmed the presence of 13 polyphenols constituents such as gallic acid, ellagic acid, and corilagin using method (Soong and Barlow, 2005). In order to make full use of longan seeds, it is necessary to further investigate the chemical consti- tuents in longan seeds. The present paper deals with the isolation and structure elucidation of the new diol.

Materials and methods

Plant material

Longan seeds were collected from a commercial longan orchard at Maoming, Guangdong, China, in September 2005 and identified by Prof. ZHENG Gongming. The seeds were sundried and ground to powder.

Equipments

¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were recorded on a Bruker DRX—400 instrument (Bruker BioSpin, Germany) in DMSO- d_6 with the residual solvent peak (δ_H 2.49 and δ_C 39.51) as reference. ESI-MS was collected on MDS SCIEX API 2000 LC-MS-MS instrument (AB MDS Sciex, Canada). For column chromatography, silica gel 60 (100–200 mesh, Qingdao Marine Chemical, Qingdao, China), Develosil ODS (10 µm, Nomura Chemical, Japan), polyamide (80–100 mesh, Taizhou Luqiao Bio chemical

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Corp., Taizhou, China), and Sephadex LH-20 (Pharmacia Fine Chemicals, Sweden) were used. TLC was performed on precoated silica gel plates (GF₂₅₄, Qingdao Marine Chemical, China) with detection under fluorescent light ($\lambda = 254$ nm), exposure in I₂ vapor, and spraying with 10% H₂SO₄ in EtOH, followed by heating.

Extraction and isolation

The powder of longan seeds (10.5 kg), defatted with petroleum ether, was extracted with 95% EtOH for three times at room temperature. The EtOH solution was combined and concentrated under vacuum. The residue was suspended in H₂O and partitioned successively with petroleum ether, CHCl₃, EtOAc, and *n*-BuOH to obtain petroleum ether- (181.2 g), CHCl₃- (39.0 g), EtOAc- (120.5 g), and *n*-BuOH-soluble (102.3 g) extracts.

The CHCl₃ extract was subjected to a silica gel column chromatography eluted with CHCl₃-MeOH (49:1 \rightarrow 4:1) to give 16 fractions. Fraction 3 was further separated by silica gel column chromatography eluted with petroleum-acetone (50:1 \rightarrow 4:1) to afford compound **1** (4.5 mg).

Results and discussion

Compound 1: colorless needles; ESI-MS *m/z*: 201 $[M - H]^-$, MS² (201): 171, 59. ¹H-NMR (400 MHz, DMSO-*d*₆) & 4.31 (1H, t, *J* = 5.2 Hz, 1-OH), 4.24 (1H, d, *J* = 4.6 Hz, 10-OH), 3.41 (1H, m, H-10), 3.35 (2H, dd, *J* = 11.7, 6.4 Hz, H-1), 1.23-1.38 (14H, m, H-3-9), 1.00 (1H, m, H-2), 0.94 (3H, d, *J* = 6.3 Hz, H-11), 0.76 (3H, d, *J* = 6.7 Hz, 2-CH₃); ¹³C-NMR (100 MHz, DMSO-*d*₆) & 14.54 (2-CH₃), 19.28 (C-11), 25.53, 26.83, 28.99, 29.14, 29.45, 32.32, 32.55 (C-3-9), 39.47 (C-2), 60.72 (C-1), 69.40 (C-10).

The negative ESI-MS of compound **1** gave a base ion peak at m/z 201 [M – H]⁻, indicating a molecular weight of 202. By the combined analyses of ESI-MS, ¹H-NMR, ¹³C-NMR, and DEPT data, its molecular formula was suggested as C₁₂H₂₆O₂. The ¹³C-NMR spectrum showed 12 resonances which were sorted by the DEPT experiment as two methyl carbons at δ 14.54 (2-CH₃) and 19.28 (C-11), two methine carbons at δ 39.47 (C-2) and 69.40 (C-10), connected with a hydroxyl group, and eight methylenes at δ 60.72 (C-1) and 25.53, 26.83, 28.99, 29.14, 29.45, 32.32, 32.55 (C-3-9), one (the signal at δ 60.72) of which a hydroxyl group was attached with a hydroxyl group. Therefore, the basic structure of compound 1 was a saturated chain contained two hydroxyl groups. ¹H-NMR spectrum showed a triplet (J = 5.2 Hz) for C-1 hydroxyl proton at δ 4.31, a doublet (J = 4.6 Hz) for C-10 hydroxyl proton at 4.24, a multiplet for C-10 proton at 3.41, a double doublet (J = 11.7, 6.4 Hz) for C-1 proton at 3.35, a multiplet for C-2 proton at 1.00, a doublet (J = 6.3 Hz) for C-11 proton at 0.94, a doublet (J = 6.7 Hz) for C-2-CH₃ protons at 0.76, and a multiplet signal for C-3-9 proton at 1.23-1.38. Thus the structure of compound 1 was concluded as 2-methyl-1,10-undecanediol (Fig. 1), and further confirmed by MS² [(201): 171, 59], but disregarding stereochemistry.



Fig. 1 Structure of compound 1 and its splitting manner

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