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Further Study on the Constituents of *Allium tuberosum* leaves

Jae Sue Choi and Chang Hak Go

Department of Nutrition and Food Science, National Fisheries University of Pusan, Pusan 608-737, Korea

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In the course of continuous work on the leaves of *Allium tuberosum* (Liliaceae), compounds 1 and 2 were isolated from the ethylacetate and butanol-soluble fraction, and identified as N-*p*-coumaroyl tyramine and bis(*p*-hydroxyphenyl) ether, respectively, on the basis of spectral data and physicochemical results.

Key words : *Allium tuberosum*, bis(*p*-hydroxyphenyl) ether, N-*p*-coumaroyl tyramine

INTRODUCTION

Allium tuberosum Rottler (Liliaceae) is a perennial herb which is cultivated widely and the leaves are used for food. According to the dictionary of Chinese drugs (Shanghai Science & Technological Publisher, 1985), they have been used for treatment of abdominal pain, diarrhea, hematemesis, snakebite and asthma. In the previous papers (Choi *et al*, 1988, 1992), the isolation of amino acids, adenosine and β-carboline alkaloid was reported. In the course of continuous work on this plant part, additional two compounds were isolated. This paper deals with the isolation and characterization of the compounds.

MATERIALS AND METHODS

The mps were taken on an Electrothermal digital melting point apparatus and are uncorrected. The IR spectrum was determined in KBr tablet on a Shimadzu IR-400 spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker-AM 300 spectrometer; Chemical shifts are given on a δ (ppm) scale with tetramethylsilane. The EIMS spectra were taken with a Hewlett-Packard 5985B GC/MS spectrometer operating at 70eV.

Isolation

This was carried out as described previously (Choi *et al*, 1992).

The EtOAc soluble fraction (10 g) was subjected to silica gel column chromatography (solvent : EtOAc) to yield compound **1** (150 mg). The BuOH soluble fraction (60 g) was subjected to silica gel column chromatography (solvent : $CHCl_3$-MeOH (gradient)) to yield compound **2** (120 mg).

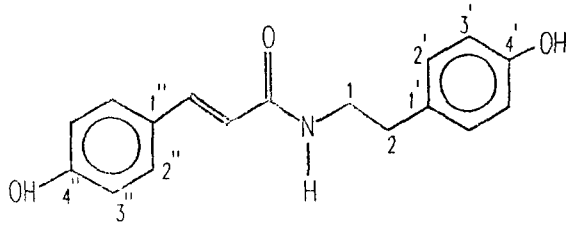
Compound 1 : Yield : 1.5×10^{-1}% (dry weight), Amorphous powder from MeOH, $FeCl_3$; +, mp; 235~236°C, MS (*m/z*, %); 283 (M^+, 2.0), 164 ($C_9O_3H_8$, 65.7), 147 ($C_9O_2H_7$, 100), 120 (C_8OH_8, 51.9), ^{1}H-NMR (DMSO-d_6, 300 MHz) δ; tyramine moiety 2.60 (2H, t, J=7.40 Hz, H-1), 3.31 (2H, t, J=7.40 Hz, H-2), 6.78 (2H, d, J=8.60 Hz, H-3' & 5'), 7.38 (2H, d, J=8.60 Hz, H-2' & 6'), coumaroyl moiety 6.36 (1H, d, J=15.70 Hz, H-α), 6.66 (2H, dd, J=8.40 & 2.0 Hz, H-3" & 5"), 7.00 (2H, dd, J=8.40 & 2.0 Hz, H-2" & 6"), 7.29 (1H, d, J=15.70 Hz, H-β), ^{13}C-NMR (DMSO-d_6, 75.5 MHz) δ; tyramine moiety 34.39 (C-2), 40.62 (C-1), 115.86 (C-3' & 5'), 129.38 (C-2' & C-6'), 129.48 (C-1'), 155.56 (C-4'), coumaroyl moiety 115.04 (C-3" & C-5"), 118.73 (C-α), 125.89 (C-1"), 129.08 (C-2" & 6"), 138.49 (C-β), 158.70 (C-4"), 165.23 (C=O).

Compound 2 : Yield : 1.2×10^{-1}% (dry weight), Amorphous prism from aqueous-MeOH, mp; 340.5°C (decomp.), IR (KBr, cm^{-1}); 3019 (OH), 2464, 1992, 1680 (aromatic), 1451, 1461, 1391, 1226, 1098, 997, 846, 760, 584, 563, 542, 431, MS (*m/z*, %); 202 (M^+, 5.5), 112 (96.0), 69 (100), ^{1}H-NMR (DMSO-d_6, 300 MHz) δ; 10.97 (1H, br. s, OH), 10.78 (1H, br. s, OH), 7.37 (2H, d, J=7.60 Hz), 5.44 (2H, d, J=7.60 Hz), ^{13}C-NMR (DMSO-d_6, 75.5 MHz) δ; 164.24, 151.43, 142.04 (×2), 100.16 (×2).

RESULTS AND DISCUSSION

An EtOAc-soluble fraction of the leaves of *A. tuberosum* was repeatedly chromatographed over silica gel to afford compound **1** as amorphous powder, mp 235~236°C. The mass spectrum of compound **1** showed a molecular ion peak at *m/z* 283 cor-

Correspondence to: Jae Sue Choi, Dept. of Nutrition and Food Science, National Fisheries University of Pusan, Pusan 608-737, Korea



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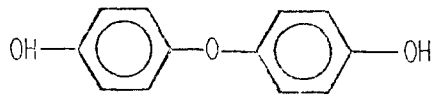

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responding to $C_{17}H_{17}NO_3$ and the ^{13}C-NMR spectrum showed 13 unique types of carbon; one α,β-unsaturated carbonyl carbon, eight aromatic carbons, two methylene carbons and two vinylic carbons. Since the formula of compound **1** shows 17 carbon atoms, four of eight aromatic carbons must be an element of symmetry. The ^{1}H-NMR spectrum of **1** showed two ortho-coupled doublets each of two protons with a J value of 8.6 Hz at δ 7.38 and 6.78 ppm, indicating the presence of a 1,4-di-substituted benzene ring and two trans-coupled vinylic protons at δ 6.36 and 7.29 with a J value of 15 Hz. The signals at δ 7.00 and 6.66 were assignable to the two ortho-coupled protons of another aromatic ring, respectively, which were long range coupled to the vinylic proton as a double doublet with J values of 8.4 and 2.0 Hz. Two triplets at 3.31 and 2.60 could be assignable to two methylene protons. These data together with the apprearance of intense peaks at *m/z* 147 ($C_9O_2H_7$, 100) and 120 (C_8OH_8, 51.9) suggested the compound **1** to be N-*p*-coumaroyl tyramine. It was further confirmed by comparison of ^{13}C-NMR spectral data with those reported in the literature (Zhao *et al*, 1992). The presence of this compound in the plants has previously been reported in the tuber of *Allium bakeri* (Okuyama *et al*, 1986), *Asimina triloba* (Zhao *et al*, 1992) and *Solanum melongena* (Yoshihara *et al*, 1978). This is the first report of its occurrence from this plant. It is of significance that *A. tuberosum* contains this amide because it shows anti-platelet aggregation effect (Okuyama *et al*, 1986) and cytotoxic activities against MCF-7 (human breast carcinoma), A-549 (human lung cancer) and HT-29 (human colon cancer) cell lines (Zhao *et al*, 1992).

The BuOH-soluble fraction of the leaves of *A. tuberosum* was also repeatedly chromatographed over silica gel to afford compound **2**. Compound **2**, $C_{12}H_{10}O_3$ (double bond equivalent=8), which gave mp 340.5°C, showed a molecular ion peak at *m/z* 202 in the mass spectrum. The IR spectrum of **2** displayed absorption bands at 3019 and 1680 cm^{-1}, indicating the presence of hydroxyl group and aromatic ring in the molecule. The ^{1}H-NMR spectrum of **2** showed two ortho-coupled doublets each of two protons with a J value of 7.60 Hz at δ 7.37 and 5.44 ppm, indicating the presence of a 1,4-di-substituted benzene ring and two singlets at δ 10.98 and 9.52 assignable to two phenolic protons, respectively. The ^{13}C-NMR spectrum of **2** showed 4 unique types of carbon, whereas the formula of this compound shows 12 carbon atoms. This is due to an element of symmetry, which has already been shown from the ^{1}H-NMR. Therefore, the structure was indicated as a symmetrical bis (*p*-hydroxyphenyl) ether from an analysis of the mass and ^{13}C-NMR. This is the first report of its occurrence in nature to our best knowledge.

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