Chemistry of Natural Compounds, Vol. 45, No. 4, 2009

PHYTOCHEMICAL STUDY OF *Convolvulus subhirsutus* GROWING IN UZBEKISTAN

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UDC 547.944/945

Eight alkaloid derivatives of tropane, among which the major ones were convolvine and convolamine; the minor ones, phyllalbin, convolidine, nortropine, phyllalbin *N*-oxide, convolvidine, and conpropine, have been isolated previously from the aerial part of *Convolvulus subhirsutus* growing in Uzbekistan [1, 2]. Quantitative analysis found 0.6% total bases in the aerial part; 1.6%, in the roots. The contents of the major alkaloids convolvine and convolamine were 45-50% of the total mixture. In continuation of research on alkaloids of this plant collected near Tepar, Tashkent Oblast′, a base (15 mg) with mp 144–145°C that was identified as the known alkaloid convolicine was isolated by chromatography over a column of Al_2O_3 from the non-phenol part of total alkaloids after removal of convolvine and convolamine [3]. The benzene eluates contained an alkaloid (10 mg) with mp 178–179°C that was identified as confolidine.

The extract was neutralized to pH 7 after removal of the alkaloids, diluted with water in a 1:1 ratio, and treated successively with hydrocarbons, EtOAc, and $CHCl_3$. Paper chromatography and comparison with authentic samples detected in the remaining aqueous phase D-mannose, D-glucose, and D-galactose. Crystals with mp 136°C that were identified as β-sitosterol were isolated from the hydrocarbon fraction. The mother liquor was treated with acetone, evaporation of which produced crystals with mp 81–82°C that were identified as acetamide. Treatment of the mother liquor with acetone:MeOH isolated veratric acid with mp 181–182°C.

The $CHCl_3$ fraction was also treated with acetone, evaporation of which produced crystals with mp 201–202°C, R_f 0.5 (system 1). The IR spectrum of the compound contained absorption bands for active H (3115 cm^{-1}, –OH), –CH (3045), an aromatic ring (1605, 1562, 1506), and a conjugated carbonyl (1702) [4, 5]. The UV spectrum showed absorption maxima at 297 and 345 nm that were characteristic of 6,7-dihydroxycoumarins [6]. The PMR spectrum of the coumarin had resonances for aromatic protons at 6.15 and 7.79 ppm as two doublets (J = 9.6 Hz) for the C-3 and C-4 protons; at 7.05, a singlet for the C-5 proton; at 6.71, a singlet for the C-8 proton. A 3H singlet for the aromatic methoxyl was observed at stronger field (3.85). Resonances for H-4 and H-8 were broadened due to through-space spin—spin coupling between them with J of H-4 and H-8 <1 Hz [7].

The molecular weight of the coumarin was confirmed by a peak with mass 192 in the GC/MS. These spectral properties indicated that the isolated coumarin was scopoletin [8], which was isolated for the first time from a plant of the genus *Convolvulus*.

Chromatography of the EtOAc fraction over a column of silica gel produced from EtOAc:hydrocarbon fractions a compound with mp 140–141°C, R_f 0.46 (system 1). GC/MS of it gave MW 208 amu. The UV spectrum exhibited maxima at 218, 245, and 330 nm that were characteristic of a conjugated aromatic system. The IR spectrum had absorption bands for a 1,3,4-trisubstituted benzene ring at 1682, 1588, 870, and 814 cm^{-1}. The PMR spectrum had a 3H triplet at strong field (1.22 ppm, J = 7.2 Hz) for resonance of the methyl of the ethyl group. The resonance for $O–CH_2$ appeared as a quartet at 4.13 (2H, J = 7.2); for the β-proton (=CH–Ar), as a 1H doublet at 6.16 (J = 16.2). Resonances for protons of a pyrocatechol system of an aromatic ring were also present at 6.71 (1H, d, J = 8.4, H-5′); 6.85 (1H, ddd, J = 1.6, H-2′); and 6.97 (1H, d, J = 1.6, H-6′) [9]. These spectral properties indicated that the isolated compound was caffeic acid ethyl ester, which was isolated for the first time from this plant. Caffeic acid and its esters are intermediates in the biosynthesis of coumarins and flavonoids. GC/MS detected in the alcohol extract peaks with MW 190 and 141 that were apparently due to the ethyl ester of umbelliferone and the amino-alcohol tropine, respectively.

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0009-3130/09/4504-0604

Thus, the two known alkaloids convolicine and confolidine were isolated from *C. subhirsutus*. In addition, scopoletin, caffeic acid ethyl ester, *β*-sitosterol, veratric acid, and acetamide were isolated for the first time from this plant. D-Glucose, D-mannose, D-galactose, umbelliferone ethyl ester, and tropine were also present.

IR spectra were recorded in KBr disks on a Perkin—Elmer Model 2000 Fourier IR spectrometer; UV spectra, in EtOH on a Hitachi spectrophotometer. NMR spectra were recorded on a Tesla BS-567A/100 MHz instrument (CD_3OD solvent, HMDS internal standard, δ–scale). We used Al_2O_3 (neutral, 100/160 μm) for column chromatography. TLC was performed on plates with KSK silica gel using $CHCl_3$:CH_3OH (40:1, system 1).

Isolation of Scopoletin and Caffeic Acid Ethyl Ester. The $CHCl_3$ part of the alcohol extract was treated with acetone. The part that was insoluble in acetone afforded crystals with mp 205-206°C, R_f 0.5 (system 1), that did not give melting point depression with an authentic sample of scopoletin. The EtOAc fraction of the alcohol extract was chromatographed over a column of silica gel. The first EtOAc:hydrocarbon fractions produced crystals with mp 140-141°C (10 mg), R_f 0.46 (system 1), caffeic acid ethyl ester.

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