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Isolation of a New Phenylpropanoid from *Codonopsis ussuriensis*

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Abstract□A new phenylpropanoid was isolated from the roots of *Codonopsis ussuriensis* (Rupr.et Maxim) Hemsley. It was colorless crystals, mp. 140-142°C and was elucidated as 4-(3-ethoxy-1-propenyl)-2,6-dimethoxyphenyl-β-D-glucopyranoside on basis of spectral data analysis.

Keywords□*Codonopsis ussuriensis*, Campanulaceae, 3-ethoxy-syringin, 4-(3-ethoxy-1-propenyl)-2,6-dimethoxyphenyl-β-D-glucopyranoside.

Codonopsis ussuriensis (Rupr. et Maxim) Hemsley (Campanulaceae) is a plant belonging to the same species as *C. pilosula* and *C. lanceolata*, and those pharmacological actions and components have been studied extensively by several researchers[1-6]. We have previously reported that an ether soluble fraction of the plant showed an increase in red blood cell number[7].

In this paper, the chemical structure of a new phenylpropanoid (Compound I) isolated from n-butanol fraction was studied.

EXPERIMENTAL METHODS

Instrumental

Melting point was recorded on a Thomas[R] Hoover capillary melting point apparatus. HPLC were done by Waters Associates Liquid Chromatograph and detected by Waters 441 UV 254 nm. ^{13}C-NMR and ^{1}H-NMR spectra were obtained on Bruker AM-300 spectrometer using TMS as an internal standard. IR and UV spectra were measured on a DIGLAB FTS-80 FT-IR and Shimadzu UV-visible recording spectrophotometer UV 240 Graphicord, respectively. Mass spectra were taken on JEOL-DX 303 Mass Spectrometer, JEOL JMA-DA 5000 Mass Data System.

Isolation

Codonopsis ussuriensis was collected in July (1988) at Kwang Neung, Kyungkido, Korea. Dried root (1.2 kg) was extracted with methanol (30 *l*) (4 h, 3 times). The methanol extract was evaporated in vacuo and fractionated with diethylether and then n-butanol.

TLC chromatogram of the n-butanol fraction on a silica gel plate ($CHCl_3$: CH_3OH: H_2O = 64: 50: 10) revealed seven spots upon vanillin sulphuric acid spray (Rf = 0.79, 0.68, 0.62, 0.56, 0.43, 0.33, 0.15). When it was subjected to column chromatography on silica gel (Merck, 7734) with a solvent system of chloroform and methanol (gradient), compound I was obtained at $CHCl_3$/MeOH (10:1), detected by TLC ($CHCl_3$: CH_3OH: H_2O = 64: 50: 10, Rf = 0.56, detector: UV and vanillin sulphuric acid spray). And the purity of compound I (T_R 6.869) was checked by HPLC system utilized Spherisorb reversed-phase C_{18} column (particle size 5 μ, 15 cm × 3.9 mm ID) and mobile phase with 30% methanol in water. The flow rate was 1.0 ml/min.

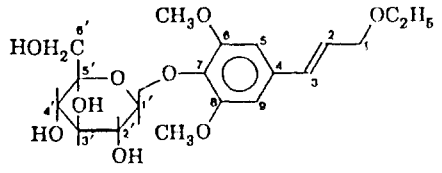
Compound I

Colorless crystal, mp. 140-142°C; UV λ_{max} (EtOH) nm 230, 265; IR ν_{max} cm^{-1} 3560, 3387, 3309, 3030, 1650, 1589; ^{1}H-NMR (CH_3OH-d_4) δ (ppm) 1.31 (3H, t, J = 7.3 Hz, $-OCH_2\underline{CH_3}$), 3.20 (2H, q, J = 7.3 Hz, $-O\underline{CH_2}CH_3$), 3.86 (6H, s, 2 × OCH_3), 4.21 (2H, dd, J = 4.3 and 1.2 Hz, $-CH=CH-\underline{CH_2}-$), 4.87 (1H, d, J = 7.4 Hz, anomeric H), 6.33 (1H, dt, J = 15.8 and 4.3 Hz, $-CH=\underline{CH}-CH_2$), 6.55 (1H, dt, J = 15.8 and 1.2 Hz, $-\underline{CH}=CH-CH_2$), 6.75 (2H, s, aromatic 2H); ^{13}C-NMR (CH_3OH-d_4) δ (ppm) Table I; Mass (EI) 210, 192, 182, 167, 149, 86 (CI) Reagent gas: methane 210, 193, 182, 167, 149, 86 (FAB) 395, 382, 167.

RESULTS AND DISCUSSION

Compound I was colorless crystals and its melting point was 140-142°C. The presence of aromatic group was shown in UV (λ_{max}^{EtOH} 265 nm) and IR

Table I. ^{13}C-NMR data of compound I comparing with that of syringin



Carbon Number	Compound I	Syringin[8]
1	63.6	63.6
2	135.2	135.2
3	131.2	131.2
4	130.0	130.0
5, 9	105.3	105.3
6, 8	154.3	154.3
7	135.8	135.8
1'	105.2	105.2
2'	75.7	75.7
3'	78.3	78.3
4'	71.3	71.3
5'	77.8	77.8
6'	62.5	62.5
OCH_3	57.0	57.0
$OCH_2\underline{CH_3}$	9.2	–
$O\underline{CH_2}CH_3$	47.9	–

spectrum (3030, 1650, 1589 cm^{-1}). In ^1H-NMR the signal of 3.86 ppm (6H) indicate the two symmetrical methoxyl radicals which are bonded to benzene ring directly. Thus, compound I has an aromatic group which two methoxyl radicals are bonded symmetrically. In ^1H-NMR spectrum the multiple peak of δ 3.43-3.82 ppm and the anomeric proton peak (δ 4.87, d, J = 7.44 Hz) reveal the presence of sugar. The hydroxyl radicals of sugar were shown in IR spectrum (3560, 3387, 3309 cm^{-1}). ^1H-NMR spectrum showed the signal of two symmetrical protons at δ 6.76 (s, 2H). And the signals of δ 4.21 (dd, J = 4.26 Hz, 1.20 Hz, 2H), 6.33 (dt, J = 15.84, 4.26 Hz, 1H), and 6.55 (dt, J = 15.84, 1.20 Hz, 1H) indicate the presence of (-CH = CH -CH_2O-) group. From the J value, we can predict that the proton 1 and 2 have trans type.

Thus benzene ring of compound I has sugar linked by β position at C-1, propenyl radical at C-4, two symmetrical methoxyl radicals and protons at C-2,6 or C-3,5. And the ethyl radical which is appeared at δ 1.31 (t, J = 7.30 Hz) and δ 3.20 (q, J = 7.30 Hz) of ^1H-NMR is attached to 3 position of propenyl radical by ether type.

From the above findings, we expected that the structure of compound I should be similiar to that of syringin[8] except ethyl radical. Therefore the spectral data of compound I was compared with the standard of syringin simultaneously. In ^1H-NMR and ^{13}C-NMR (Table I), compound I and syringin have the same spectra except ethyl radical signals of compound I. In HPLC, compound I showed a peak at 6.069 min while syringin showed a peak at 6.162 min, and IR spectra of them have similiar signal bands.

From mass spectra, molecular peak could not be found, but EI and CI spectra showed m/z 210 base peak. However, the numbers of carbon and proton were determined from CMR and PMR spectra. Therefore by the comparison with the spectral data of syringin, compound I is elucidated as 3-ethoxy syringin, 4-(3-ethoxy-1-propenyl)-2,6-dimethoxyphenyl-β-D-glucopyranoside, $C_{19}H_{28}O_9$ (MW = 400).

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