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A New Phenolic Aldehyde from the Seeds of *Phytolacca americana*

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商陸種子의 新훼놀성 알데하이드

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Caffeic aldehyde was isolated from the seeds of *Phytolacca americana*. This is the first reported occurrence of the compound in nature.

Introduction

The genus *Phytolacca* has been extensively investigated[1,2] and previous works on the seeds of *Phytolacca americana* have yielded 3-acetyl-aleuritolic acid[3] and a new lignan, americanin A[4]. We now wish to report the isolation of a new naturally occurring phenolic aldehyde from the seeds of *Phytolacca americana*.

The compound, $C_9H_8O_3$, mp 203~4°, M^+(m/e) 164, gave a green colouration in $FeCl_3$ reaction and its IR spectrum showed the presence of OH (3240cm^{-1}), α,β-unsaturated CO(1655cm^{-1}), *trans*-double bond (1615 and 980cm^{-1}) and an aromatic system (1595, 1530 and 1449cm^{-1}). The formation of a di-O-methyl ether, mp 81~3° and a diacetate, mp 115° indicated the presence of two phenolic groups. The NMR spectrum of the diacetate showed a singlet (6H) at δ 2.31, a double doublets centeredat 6.63(1 H, J=8 and 16Hz, a doublet at 7.4 (1H, J=16 Hz), a doublet at 9.64 (1H J=8Hz) and signals due to three aromatic protons at from 7.20 to 7.39.

These evidences clearly suggested that this compound is 3,4-dihydroxycinnamic aldehyde. This suggestion was confirmed by the formation of 3,4-dimethoxybenzoic acid and 3,4-dimethoxycinnamic acid(methylester) from the dimethyl ether by oxidation with $KMnO_4$ and Ag_2O, respectively.

To our knowledge this compound has not been previously reported in the literature.

Experimental

Isolation of caffeic aldehyde The acetone extract of the seeds of *P. americana* was extracted with $CHCl_3$ followed by H_2O. The water soluble fraction was chromatographed over Silica gel using 3% MeOH-$CHCl_3$ as an eluent and crystallized from MeOH to give brown powdery crystals of caffeic aldehyde, mp 203~4°, UVλ_{EtOH}^{max}nm(log ε): 226(4.05), 242(3.97), 255(4.00), 350(4.34), with $AlCl_3$ 226(4.04), 387(4.22), with $AlCl_3$+HCl 226(4.09), 240(4.04), 255(4.01), 350 (4.27); with H_3BO_3/NaAc 267(4.06), 321~31 (3.99), 376 (4.42). MS m/e(%); 164(M^+, 61),

147(22), 136(28), 118(22), 110(51), 89(100), 77(87), 63(96), 53(93), 39(87), 29(32). Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91. Found; C, 65.82; H, 4.70.

Acetylation of caffeic aldehyde Caffeic aldehyde (100mg) was acetylated with Ac_2O (2ml) and pyridine (1ml) in the usual way.

The reaction product was crystallized from benzene-ether (4:1) to give yellowish prisms, mp 115°, IRν_{max}: 1757 and 1200cm^{-1}(acetate), no OH band.

Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.92; H, 4.85. Found: C, 62.88; H, 4.84.

Methylation of caffeic aldehyde To a solution of caffeic aldehyde (30mg) in acetone (20ml) was added 1ml of $(CH_3)_2SO_4$ and 0.5g of K_2CO_3. The mixture was refluxed on the steam bath for 3hr and filtered. The filtrate was evaporated, and extracted with ether. The ether layer was washed with $NaHCO_3$ and then H_2O, dried and evaporated. The residue was crystallized from MeOH to give dimethylether, mp 81-3°. (Lit.[5], mp 82-83°). NMR ($CDCl_3$) δ: 3.96(S, 2×Meo), 6.63(dd, 1H, J=8 and 17Hz), 6.8~7.25 (3H, aromatic H), 7.46(d, 1H, J=17Hz) 9.77(d, 1H, J=Hz).

$KMnO_4$-oxidation of dimethylether To a solution of dimethylether (50mg) in acetone (10ml) was added 1ml of 10% KOH and then an acetone solution of $KMnO_4$ dropwise at room temperature until colour of $KMnO_4$ did not disappear. After degradating an excess of $KMnO_4$ by addition of EtOH, the reaction mixture was filtered and chromatographed over Silica gel using benzene-ether (4:1) as an eluent to give 3,4-dimethoxybenzoic acid, mp 174-5°, which was identical with an authentic sample by direct comparison(TLC, mmp).

Ag_2O-oxidation of dimethylether To a suspension of Ag_2O(1g) in 10% NaOH (20ml) was added a sample (100mg) and stirred for 10min at 60°, and filtered. The filtrate was acidified with HCl, extracted with ether, and the ether solution was washed, dried and methylated with CH_2N_2 in an usual way to give 3,4-dimethoxycinamic acid methylester, mp 60°, which was identical with an authentic sample.

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