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Cirsiumaldehyde from *Gastrodia elata*

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Abstract – In the course of continous work on tubers of *Gastrodia elata*, a new constituent was isolated from the ethyl acetate soluble fraction prepared from the methanol extract. The structure of the compound was identified as α,α'-[bis-2-(5-carboxaldehydo)furanyl]-dimethyl ether from the elemental analytical and spectroscopic data. This compound was once isolated from *Cirsium chlorolepis* and named as cirsiumaldehyde. This is the first furan type compound isolated from *Gastrodia elata*.

Key words – *Gastrodia elata*, α,α'-[bis-2-(5-carboxaldehydo)furanyl]-dimethyl ether, cirsiumaldehyde, furan.

The steamed and dried tubers of *Gastrodia elata* Blume (Orchidaceae) have been considered as one of a very important herb medicines and used for the treatment of headaches, migraine, dizziness, childhood convulsions, epilepsy, rheumatism, neuralgia, and other neuralgic and nervous affections in oriental traditional or folk medicines(Bensky and Gamble, 1986, Tang and Eisenbrand, 1992). In the course of our search for plants with anti-platelet and/or anti-thrombotic potentials, several solvent fractions prepared from the MeOH extract of the tubers of *G. elata* attenuated the thrombotic symptoms in both mouse and rat models of thrombosis (Paik *et al.*, 1995). In this paper, we report the isolation of the first furan type component, α,α'-[bis-2-(5-carboxaldehydo)furanyl]-dimethyl ether, from the EtOAc fraction which is one of the solvent fractions with anti-thrombotic activities.

Experimental

Melting point was determined on a Mitamura-Riken melting point apparatus and uncorrected. IR spectrum was recorded on a Jasco FT/IR-5300 spectrometer and ^{1}H- and ^{13}C-NMR spectra were taken at 300 MHz and 75.5 MHz respectively on a Varian Gemini-2000 spectrometer with tetramethylsilane as the internal standard. The elemental analysis was performed with a GmbH Vario EL Elemental Analysensystem by Seoul Branch Analytical Lab, Korea Basic Science Institute.

Plant materials – Steamed and dried tubers of *Gastrodia elata* were purchased from a crude drug market in Seoul and were identified by Prof. Hyung Joon Chi, Natural Products Research Institute, Seoul National University.

Isolation of the compound – The steamed and dried tubers of *Gastrodia elata* (6 Kg) were refluxed with methanol three times for six hours each. The concentrated MeOH extract was partitioned between $CHCl_3$ and H_2O and the H_2O layer was further extracted with EtOAc to obtain EtOAc soluble fraction (40 g). 25 g of the EtOAc fr. was chromatographed on a silica gel (4 Kg) column eluting with $CHCl_3$ containing increasing propotions of MeOH. The subfraction (2.5 g) eluted with $CHCl_3$:MeOH=20:1 was re-chromatographed with silica gel and eluted with $CHCl_3$: MeOH =100:1 affording the pale yellow colored com-

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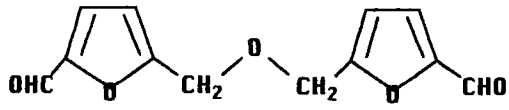
pound.

mp 114-115°C (from EtOAc-*n*-hexane), Anal. calcd. for $C_{12}H_{10}O_5$: C, 61.53; H, 4.31, found: C, 61.37; H, 4.33; IR ν_{max} (KBr) cm^{-1}; 1670, 1523; ^{1}H-NMR ($CDCl_3$); δ 4.63 (4H, s), 6.56 (2H, d, J=3.6 Hz), 7.21 (2H, d, J=3.6 Hz), 9.64 (2H, s), ^{13}C-NMR ($CDCl_3$); δ 64.59, 111.92, 121.96, 152.90, 157.32, 177.90.

Results and Discussion

The present compound, mp 114-115°C, was obtained as pale yellow crystal. The IR spectrum revealed the presence of a carbonyl group at 1,670 cm^{-1}. The ^{1}H-NMR spectrum showed one aldehyde peak at δ 9.64 (s), two aromatic doublets at δ 7.21 and 6.56 and one oxygenated methylenic singlet at δ 4.63 with the proton proportions of 1:1:1:2. The ^{13}C-NMR spectrum showed only six peaks, one at δ 177.90 ascribable to the carboxylic carbon, four aromatic carbon peaks at δ 157.32, 152.90, 121.96 and 111.92 and one for oxygenated methylenic carbon at δ 64.59. The elemental analysis showed neither nitrogen nor sulfur present in this compound and indicative of the molecular formula as $C_{12}H_{10}O_5$. The elemental analytical data and the ^{1}H- and ^{13}C-NMR spectra are suggestive of a dimeric structure with two 5-membered furan rings with two aldehyde groups. The two aromatic proton signals with J=3.6 Hz of furan are suggestive of 2,5-disubstitution (Silverstein *et al.*, 1991). On the basis of the above discussed data, the structure of the compound was determined as α,α'-[bis-2-(5-carboxaldehydo)furanyl]-dimethyl ether. This is the first report on the isolation of the furan type compound from *Gastrodia elata*. The literature survey revealed that the present compound was once isolated from *Cirsium chlorolepis* and named as cirsiumaldehyde (Shen and Mu, 1990).



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