Natural Product Sciences
8(4) : 137-140 (2002)

The Constituents of the Aerial Part of *Gastrodia elata* Blume

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Abstract – From the MeOH extract of the aerial part of *Gastrodia elata* Blume (GEB) (Family: Orchidaceae), eight compounds have been isolated on repeated column chromatography, and their structures were elucidated as dotriacontanoic acid (**1**), beta-sitosterol (**2**), 4-hydroxybenzaldehyde (**3**), docosanoic acid oxiranylmethyl ester (**4**), hentriacotanoic acid (**5**), octadecanoic acid (**6**), benzoic acid (**7**) and gastrodin (**8**) on the basis of their spectral evidences including EI-Mass and 2D-NMR spectrum. All of them were obtained from the aerial part of *Gastrodia elata* Blume for the first time, in which compound **4** is a novelty to our best knowledge. It is also known that a phenolic glucoside, gastrodin is a major constituent just like Gastrodia rhizome.
Keywords – *Gastrodia elata,* Orchidaceae, gastrodin, docosanoic acid oxiranylmethyl ester

Introduction

Gastrodia elata Blume belongs to Orchidaceae, which is a perennial parasitic herbaceous plant, being growing in the woods of the central provinces of China, Korea and Japan (Soka, T., 1985), its rhizome has been traditionally used as a tonic, a sedative and an antispasmodic (Zhong Yao Zi, 1961), and also listed officially in the Chinese Pharmacopoeia as important Chinese herbal medicines called Rhizome *Gastrodia* (Chinese name: Tianma) for the medical treatment of headaches, migraine, dizziness, epilepsy, rheumatism, neuralgia, paralysis and other neuralgic and nervous disorders (Pharmacopoeia of China, 2000; Tang, W., *et al.*, 1992). The recent research reports have revealed that this plant and its active constituents have some very beneficial properties such as aiding in expelling all kinds of toxins from the body, enhancing strength and virility, improving the circulation and facilitating memory consolidation and retrieval (Hayashi, J., *et al.*, 2002; Hsieh, M. T., *et al.*, 1997; Wu, C. R. *et al.*, 1996). To date, the constituents of the tubers of this plant have been investigated by phytochemical studies, which have revealed the presence of phenolic compounds including gastrodin as a major constituent, together with 4-hydroxybenzaldehyde, 4-hydroxybenzyl alcohol, parishin, 4,4-dihydroxybenzyl sulfoxide, vanillin, vanillyl alcohol, etc. (Zhou, J., *et al.*, 1979; Taguchi, H., *et al.*, 1981; Noda, N., *et al.*, 1995; Lin, J. H., *et al.*, 1996; Yun, C., *et al.*, 1997), beta-sitosterol, organic acids and polysaccharides (Zhong Hua Ben Cao, 1996), but there is not any report on the studies of the aerial part of this plant. For the purpose of further use and development of *Gastrodia elata* Blume, we have investigated the MeOH extract of its aerial part. As a result, eight compounds were obtained for the first time. In this paper, we describe the isolation of eight compounds and their structural elucidation on the basis of their spectral evidences, determined as dotriacontanoic acid (**1**) (450 mg), beta-sitosterol (**2**) (15 mg), 4-hydroxybenzaldehyde (**3**) (20 mg), docosanoic acid oxiranylmethyl ester (**4**) (15 mg), hentriacotanoic acid (**5**) (20 mg), octadecanoic acid (**6**) (100 mg), benzoic acid (**7**) (15 mg) and gastrodin (**8**) (550 mg). Among them, compound **4** is a new compound and gastrodin is also a major constituent similar to its rhizome.

Experimental

Plant materials – The aerial parts of GEB were collected at mountain of DaeAm of KangWon province of Korea in June 2001 and identified by Prof. Chang-Soo Yook, college of Pharmacy, KyungHee University.

General experimental procedures – Melting points (uncorrected) were measured using a Boetius micromelting point apparatus. EI-MS on JEOL JMS-01SG and JMS-

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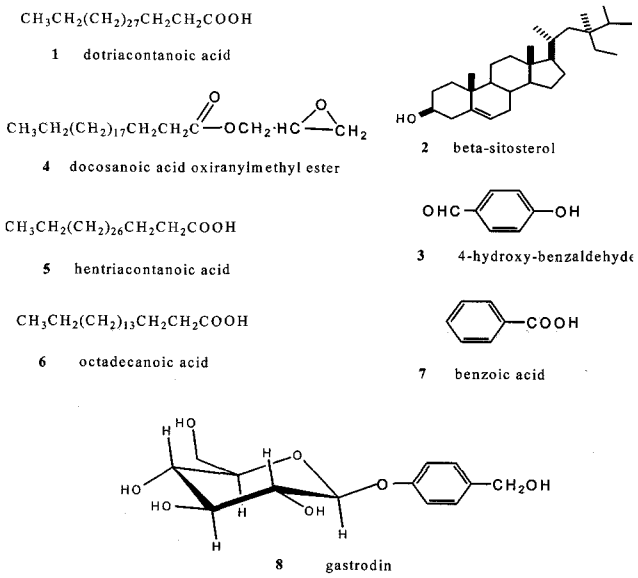

Scheme 1. the structures of compounds **1-8.**

DX303HF instruments, and NMR spectra were measured in $CDCl_3$ and CD_3OD on a JEOL-α-500 spectrometer and chemical shifts were relative to tetramethylsilane (TMS). Column chromatography (CC) was carried out on silica gel 230-400 mesh (Merck). TLC was performed on precoated silica gel 60GF254 (Merck).

Extraction and isolation – The dried aerial parts of GEB (2 kg) were extracted with MeOH and then the methanolic extract (60 g) was dissolved with in water and extracted with ether and butanol successively. The ether extract (25 g) gave compounds **1-5** upon a series of silica gel column chromatography eluting using n-hexane-EtOAC (6:1→2:1). On the other hand, the butanol extract (15 g) was purified by silica gel column chromatography repeatedly with developing solvent ($CHCl_3$:MeOH=10:1→7:1) to obtain compounds **6-8**.

Compound **1** (dotriacontanoic acid): white powder, mp: 67.4~68.5°C, its EI-MS (*m/z*) 480 $[M]^+$, 424, 396, 368, 340, 185, 129, 85, 57. ^{1}H-NMR (500MHz, *J* in Hz, δ in ppm, in $CDCl_3$) δ 0.91 (3H, t, *J*=7.5, H-1), 1.28~1.37 (m, H-2~H-29), 1.66 (2H, m, H-30) and 2.37(2H, t, *J*=7.0, H-31). ^{13}C-NMR (125MHz, in $CDCl_3$, δ in ppm) δ: 179.71 (C-32), 34.19 (C-31), 32.16 (C-3), 29.93, 29.90, 29.89, 29.87, 29.82, 29.67, 29.59, 29.47, 29.30 (C-4~C-29), 24.93 (C-30), 22.92 (C-2) and 14.32 (C-1).

Compound **2** (β-sitosterol): white needle crystal, mp 139~140°C. EI-MS (*m/z*): 396 $[M-H_2O]^+$, 329, 303, 255, 145, 107, 91. ^{13}C-NMR (125MHz, in $CDCl_3$, δ in ppm) δ: 141.01 (C-1), 121.95 (C-6), 72.08 (C-3), 57.03 (C-9), 56.34 (C-14), 50.42 (C-8), 46.13 (C-17), 42.58 (C-10), 42.55 (C-22), 40.04 (C-4), 37.51 (C-1), 36.76 (C-13), 36.39 (C-20), 34.22 (C-7), 32.17 (C-11), 31.91 (C-24), 29.93 (C-12), 29.45 (C-25), 28.48 (C-15), 26.40 (C-16), 24.55 (C-2), 23.34 (23), 21.34 (C-28), 20.04 (C-19), 19.62 (C-18), 19.29 (C-21), 19.03 (C-29), 12.22 and 12.10 (C-26 and 27). ^{1}H-NMR(500MHz, in $CDCl_3$, δ in ppm) δ: 5.37 (1H, d, *J*= 5.0Hz, H-6), 3.51 (1H, m, H-3), 1.06 (s, H-19), 0.95 (d, *J*=8.0Hz, H-21), 0.85~0.95 (H-26, 27, 29) and 0.71 (s, H-18).

Compound **3** (4-hydroxybenzaldehyde): white powder, mp: 118~119°C. EI-MS (*m/z*): 122 $[M]^+$, 93, 65, 53. ^{1}H-NMR (500MHz, in $CDCl_3$, *J* in Hz, δ in ppm) δ : 9.88 (1H, s, CHO), 7.84 (2H, d, *J*=8.5, H-2 and 5), 7.01 (2H, d, *J*=8.5, H-3 and H-4). ^{13}C-NMR (125MHz, in $CDCl_3$, δ in ppm) δ: 191.49 (C-7), 161.97 (C-4), 132.76 (C-1), 130.08 (C-2 and 6), 116.27 (C-3 and 5).

Compound **4** (docosanoic acid oxiranylmethyl ester): white powder, mp: 68.2~69.5°C. EI-MS (*m/z*): 396 [M]+, 368, 340, 312, 267, 239, 97, 83, 73, 67. ^{1}H-NMR (500 MHz, in $CDCl_3$, *J* in Hz, δ in ppm) δ: 0.90 (3H, t, *J*=6.5, H-1), 1.35~1.28 (m, H-2~H-19), 1.65 (2H, m, H-20), 2.37 (2H, t, *J*=7.5Hz, H-21), 3.72 (1H, dd, *J*=11.5 and 4.0, H-1'a), 3.63 (1H, dd, *J*=11.5 and 4.0, H-1'b), 3.95 (1H, m, H-2') and 4.22 (2H, qd, *J*=11.5 and 4.5, H-3'). ^{13}C-NMR (125 MHz, in $CDCl_3$, δ in ppm) δ: 174.56 (C-22), 70.54 (C-3'), 65.42 and 63.61 (C-1' and C-2'), 34.40 (C-21), 32.15 (C-3), 29.92, 29.91, 29.89, 29.87, 29.88, 29.67, 29.82, 29.58, 29.47, 29.36 (C-4~C-19), 25.15 (C-20) and 14.32 (C-1).

Compound **5** (hentriacontanoic acid): white powder, mp: 59~61°C; Its EI-MS (*m/z*) 466 $[M]^+$, 438, 422, 410, 395, 353, 325, 297, 129. ^{1}H-NMR (500MHz, in $CDCl_3$, *J* in Hz, δ in ppm) δ: 0.90 (3H, t, *J*=7.5, H-1), 1.27~1.32 (m, H-2~H-28), 1.67 (2H, m, H-29) and 2.36 (2H, t, *J*=7.5, H-30). ^{13}C-NMR (125MHz, in $CDCl_3$, δ in ppm) δ: 179.43 (C-31), 34.18 (C-30), 32.21 (C-3), 29.93~29.18(C-4~C-28), 24.94 (C-29), 22.92 (C-2) and 14.23 (C-1).

Compound **6** (octadecanoic acid): white powder, mp: 68~70°C, its EI-MS (*m/z*) 285 $[M+H]^+$, 257, 228, 214, 186, 157, 130, 97. ^{1}H-NMR (500MHz, in CD_3OD, *J* in Hz, δ in ppm) δ: 0.92 (3H, t, *J*=7.0, H-1), 1.28~1.33 (m, H-2~H-15), 1.67 (2H, m, H-16) and 2.36 (2H, t, *J*=7.5, H-17). ^{13}C-NMR (125MHz, in CD_3OD, δ in ppm) δ: 176.65 (C-18), 33.86 (C-17), 31.90 (C-3), 29.93~29.18 (C-4~C-15), 24.95 (C-16), 22.56 (C-2) and 13.28(C-1).

Compound **7** (benzoic acid): white pallelet crystal., mp: 123~124°C. ^{1}H-NMR (500MHz, in CD_3OD, *J* in Hz) δ ppm: 8.05 (2H, dt, *J*=8.5 and 1.5, H-2 and 6), 7.61 (1H, dt, *J*=8.5 and 1.5, H-4), 7.47 (2H, dt, *J*=8.5 and 1.5, H-3 and 5). ^{13}C-NMR (125MHz, in $CDCl_3$) δ ppm: 168.72 (C-7), 132.85 (C-4), 129.54 (C-2 and 6), 128.28 (C-3 and 5).

Compound **8** (gastrodin): white powder, mp: 154~157°C.

EI-MS (*m/z*): a molecular peak at 288, other fragments 165, 125 [M-glucose], 74, and 62. ^{1}H-NMR (500MHz, in CD_3OD, *J* in Hz, δ in ppm) δ: 7.31 (1H, d, *J*=8.7, H-2, 6), 7.25 (2H, d, *J*=8.7, H-3, 5), 4.92 (1H, d, *J*=7.0, H-1), 4.56 (2H, s, H-7), 3.92 (1H, brd, *J*=11.5, H-6), 3.74 (1H, dd, *J*=11.5 and 7.0, H-6) and 3.59~3.44 (m, H-2~H-5). ^{13}C-NMR (125MHz, in CD_3OD, δ in ppm) δ: 157.28 (C-4), 135.52 (C-1), 128.37 (C-2 and 6), 116.62 (C-3 and 5), 101.24 (glucose C-1'), 76.89 (C-3'), 76.82 (C-5'), 73.78 (C-2'), 70.24 (C-4'), 63.72 (C-7) and 60.48 (C-6').

Results and Discussion

The structures of compounds **1~3** and compounds **5~7** could be determined as dotriacontanoic acid (**1**) (Liu, Y. W., 1981), beta-sitosterol (**2**) (Charles, J. P., 1993), 4-hydroxybenzaldehyde (**3**) (Charles, J. P., 1993), hentriacotanoic acid (**5**) (Yogendra, N., 1983) octadecanoic acid (**6**) (Carballeira, N. M., 2001) and benzoic acid (**7**) (Charles, J. P., 1993) by spectral analysis and direct comparison with reported data.

Compound **4** was a white powder, its EI-MS (*m/z*) showed a molecular peak at 396, with other significant fragments such as (*m/z*) 368, 340, 312, 267, 239, 97, 83, 73, 67, which indicated existing a long open chain aliphatic system. ^{1}H-NMR spectrum suggested a terminal methyl group at δ 0.90 (3H, s), several methylenes having a long open chain at δ1.28~1.35, one methylene at δ1.65 (2H, m) and one methylene adjacent to carbonyl group at δ2.37 (2H, t, *J*=7.5), and moreover, there exist two AB patterns protons at δ3.72 (1H, dd, *J*=11.5 and 4.0), 3.63 (1H, dd, *J*=11.5 and 4.0), 3.95 (1H, m) and 4.22 (2H, qd, *J*=11.5 and 4.5), respectively, which were assigned to an epoxide group -$\underline{CH_2CHOCH_2}$-. ^{13}C-NMR data showed signals owing to one ester carbonyl group at δ174.56, two oxygen-bearing methylenes at δ70.54, 65.42 or 63.61, one oxygen-bearing methine at δ65.42 or 63.61, and a long chain carbons at δ34.40, 32.15, 29.92, 29.91, 29.89, 29.87, 29.88, 29.67, 29.82, 29.58, 29.47, 29.36, 25.15 and 14.32. From EI-MS and NMR data maybe deduce its molecular formula $C_{25}H_{48}O_3$. Thus, from above data, compound 4 was determined as docosanoic acid oxiranylmethyl ester. To our best knowledge, compound 4 was a new compound.

Compound **8** was obtained as white powder, had a molecular ion peak at (*m/z*) 288, assumed its molecular formula $C_{13}H_{18}O_7$, which was also confirmed by its NMR spectrum. The characteristic ^{1}H-NMR signals showed four aromatic protons including AAXX system attributable to a 1,4-disubstituted aromatic ring, chemical shifts were 7.31 (1H, d, *J*=8.7, H-2, 6), 7.25 (2H, d, *J*=8.7, H-3, 5) and one sugar linkage at C-4 as a β-configuration at δ 4.92 (*J*=7.0 Hz). ^{13}C-NMR(125MHz, in CD_3OD) indicated 13 carbons including six aromatic carbons at δ157.28 (C-4), 135.52 (C-1), 128.37 (C-2 and 6), 116.62 (C-3 and 5), one oxygen-bearing methylene at δ63.72 (C-7) and one glucose at δ101.24 (glucose C-1), 76.89 (C-3), 76.82 (C-5), 73.78 (C-2), 70.24 (C-4) and 60.48 (C-6). Thus it was found compound **8** was phenolic glycoside. By comparison with published data (Baek, N. I., Choi, S. Y., *et al*, 1999), compound **8** was known as gastrodin.

References

Baek, N. I., Choi, S. Y., Park, J. K., Cho, S. W., Ahn, E. M., Jeon, S. G., Lee, B. R., Bahn, J. H., Kim, Y. K. and Shon, I. H., Isolation and identification of succinis semialdehyde dehydrogenase inhibitory compound from the rhizome of *Gastrodia elata* Blume, *Arch. Pharm. Res.*, **22**(2), 219-224 (1999).

Carballeira, N. M., Cruz, H., Hill, C. A., De Voss, J. J. and Garson, M., Identification and total synthesis of novel fatty acids from the *Siphonarid limpet siphonaira* denticulate, *Journal of Natural Products*, **64**(11), 1426-1429 (2001).

Charles, J. P. and Jacqlynn, B., The Aldrich Library of ^{13}C and ^{1}H FTNMR Spectra, EDITION I, USA, **3**, 595 (1993).

Charles, J. P. and Jacqlynn B., The Aldrich Library of ^{13}C and ^{1}H FTNMR Spectra, EDITION I, USA, **2**, 943, 1063 (1993).

Hayashi, J., Sekine, T., Deguch, S., Lin, Q., Horie, S., Tsuchiya, S., Yano, S., Watanabe, K. and Ikegani, F., Phenolic compounds from *Gastrodia* rhizome and relaxant effects of related compounds on isolated smooth muscle preparation, *Phytochemistry*, **59**, 513-519 (2002).

Hsieh, M. T., Wu, C. R. and Chen, C. F., Gastrodin and *p*-hydroxybenzyl alcohol facilitate memory consolidition and retrieval but not acquisition on the passive avoidance task in rats, *Journal of Ethnopharmacology*, **56**, 45~54 (1997).

Lin, J. H., Liu, Y. C., Hau, J. P. and Wen, K. C., Parishins B and C from rhizomes of *Gastrodia elata*, *Phytochemistry*, **42**, 549-551 (1996).

Liu, Y. W., Antituberculous constituents of *Gentiana rhodantha*, *Zhong Yao Tong Bao*, **10**(12), 33-34 (1985).

Noda, N., Kobayashi, Y., Miyahara, K. and Fukahori, S., 2,4-Bis (4-hydroxybenzyl)phenol from *Gastrodia elata*, *Phytochemistry*, **39**, 1247-1248 (1995).

Soka, T., Dictionary of Chinese Drugs, Shanghai Science Technology Shogaukan (Eds.), Shogkukan Press, Tpkyo, 1870-1873 (1985).

Taguchi, H., Yoshioka, I., Yamasaki, K. and Kim, I. H., Studies on the constituents of *Gastrodia elata* Bl.ume, *Chemical and Pharmaceutical Bulletin*, **29**, 55-62 (1981).

Tang, W. and Eisenbrand, G., Chinese Drugs of Plant Origin, 71. *Gastrodia elata* Bl. SpringerVerlag, Berlin, Heidelberg, 545-548 (1992).

The Pharmaceutical Institute, Chinese Academy of Medical Sciences, Peking, *Zhong Yao Zi*, **I**, 88(1961).

The State Pharmacopoeia Commission of P. R. China, Pharmacopoeia of the Peoples Republic of China (Vol. I), Chemical Industry Press, Beijing, 29 (2000).

The State Traditional Drugs Administration, *Zhong Hua Ben Cao*, Shanghai Science and Technology Press, 2323-2330, 1996.11.

Wu, C. R., Hsieh, M. T., Huang, S. C., Peng, W. H., Chang, Y. S. and Chen, C. F., Effects of *Gastrodia elata* and its active compounds on scopolamine-induced amnesia in rats, *Planta Medica*, **62**(4), 317-321 (1996).

Yogendra, N., S. and Raghunath, S. T., heptatriacontan-4-one, tetratriacontanyl octacosanoate and other constituents from *Pedalium murex*, *Phytochemistry*, **22**(4), 973-974 (1983).

Yun-Choi, S. H. and Pyo, M. K., Isolation of 4,4-dihydroxy-benzylsulfoxide from *Gastrodia elata*, *Archive Pharmaceutical Research*, **20**, 91-92 (1997).

Zhou, J., Yang, Y. B. and Yang, T. R., The chemistry of *Gastrodia elata* Bl. 1., The isolation and identification of chemical constituents of *Gastrodia elata* Bl. (Chinese), *Acta Chimica Sinica*, **37**, 183-189 (1979).

(Accepted October 15, 2002)