한국농화학회지 제 39권 제 1호(1996)
Agricultural Chemistry and Biotechnology
Vol. 39, No. 1, pp. 89~94(1996)

Isolation and Identification of Sesquiterpene *o*-Naphthoquinones, Mansonones E, F and H, from the Root Bark of *Ulmus davidiana* Planch

Jong-Pyung Kim[1], Won-Gon Kim[1], Hiroyuki Koshino[2], Jong Hee Park[3], Jin Jung[4] and Ick-Dong Yoo[1]*

[1]Korea Research Institute of Bioscience and Biotechnology, Korea Institute of Science & Technology, P. O. Box 115, Yusong, Taejon 305-600, Korea, [2]The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama, 351-01, Japan, [3]College of Pharmacy, Pusan National University, Pusan 609-735, Korea, [4]Department of Agricultural Chemistry, Seoul National University, Suwon 441-744, Korea

Abstract : Three sesquiterpene *ortho*-naphthoquinones were isolated from the methanolic extract of root bark of *Ulmus davidiana* Planch whose stem and root bark have been used as an oriental medicine for the treatment of edema, mastitis, gastric cancer and inflammation. The structures of these compounds were established on the basis of spectral data obtained from UV-vis, IR, HR-EIMS and NMR spectrometry, including the pulse field gradient (PFG)-HMQC and HMBC techniques. Their structures were determined as 2,3-dihydro-3,6,9-trimethylnaphtho(1,8-*b,c*)pyran-7,8-dione, 3,6,9-trimethylnaphtho(1,8-*b,c*)pyran-7,8-dione and 2,3-dihydro-4-hydroxy-3,6,9-trimethylnaphtho(1,8-*b,c*)pyran-7,8-dione, which were identified as mansonones E, F and H, respectively. These compounds have originally been isolated from *Mansonia altissima* Chev, but have never been isolated from *Ulmus davidiana* Planch. Especially, mansonone H was isolated for the first time from Ulmaceae. The mismatched carbon chemical shifts of mansonones E and F in the reported literature were corrected by the aid of the PFG-HMBC spectral data.(Received January 6, 1996; accepted January 30, 1996).

Introduction

Ulmus davidiana Planch (Ulmaceae) is a deciduous tree which is distributed widely in Korea, Japan and China. The stem and root bark of this species have been used as an oriental medicine for the treatment of edema, mastitis, gastric cancer and inflammation.[1-4] As a part of our search for new biologically active substances from the traditional medicines,[5,6] we made a survey of the cytotoxicity of *Ulmus davidiana* against the human cancer cellines. The 80% aqueous methanolic extracts of root bark of this species showed high cytotoxicity (data not shown in this paper). Therefore, the chemical constituents of this cytotoxic extract were investigated. Up to now, two flavonoids, (+)-catechin and (+)-catechin 5-O-β-D-apiofuranoside, have so far been isolated from this plant species.[7] From the 80% aqueous methanolic extracts of root bark of this species, three cytotoxic compounds were isolated, and their structures were determined by their physico-chemical properties and various spectral data. In particular, PFG-HMQC and HMBC techniques[8-10] were applied for the first time for the structural determination of these compounds. The present paper describes the isolation and structural elucidation of these compounds.

Materials and Methods

Plant material

The root bark of *Ulmus davidiana* was collected from Mt. Wonhyo, Kyungnam Province, Korea, in May 1994. Fresh root bark was dried in a dark, well-ventilated place. The voucher specimen is deposited in the Herbarium of College of Pharmacy, Pusan National University.

Reagents and solvents

Most solvents used in the extraction and chromatography were GR or redistilled EP grade. The packing materials for column chromatographies were Sephadex LH-20 (Pharmacia, bead size 25-100 μm), silica gel (Merck, Kieselgel 60, 70-230 mesh) and C-18 resin (YMC-gel ODS-A, 60-230/70 μm).

General experimental procedures

NMR spectra were recorded on a JEOL α-600 NMR spectrometer at 600.05 MHz for ^1H, and 150.8 MHz for

---

Key words : *Ulmus davidiana* Planch, root bark, sesquiterpene *o*-naphthoquinones, mansonones E, F and H, structure
*Corresponding author

^{13}C in $CDCl_3$ or CD_3OD with TMS as an internal standard. Chemical shifts are expressed as δ (ppm) from TMS and coupling constants are given in Hz. All one-bond ^1H-^{13}C connectivities and ^1H-^{13}C long range correlations were established by heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond coherence (HMBC) spectra, respectively, using pulse field gradient (PFG) techniques recorded on a JEOL α-600 NMR spectrometer. PFG was applied by 600.5/150.8 MHz with $^nJ_{CH}=8.3$ Hz for HMBC and $^1J_{CH}=145$ Hz for HMQC, using a gradient of GRAD 1=20% (28.8 G cm^{-1}) and GRAD 2=10% (14.4 G cm^{-1}). Molecular weights were determined by the high resolution electron impact mass spectra (HR-EIMS) and EIMS recorded on a JEOL JMS-HX 110A mass spectrometer and Hewlett Packard Model HP 5989A EIMS system, respectively. UV-vis spectra were taken in MeOH on a Shimazu UV-260 spectrophotometer. IR spectra were obtained with a Laser Precision Analect RFX-65S FT-IR spectrometer using KBr discs. Specific rotations ($[\alpha]_D$) were measured in MeOH on a Polartronic polarimeter (Universal, Schmitd+Haensch, Germany) at 22℃. Thin-layer chromatography (TLC) was performed using Merck silica gel glass-backed plates (Kiesel gel $60F_{254}$, 0.25 mm thick: analytical, and 0.5 mm thick: preparative) without activation. Preparative HPLC was performed on a C-18 Maxsil column (22.5 mm×250 mm, 5 μm, Phenomenex) using a water-methanol system as a mobile phase, and by monitoring with a Waters photodiode-array detector (190-650 nm).

Extraction and isolation

Air dried root bark (4 kg) was milled and extracted with 80% aqueous methanol at room temperature for 3 days. The methanolic extract was filtered and concentrated under reduced pressure. The crude product (185 g) was subjected to successive extraction with *n*-hexane and $CHCl_3$. The *n*-hexane extract (8.7 g) was applied to a silica gel column eluted with *n*-hexane : EtOAc (50 : 1)~(1 : 1). The (20 : 1) eluted fraction was subjected to a 40% MeOH equilibrated C-18 column and eluted with 40% and 60% aqueous MeOH, consecutively. The preparative HPLC (70% aqueous MeOH, flow rate 7.0 ml/min, RT 16.7 min) of the 60% MeOH eluted fraction (285 mg) gave 183 mg of pure **1**. The $CHCl_3$ layer was concentrated under vacuum, and the residue (6.4 g) was subjected to column chromatography on a silica gel eluted with $CHCl_3$, $CHCl_3$-MeOH mixture in increasing proportion of MeOH. The fractions were collected and combined by monitoring with analytical TLC to afford four fractions in order of increasing polarity. Among them, fraction I was rechromatographed on a silica gel column ($CHCl_3$: MeOH=100 : 1) and a Sephadex LH-20 column ($CHCl_3$: MeOH=1 : 1), followed by C-18 column chromatography eluted with 40% and 60% aqueous MeOH, consecutively. The 60% aqueous MeOH eluted fraction was subjected to preparative silica gel TLC and HPLC (75% aqueous MeOH, flow rate 7.5 ml/min, RT 22.5 min) to give 96.3 mg of **2**. From fraction II, **3** (10.3 mg) was purified by Sephadex LH-20 column chromatography, preparative silica gel TLC and HPLC (58% aqueous MeOH, flow rate 7.5 ml/min, RT 27.5 min), consecutively. The purity of each compound was confirmed by HPLC on a Cosmosil C-18 column (4.6×150 mm, 5 m) at a flow rate of 1.0 ml min^{-1}.

Results

Mansonone E (1)

Orange needles. Mp. 148℃, $[\alpha]_D^{22}+72.4°$ (c=1.24), UV-vis λ_{max}^{MeOH} nm (log ε): 220 (3.87), 264 (4.15), 370 (2.99), 448 (3.03). IR ν_{max} cm^{-1} (KBr): 1690, 1640, 1610, 1584. HR-EIMS *m/z* 242.0993 ($C_{15}H_{14}O_3$ requires 242.0943). EIMS *m/z* (relative intensity): 244 $[M+2]^+$ (11), 242 $[M]^+$ (32), 214 $[M\text{-}CO]^+$ (100), 199 $[M\text{-}CO\text{-}Me]^+$ (76), 186 $[M\text{-}CO\text{-}CO]^+$ (13), 171 $[M\text{-}CO\text{-}CO\text{-}Me]^+$ (42). ^1H and ^{13}C NMR: Tables 1 and 2.

Mansonone F (2)

Violet needles. Mp. 215℃, UV-vis λ_{max}^{MeOH} nm (log ε): 234 (4.48), 255 (sh), 336 (3.18), 558 (3.06). IR ν_{max} cm^{-1} (KBr): 1683, 1629, 1600, 1577. HR-EIMS *m/z* 240.0755 ($C_{15}H_{12}O_3$ requires 240.0786). EIMS *m/z* (relative intensity): 242 $[M+2]^+$ (15) 240 $[M]^+$ (38), 212 $[M\text{-}CO]^+$ (100), 197 $[M\text{-}CO\text{-}Me]^+$ (39), 184 $[M\text{-}CO\text{-}CO]^+$ (15), 169 $[M\text{-}CO\text{-}CO\text{-}Me]^+$ (40). ^1H and ^{13}C NMR: Tables 1 and 2.

Mansonone H (3)

Dark brown platelet. Mp. 162℃, $[\alpha]_D^{22}+136.5°$ (c=0.24), UV-vis λ_{max}^{MeOH} nm (log ε): 220 (3.85), 274 (3.91), 298 (3.64), 389 (4.48). UV-vis $\lambda_{max}^{MeOH+NaOH}$ nm 220, 240, 274, 283(sh), 423, 555. IR ν_{max} cm^{-1} (KBr): 3430, 1690, 1662, 1639, 1610, 1583. HR-EIMS *m/z* 258.0902 ($C_{15}H_{14}O_4$ requires 258.0892). EIMS *m/z* (relative intensity): 260 $[M+2]^+$ (24), 258 $[M]^+$ (28), 243 $[M\text{-}Me]^+$ (54), 230 $[M\text{-}CO]^+$ (100), 215 $[M\text{-}CO\text{-}Me]^+$ (56), 202 $[M\text{-}CO\text{-}CO]^+$ (20), 187 $[M\text{-}CO\text{-}CO\text{-}Me]^+$ (16). ^1H and ^{13}C NMR: Tables 1 and 2.

Discussion

Mansonones E(**1**), F(**2**) and H(**3**) showed close similarities in their physico-chemical properties. The quinoid nature of these compounds was indicated by the carbonyl absorptions (1680-1690 cm^{-1}) in their IR spectra and

Table 1. ^{1}H NMR spectral data of compound 1-3*

H	1	2	3
2	4.23 (1H, *dd*, 10.7, 5.1) 4.41 (1H, *dd*, 10.7, 3.9)	7.08 (1H, *d*, 1.2)	4.28 (1H, *dd*, 10.3, 3.5) 4.40 (1H, *brd*, 10.3)
3	3.10 (1H, *m*)		3.21 (1H, *m*)
4	7.35 (1H, *d*, 7.8)	7.47 (1H, *d*, 8.3)	
5	7.25 (1H, *d*, 7.8)	7.41 (1H, *d*, 8.3)	6.33 (1H, *s*)
3-Me	1.37 (3H, *d*, 6.8)	2.11 (3H, *d*, 1.2)	1.24 (3H, *d*, 7.3)
6-Me	2.63 (3H, *s*)	2.70 (3H, *s*)	2.48 (3H, *s*)
9-Me	1.94 (3H, *s*)	1.97 (3H, *s*)	1.85 (3H, *s*)

*Recorded in $CDCl_3$ (**1**,**2**) and CD_3OD (**3**), chemical shift values are reported as δ (ppm) from TMS at 600.05 MHz; number of protons, signal multiplicity and coupling constants (Hz) are shown in parentheses; *s*: singlet, *d*: doublet, *brd*: broad doublet, *dd*: doublet of doublet, *m*: multiplet.

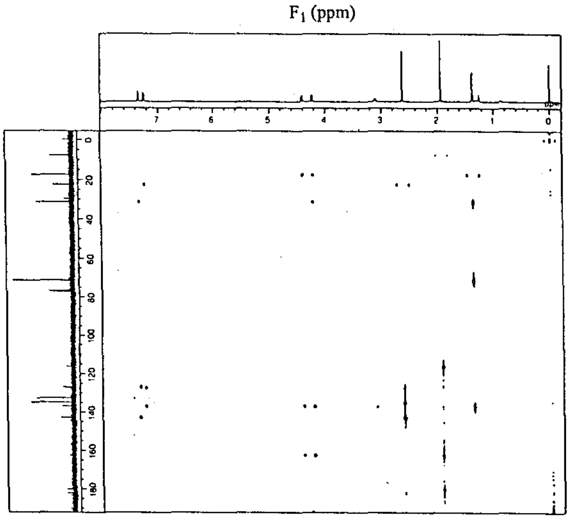

Fig. 1. PFG-HMBC spectrum of mansonone E. The spectrum was recorded on a JEOL α-600 NMR spectrometer operating at 600.05 MHz (^{1}H)/150.80 MHz (^{13}C) in $CDCl_3$. All measuring conditions are given in Materials and Methods.

the appearance of relatively intense $[M+2]^+$ ion peaks in the EIMS spectra, which is characteristic of *ortho*-naphthoquinone but not that of *para*-naphthoquinone.[11]

The molecular formula of **1** was determined to be $C_{15}H_{14}O_3$ on the basis of HR-EIMS (*m/z* $[M]^+$ 256.0751) and ^{13}C NMR data. Its ^{1}H NMR spectrum showed eight signals as shown in Table 1. Two aromatic protons at δ 7.25 and 7.35 were mutually *ortho*-coupled ($J=7.8$ Hz). The presence of the group $-CH(CH_3)-CH_2-O-$ is argued from the methylene protons at δ 4.23 and 4.41 and a methine proton at δ 3.10 which evidently coupled with the alipathic methyl doublet at δ 1.37. The strongly deshielded aromatic methyl signal appeared as singlet at δ 2.63 indicating its *peri* position to the quinone carbonyl.

The ^{13}C NMR spectrum of **1** showed fifteen carbons having two carbonyl carbons of quinone resonating at δ 180.2 and 182.2. By the aid of PFG-HMQC spectrum, all protonated carbons were assigned as shown in Table 2. It was revealed that the carbon at δ 71.4 is an oxymethylene carbon and the methine proton at δ 3.10 directly linked to the carbon at δ 31.3. From the chemical shift, the carbon at δ 162.4 was considered as an sp^2 quaternary carbon to which an oxygen atom is directly linked.

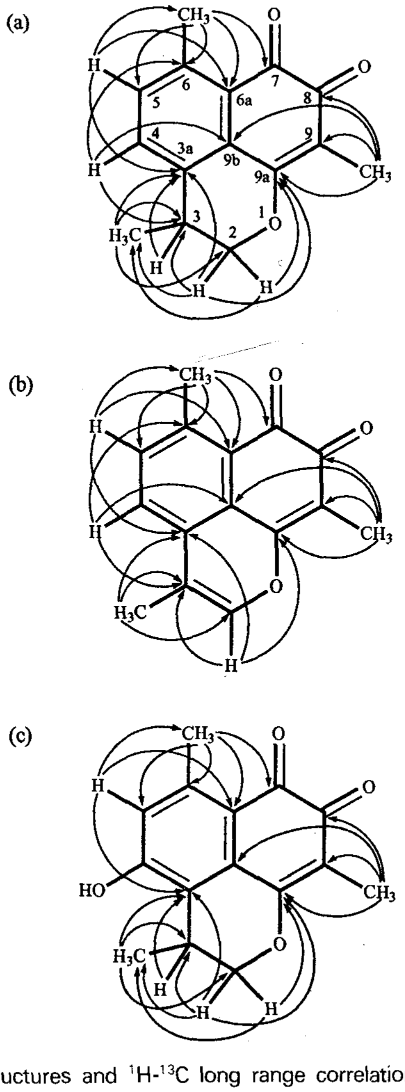

Fig. 2. Structures and ^{1}H-^{13}C long range correlations of mansonones E(a), F(b) and H(c) observed in their PFG-HMBC spectra. Arrows indicate the ^{1}H-^{13}C long range correlations.

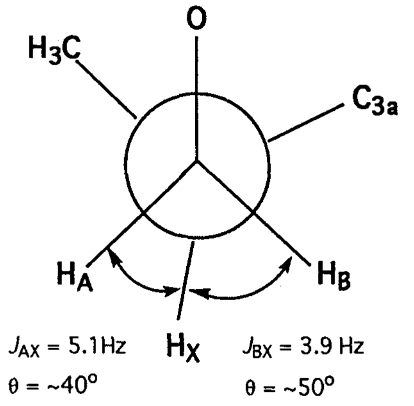

Fig. 3. Conformation of the heterocyclic ring of mansonone E.

The complete structure of **1** was achieved from the ^1H-^{13}C long range correlations in the PFG-HMBC spectrum (Fig. 1). As shown in Fig. 2(a), the methyl protons at δ 1.37 (3-Me) showed three correlations within the heterocyclic ring due to the ^3J couplings with C-2 (δ 71.4) and C-3a (δ 136.9), and the ^2J coupling with C-3 (δ 31.3). The ^1H-^{13}C long range correlations from the olefinic methine protons (δ 4.23 and 4.41) to C-9a (δ 162.4) indicated the presence of an ether bond between C-2 and C-9a. The aromatic proton at δ 7.35 (H-4) showed long range correlations to C-6 (δ 142.8), C-9b (δ 126.8) and C-3 (δ 31.3). The other aromatic proton at δ 7.25 (H-5) was coupled to the quaternary carbons at δ 136.9 (C-3a) and δ 127.3 (C-6a), and to the methyl carbon at δ 22.5 (6-Me). The ^4J coupling from the methyl protons at δ 2.63 (6-Me) to C-7 (δ 182.2) proved the *peri* relationship between this methyl group and the carbonyl group. The remaining methyl protons at δ 1.94 displayed long range correlations to C-9a, C-9b and the carbonyl carbon at δ 180.2 (C-8). From these observations, the chemical shift assignments of four quaternary carbons, C-3a, C-6a, C-9a and C-9b, were established. Although the connectivity between two carbonyl carbons (C-7 and C-8) could not be proved, its *o*-quinone structure has been suggested by the physico-chemical properties. Therefore, the structure of **1** was established as 2,3-dihydro-3,6,9-trimethylnaphtho(1,8-*b,c*)pyran-7,8-dione, which has been known as mansonone E.[12)]

The optical activity ($[\alpha]_D$ +72.4°) and ^1H NMR data of **1** indicated that the methyl group (3-Me) attached to the asymmetric carbon (C-3) is an *quasi* axial position, because the signal of methylene group in the heterocyclic ring appeared as doublet of doublet at δ 4.23 (J_{AB}=10.7 Hz, J_{AX}=5.1 Hz) and 4.41 (J_{AB}=10.7 Hz, J_{BX}=3.9 Hz). From these coupling constants, the dihedral angles were calculated about 40°($\phi_{H_XH_A}$) and 50°($\phi_{H_XH_B}$) by Karplus equation ($J_{HH'}=8.5\cos^2\theta-2.8$)[13)] (Fig. 3).

The molecular formula of **2** was determined as $C_{15}H_{12}O_3$ by the HR-EIMS [*m/z* 240.0775 (M^+)] and ^{13}C NMR

Table 2. ^{13}C NMR spectral data of 1-3*

C	1	2**	3**
2	71.4	140.4	73.8
3	31.3	112.1	27.5
3a	136.9	129.5	118.9
4	132.6	128.4	156.0
5	134.9	136.4	121.8
6	142.8	146.6	148.3
6a	127.3	126.3	129.2
7	182.2	182.0	183.2
8	180.2	178.0	180.2
9	116.8	113.4	114.8
9a	162.4	161.7	165.6
9b	126.8	124.0	129.4
3-Me	17.5	12.6	17.4
6-Me	22.5	23.2	23.8
9-Me	7.8	7.7	7.9

*Recorded in $CDCl_3$ (**1**,**2**) and CD_3OD (**3**), chemical shift values are given as δ (ppm) from TMS at 150.8 MHz; **Assignments are differnet from those in the literature.[15] All carbons were assigned with the aid of PFG-HMQC and PFG-HMBC experiments whose measuring conditions are stated in Materials and Methods.

data. Its ^1H NMR spectrum was very similar to that of **1**. However, it was mainly differed in the heterocyclic ring region (Table 1). The olefinic methine proton at δ 7.09 and the methyl protons at δ 2.11 appeared as doublet (J=1.2 Hz) due to their allylic coupling. The high chemical shift value of this allylic coupled olefinic methin proton suggested the presence of the fragment -C(CH_3)=CH-O-, which must be a part of heterocyclic ring.

Its ^{13}C NMR and PFG-HMQC spectra also showed some similarities to those of **1**; fifteen carbons including three methyl carbons (δ 7.7, 12.6 and 23.2), two aromatic carbons (δ 128.4 and 136.4) and two carbonyl carbons (δ 178.0 and 182.0). The carbon at δ 140.4 was assigned to be an olefinic methine carbon to which the proton at δ 7.08 attached.

The long range correlations observed from the PFG-HMBC spectrum were almost the same as those of **1** [Fig. 2(b)]. However, only the correlations in the heterocyclic ring region showed some difference. The doublet methyl protons at δ 2.11 (3-Me) coupled to C-3 (δ 111.2), C-3a (δ 129.5) and C-2 (δ 140.4), and the methine proton at δ 7.08 (H-2) showed ^2J and ^3J couplings with C-3, C-3a, C-9a and methyl carbons of 3-Me. All of these observations led to the conclusion that the structure of **2** is 3,6,9-trimethylnaphtho(1,8-*b,c*)pyran-7,8-dione, which has been known as mansonone F.[12)]

Compound **3** showed the $[M]^+$ ion at *m/z* 228.0902 in the HR-EIMS spectrum, which corresponds to the empirical formula of $C_{15}H_{14}O_4$. It exhibited the characteristic IR absorption of hydroxyl group at 3430 cm^{-1}. The bathochromic shift of UV-vis spectrum on adding NaOH suggested that this hydroxyl group is phenolic.

When compared with **1**, its ^{1}H and ^{13}C NMR spectra were only differed in the aromatic region. Only an aromatic proton signal was observed as singlet at δ 6.33 in the ^{1}H NMR spectrum of **3**. This fact suggested that one of two *ortho*-coupled aromatic protons was substituted by the phenolic hydroxyl group. This was confirmed by the ^{13}C signal at δ 156.0 which is considered as the chemical shift of hydroxyl group attached aromatic carbon. Because of the β-effect of hydroxyl group, C-3a and C-5 appeared with up-field shift to δ 118.9 and 121.8, respectively. The long range correlations in the PFG-HMBC spectrum [Fig. 2(c)], from the protons at δ 1.24 (3-Me) to C-4 (δ 156.0), and from the aromatic proton at δ 6.33 to C-3a, C-6a and methyl carbon at δ 23.8 (6-Me) confirmed the position of hydroxyl group in C-4. Therefore, the structure of **3** was determined to be 2,3-dihydro-4-hydroxy-3,6,9-trimethylnaphtho(1,8-*b,c*)pyran-7,8-dione, which has been known as mansonone H.14)

When compared with the literature,15) however, the carbon assignments of C-3a, C-6a, and C-9b of **1** and **2**, which have been made with the aid of DEPT experiments, were not compatible with our data obtained by the PFG-HMBC spectra in the same solvent. They have been reported as δ 126.90, 136.85 and 127.40 in mansonone E(**1**) and δ 123.91, 129.45 and 126.25 in mansonone F(**2**), respectively. Thus, we correct these mismatched carbon chemical shifts as shown in Table 2.

Mansonones, a group of sesquiterpene *o*-naphthoquinones,16) have originally been isolated from the West African tree *Mansonia altissima* Chev12,14,17-20) and several plant species.15,21-24) Mansonones E and F also have been observed to accumulate in the sapwood of *Ulmus americana* and other elm species in response to infection by *Ceratocystis ulmi*, or other stresses.25-27) However, these compounds have never been isolated from *Ulmus davidiana*. Especially, mansonone H has been isolated only from *Mansonia altissima* Chev16) and *Helicters angustifolia*.15)

References

1. Cho, M. Y. (1989) In 'Colored Illustrations of Plants of Korea', pp. 107-109, Academy press, Seoul, Korea.
2. Lee, C. B. (1985) In 'Korea Encyclopedia of Plants', pp. 280-281, Hyangmoonsa, Seoul, Korea.
3. Shanghai Science and Technological Publisher. (1985) In 'The Dictionary of Chinese Drugs', Vol. 4, p. 2771. Shougakukan, Tokyo.
4. Lee, S. J. (1966) In 'Korean Folk Medicine', Monographs Series No. 3, p. 39, Publishing center of Seoul National University, Seoul, Korea.
5. Lee, I. K., C. J. Kim, K. S. Song, H. M. Kim and I. D. Yoo (1995) Two more benzylated dihydroflavonols from *Cudrania triscuspidata*. *J. Natural Products* **58**, 1614-1617.
6. Lee, I. K., C. J. Kim, K. S. Song and I. D. Yoo (1996) Cytotoxic benzyl dihydroflavonols from *Cudrania triscuspidata*. *Phytochemistry* **41**, 213-216.
7. Son, B. H., J. H. Park and O. P. Zee (1989) Catechin glycoside from *Ulmus davidiana*. *Arch. Pharm. Res.* **12**, 219-222.
8. Hurd, R. E. and B. K. John (1991) Gradient-enhanced proton detected heteronuclear multiple-quantum coherence spectroscopy. *J. Magn. Reson.* **91**, 648-653.
9. Tyburn, J. M., I. M. Brereton and D. M. Doddrell (1992) Coherence selection in gradient-enhanced, heteronuclear correlation spectroscopy. *J. Magn. Reson.* **97**, 305-312.
10. Willker, W., D. Leibfritz, R. Kerssebaum and W. Bermel (1993) Gradient selection in inverse heteronuclear correlation spectroscopy. *J. Magn. Reson. Chem.* **31**, 287-292.
11. Oliver, R. W. A. and R. M. Rashman (1971) Mass spectrometry of quinones. Part II. A study of the distinguishing features found in the mass spectra of 1,2- and 1,4-naphthaquinones. *J. Chem. Soc. (B)*, 341-344.
12. Marini-Bettòlo, G. B. M., C. G. Casinovi and C. Galeffi (1965) A new class of quinones: Sesquiterpenoid quinones of *Mansonia altissima* Chev. *Tetrahedron Letters* **52**, 4857-4864.
13. Karplus, M. (1959) Contact electro-spin coupling of nuclear magnetic moments. *J. Chem. Phys.* **30**, 11-15.
14. Tanaka, N., M. Yasue and H. Imamura (1966) The quinoid pigments of *Mansonia altissima* wood. *Tetrahedron Letters* **24**, 2767-2773.
15. Chen, C. M., Z. T. Chen and Y. L. Hong (1990) A mansonone from *Helicters angustifolia*. *Phytochemistry* **29**, 980-982.
16. Thomson, R. H. (1987) Naphthoquinones, In 'Naturally Occurring Quinones III: recent advances', pp. 127-343, Chapman and Hall, New York, USA.
17. Shimada, K., M. Yasue and H. Imamura (1967) The structure of Mansonone I, a new pigment from *Mansonia altissima*. *J. Japan Wood Res. Soc.* **13**, 126.
18. Marini-Bettòllo, G. B., C. G. Casinovi, C. Galeffi and F. D Monache (1966) Sui chinoni sesquiterpenici della *Mansonia altissima* Chev. *Ann. Ist. Super. Sanita* **2**, 327-341.
19. Galeffi, C., C. G. Casinovi, E. Miranda delle Monache and G. B. Marini Bettòlo (1968) Chinoni sesquiterpenici della *Mansonia altissima* Chev. ~Nota II. *Ann. Ist Super. Sanita* **4**, 305-316.
20. Galeffi, C., E. Miranda delle Monache, C. G. Casinovi and G. B. Marini Bettòllo (1969) A new quinone from the heartwood of *Mansonia altissima* Chev: mansonone L. *Tetrahedron Letters* **40**, 3583-3584.
21. Ali, S., P. Singh and R. H. Thomson (1980) Naturally occurring quinones. Part 28. Sesquiterpenoid quinones and related compounds from *Hibiscus tiliaceus*. *J. C. S. Perkin Trans I*, 257-259.
22. Neelakantan, S., V. Rajagopalan and P. V. Raman (1983) Thespesone and thespone, two new mansonones of heartwood of *Thespesia populnea* Sol. ex Corr. (Fam. Malvaceae).

Indian J. Chem. **22B**, 95-96.

23. Letcher, Roy M. and I. M. Shirley (1992) *o*-Naphthoquinones from the heartwood of *Azanza garkeana*. *Phytochemistry* **31**, 4171-4172.
24. Ogihara, K., J. Zhao, M. Higa and S. Yogi (1992) Studies on the constituents of *Aristolochia liukiuensis* II. *Bull. Coll. Sci. Univ. Ryukus* **54**, 17-28.
25. Overeem, J. C. and D. M. Elgersma (1970) Accumulation of mansonones E and F in *Ulmus hollandica* infected with *Ceratocystis ulmi*. *Phytochemistry* **9**, 1949-1952.
26. Elgersma, D. M. and J. C. Overeem (1971) The relation of mansonones to resistance against Dutch elm disease and their accumulation, as induced by several agents. *Neth. J. Plant Pathol.* **77**, 168-174.
27. Dumas, M. T., G. M. Strunz, M. Hubbes and R. S. Jeng (1983) Isolation and identification of six mansonones from *Ulmus americana* infected with *Ceratocystis ulmi*. *Experientia* **39**, 1089-1091.

당느릅나무로부터 Sesquiterpene *o*-Naphthoquinone류 화합물, Mansonone E, F 및 H의 분리와 구조 결정

김종평,[1] 김원곤,[1] Hiroyuki Koshino,[2] 박종희,[3] 정 진,[4] 유익동[1]* ([1]한국과학기술연구원 생명공학연구소, [2]일본 이화학연구소, [3]부산대학교 약학대학, [4]서울대학교 농화학과)

초록 : 한방에서 종기, 치질, 위암 및 염증의 치료목적으로 사용되어온 당느릅나무 (*Ulmus davidiana* Planch) 근피의 메탄올 추출물로부터 sesquiterpene *o*-naphthoquinone류 화합물 세가지를 분리 정제하였다. 이들의 구조를 UV-vis, IR, EIMS, HR-EIMS 및 여러 가지 NMR 스펙트럼, 특히 새로운 기법인 pulse field gradient (PFG)-HMQC 및 HMBC 스펙트럼의 분석에 의하여 결정하였다. 그 결과 이들은 2,3-dihydro-3,6,9-trimethylnaphtho(1,8-*b*,*c*)pyran-7,8-dione, 3,6,9-trimethylnaphtho(1,8-*b*,*c*)pyran-7,8-dione 및 2,3-dihydro-4-hydroxy-3,6,9-trimethylnaphtho(1,8-*b*,*c*)pyran-7,8-dione으로 동정되었으며, 각각 mansonone E, F 및 H로 밝혀졌다. 이 화합물들은 당느릅나무에서는 처음 분리되었으며, 특히 mansonone H는 아프리카 열대식물인 *Mansonia altissima* Chev 및 *Helicters angustifolia*에서 분리된 후 자연계에서 처음으로 분리되었다. 문헌에 잘못 보고된 mansonone E 와 F의 C-3a, C-6a 및 C-9b의 세 사급탄소의 chemical shift를 최신 PFG-NMR기법에 의하여 동정하여 교정하였다.

---

*연락저자