Lignans from the Bark of *Magnolia kobus*

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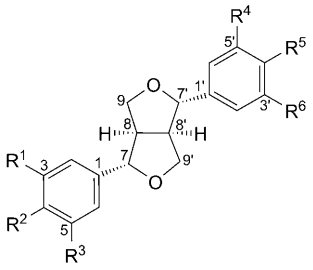
The Et_2O-soluble fraction from the bark of *Magnolia kobus* led to the isolation of two new lignans, (+)-(7α,7′α,8α,8′α)-3′,4,4′,5,5′-pentamethoxy-7,9′:7′,9-diepoxylignan-3-ol (**1**) and (+)-(7α,7′α,8α,8′α)-4,5-dimethoxy-3′,4′-(methylenedioxy)-7,9′:7′,9-diepoxylignan-3-ol (**2**), along with five known lignans **3**–**7**. Their structures were established on the basis of various spectroscopic analyses including 1D- (^{1}H, ^{13}C, and DEPT) and 2D-NMR (COSY, NOESY, HMQC, and HMBC) and by comparison of their spectral data with those of related compounds.

Introduction. – *Magnolia kobus* DC belongs to the Magnoliaceae family. It is a medium-sized deciduous tree native to Japan also found in China and Korea [1]. It is a valuable decorative plant in Japan and is known under the local name Kobusi. Young buds of *M. kobus* are important ingredients in the Chinese medicine 'Shin-I' which is used as a sedative or an analgesic. In Japan, 'Shin-I' is taken internally for the treatment of headaches or colds [2]. Earlier chemical studies on *M. kobus* revealed it to be a source of bioactive terpenes and lignans [3–6]. Lignans have evoked a great deal of interest due to their widespread occurrence in nature [7–9] and use in traditional medicines [10][11]. Furofuran lignan, one of the major subclasses of the lignan family, exhibit a wide variety of biological activities including antitumor, antimitomic, antiviral [12], antioxidant, antihypertensive [13][14], and antidiabetic activity [15], and inhibition of the platelet-activating factor (PAF) [16].

In the present study, two new furofuran lignans, (+)-(7α,7′α,8α,8′α)-3′,4,4′,5,5′-pentamethoxy-7,9′:7′,9-diepoxylignan-3-ol (**1**) and (+)-(7α,7′α,8α,8′α)-4,5-dimethoxy-3′,4′-(methylenedioxy)-7,9′:7′,9-diepoxylignan-3-ol (**2**), along with five known compounds, (+)-sesamin (**3**), (+)-yangambin (**4**), (+)-kobusin (**5**), (+)-eudesmin (**6**), and (+)-magnolin (**7**), were isolated from the bark of *M. kobus* (*Fig. 1*). Their structures were established on the basis of various spectroscopic analyses including 1D- (^{1}H, ^{13}C, and DEPT) and 2D-NMR (COSY, NOESY, HMQC, and HMBC) and by comparison of their spectral data with those of related compounds.

Results and Discussion. – Extensive chromatographic separation and purification of the Et_2O-soluble fraction from the EtOH extract of *M. kobus* bark led to the isolation of the two new furofuran lignans **1** and **2**, along with the five known lignans **3**–**7**.

Compound **1** was obtained as white crystals and displayed a molecular-ion peak at *m*/*z* 432 (M^+) in the EI-MS. Its molecular formula could be determined as $C_{23}H_{28}O_8$ by



	R^1	R^2	R^3	R^4	R^5	R^6
1	OH	MeO	MeO	MeO	MeO	MeO
2	OH	MeO	MeO	H	O–CH_2–O	
3	O–CH_2–O		H	H	O–CH_2–O	
4	MeO	MeO	MeO	MeO	MeO	MeO
5	O–CH_2–O		H	H	MeO	MeO
6	MeO	MeO	H	H	MeO	MeO
7	MeO	MeO	MeO	H	MeO	MeO

Fig. 1. *Compounds* **1**–**7**, *isolated from the bark of* M. kobus

its HR-EI-MS peak at *m*/*z* 432.1459 (M^+). The ^{1}H- and ^{13}C-NMR signals of **1** (*Table*) were assigned by the interpretation of the DEPT, COSY, NOESY (*Fig. 2*), HMQC, and HMBC data (*Fig. 2*). On the basis of these spectroscopic evidences and of comparison with lignans of the furofuran type [17–21] and of the (+)-sesamin type [18][22][23], **1** was characterized as (+)-(7α,7′α,8α,8′α)-3′,4,4′,5,5′-pentamethoxy-7,9′:7′,9-diepoxylignan-3-ol, *i.e.*, with (7*S*,7′*S*,8*R*,8′*R*) configuration (*Fig. 1*).

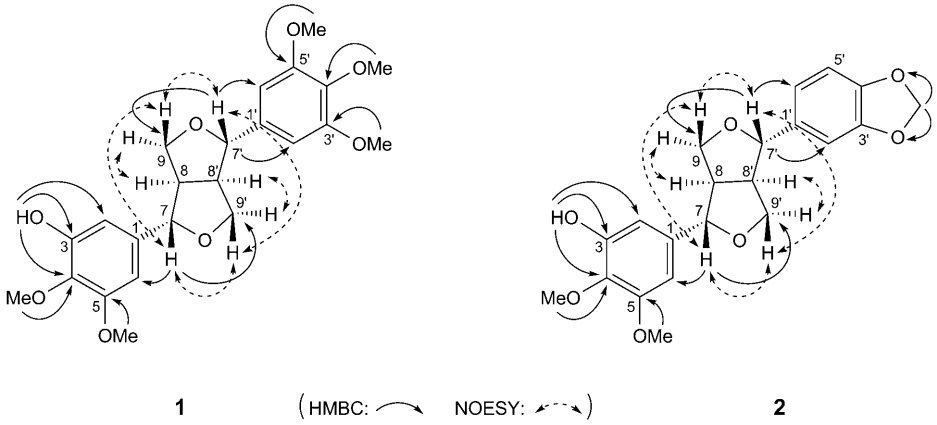


Fig. 2. *Key NOE and HMBC of compounds* **1** *and* **2**

The ^{13}C-NMR spectrum of **1** showed the signals for 23 C-atoms which were distinguished by DEPT experiments as five Me, two CH_2, and eight CH groups, and eight quaternary C-atoms. The ^{1}H-NMR spectrum of **1** showed signals for two CH groups at δ(H) 3.07–3.15 (*m*, 2 H), two benzylic OCH moieties at δ(H) 4.73 (*d*, *J* = 4.5 Hz, 1 H) and 4.75 (*d*, *J* = 4.5 Hz, 1 H), two oxygenated CH_2 groups at δ(H) 4.27–4.35 (*m*, 2 H) and 3.91–3.94 (*m*, 2 H), and two 1,3,4,5-tetrasubstituted benzene rings at δ(H) 6.53 (*d*, *J* = 2.0 Hz, 1 H) and 6.59 (*s*, 3 H), which were assigned to a lignan of the furofuran type by comparison with data reported previously [17][18]. This observation was further confirmed by the corresponding ^{13}C-NMR signals at δ(C) 54.08 and 54.31 (2 CH), 85.60 and 85.99 (2 benzylic OCH), at 71.73 and 72.15 (2 oxygenated CH_2), 134.84, 136.71, 137.32, 137.45, 149.31, 152.50, and 153.39 (8 aromatic C), and 101.67, 102.81, 105.46 (4 aromatic CH), as established by DEPT and ^{1}H, ^{13}C one-bond (HMQC) experiments. The ^{1}H-NMR spectrum showed the signals for a OH group at δ(H) 5.86 (br. *s*) and five MeO groups at δ(H) 3.84, 3.88, and 3.90 (3*s*), all being substituents at benzene rings. The ^{1}H- and ^{13}C-NMR data of **1** was

Table. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$; 500 and 125 MHz, resp.) *of Compounds* **1**–**2**. δ in ppm, J in Hz.

Position	**1**		**2**	
	δ(C)	δ(H)	δ(C)	δ(H)
C(1)	137.32	–	137.41	–
H–C(2)	105.46	6.59 (*s*)	105.48	6.57 (*d*, *J* = 1.5)
C(3)	149.31	–	149.31	–
C(4)	134.84	–	134.83	–
C(5)	152.50	–	152.50	–
H–C(6)	101.67	6.53 (*d*, *J* = 2.0)	101.66	6.50 (*d*, *J* = 1.5)
H–C(7)	85.99	4.75 (*d*, *J* = 4.5)	85.77	4.72 (*d*, *J* = 3.0)
H–C(8)	54.08	3.07–3.15 (*m*)	54.26	3.06–3.11 (*m*)
CH_2(9)	72.15	4.27–4.35 (*m*), 3.91–3.94 (*m*)	71.74	4.25–4.30 (*m*), 3.90–3.92 (*m*)
C(1′)	136.71	–	135.00	–
H–C(2′)	102.81	6.59 (*s*)	106.48	6.86 (*s*)
C(3′)	153.39	–	147.95	–
C(4′)	137.45	–	147.10	–
C(5′) or H–C(5′)	153.39	–	108.16	6.80 (*d*, *J* = 8.0)
H–C(6′)	102.81	6.59 (*s*)	119.35	6.82 (*d*, *J* = 8.0)
H–C(7′)	85.60	4.73 (*d*, *J* = 4.5)	85.66	4.71 (*d*, *J* = 3.0)
H–C(8′)	54.31	3.07–3.15 (*m*)	54.16	3.06–3.11 (*m*)
CH_2(9′)	71.73	4.27–4.35 (*m*), 3.91–3.94 (*m*)	71.91	4.25–4.30 (*m*), 3.90–3.92 (*m*)
OCH_2O	–	–	101.04	5.96 (*s*)
OH–C(3)	–	5.86 (br. *s*)	–	5.84 (*s*)
MeO–C(4)	60.91	3.90 (*s*)	60.92	3.89 (*s*)
*Me*O–C(5)	55.89	3.88 (*s*)	55.89	3.88 (*s*)
*Me*O–C(3′)	56.15	3.88 (*s*)	–	–
*Me*O–C(4′)	60.80	3.84 (*s*)	–	–
*Me*O–C(5′)	56.15	3.88 (*s*)	–	–

very similar to that of (+)-yangambin (**4**) which was also isolated and characterized in the present study. The presence of an OH group at C(3) of **1** instead of an MeO group in **4** was confirmed by the 2D-NMR data, *i.e.*, by the HMBCs δ(H) 5.86 (br. *s*, OH)/C(3), C(2) and C(4) (*Fig. 2*). The equivalence of the δ(H) of H–C(7) and H–C(7′), H–C(8) and H–C(8′), and H–C(9) and H–C(9′) required a symmetrical relative configuration for the aryl substituents [18][19] which could be either axial,axial or equatorial,equatorial. The equatorial,equatorial position of the aryl substituents was assigned on the basis of the following features of the ^{1}H- and ^{13}C-NMR spectra [18–21]: *i*) The chemical shifts of the fusion sites C(8) and C(8′) of **1** were δ(C) 54.08 and 54.31, respectively, while for furofuran lignans with diaxial aryl substituents, C(8) and C(8′) appear more upfield (δ(C) 49.0–49.5). *ii*) The chemical shifts of CH_2(9) and CH_2(9′) of **1** were δ(H) 4.27–4.35 (*m*, 2 H, H_α), and at 3.91–3.94 (*m*, 2 H, H_β), while these protons appear more upfield at δ(H) 3.65–4.0 (*m*, 2 H, H_α) and 3.30–3.65 (*m*, 2 H, H_β) if the aryl substituents are axial. *iii*) Small coupling constants were observed for H–C(7) and H–C(7′) (J = 4.5 Hz) of **1**. This observation was further confirmed by the NOEs H_{ax}–C(7′)/H_{ax}–C(9) and H_{ax}–C(9′) and H_{ax}–C(7)/H_{ax}–C(9) and H_{ax}–C(9′) (*Fig. 2*) confirming that the aryl substituents are diequatorial. According to *Freudenberg* and *Sidhu* [22], all sesamin-type lignans with a positive $[\alpha]_D$ have the same absolute configuration (*R*) at the fusion sites C(8) and C(8′). Hence, **1** with an $[\alpha]_D$ of +42.6 should have (8*R*,8′*R*)-configuration. Moreover, the aryl substituents of **1** being diequatorial and $[\alpha]$ being positive, the (7*S*,7′*S*)-configuration of **1** is confirmed. Indeed all (+)-(8*R*,8′*R*)-sesamin type-lignans with diequatorial aryl substitution belong to the same series with the absolute configuration (*S*) at the benzylic C(7) and C(7′) atoms [18][23].

Compound **2** was obtained as white crystals and exhibited a molecular-ion peak at *m/z* 386 (M^+) in the EI-MS. Its molecular formula could be established as $C_{21}H_{22}O_7$ from the HR-EI-MS peak at *m/z* 386.1374 (M^+). Most of the ^{1}H- and ^{13}C-NMR signals (*Table*) of **2** were similar to those of **1**. On the basis of dextrorotatory nature and relative configuration, the absolute configuration of **2** must be the same as that of **1** [18–20][22][23]. Therefore, the structure of **2** was established as (+)-(7α,7′α,8α,8′α)-4,5-dimethoxy-3′,4′-(methylenedioxy)-7,9′:7′,9-diepoxylignan-3-ol with (7*S*,7′*S*,8*R*,8′*R*) configuration (*Fig. 1*).

The ^{1}H-NMR signal of **2** at δ(H) 5.96 (*s*, 2 H) and its corresponding ^{13}C-NMR signal at δ(C) 101.04, established from an HMQC experiment, suggested a OCH_2O group in the molecule. The major changes observed in the ^{1}H- and ^{13}C-NMR spectra of **2** as compared to **1** are: *i*) appearance of an extra CH signal at δ(H) 6.80 (*d*, *J* = 7.5 Hz, H–C(5′)); *ii*) more downfield shifted signals for H–C(6′) and H–C(2′ (δ(H) 6.82 (*d*, *J* = 8.5 Hz) and 6.86 (*s*, resp.) and for C(6′) and C(2′) (δ(C) 119.35 and 106.48, resp.); *iii*) downfield and upfield shifted quaternary C-atom signals (δ(C) 147.10 (C(4′)) and 147.95 (C(3′)). The OCH_2O group was located at C(3′) and C(4′) based on the HMBC δ(H) 5.96 (*s*, OCH_2O)/C(3′) and C(4′) (*Fig. 2*). The $[\alpha]_D$ of **2** was positive, and the relative configuration of the two aryl substituents were established as equatorial,equatorial on the basis of spectral features similar to those of **1**.

The known compounds **3**–**7** (*Fig. 1*) were identified by comparison of their spectral data with literature values as follows: (+)-sesamin (**3**) [5][24], (+)-yangambin (**4**) [23][25], (+)-kobusin (**5**) [5][19], (+)-eudesmin (**6**) [5][19], and (+)-magnolin (**7**) [17][26].

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Experimental Part

General. TLC: precoated silica gel *60 F_{254}* (SiO_2, 0.2 mm; *Merck*) plates; developed with solvent system *A*, toluene/HCOOEt/HCOOH 5 : 4 : 1 and 7 : 2 : 1 (*v/v/v*) and visualized under UV light at 254 and 365 nm, resp. Column chromatography (CC): SiO_2 *60* (40–100 μm; *Kanto Chemical Co.*); *Adventec-SF-1600* automated fraction collector. M.p.: *Electrothermal-IA-9200* melting point apparatus (*Electrothermal Engg. Ltd.*, U. K.). Optical rotations: *Jasco-P-1020* polarimeter. UV Spectra: *Hewlett-Packard-8452A* diode-array spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Nexus-FT-IR* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Varian-Unity-Inova-500* spectrophotometer; at 500 (^{1}H) and 125 MHz (^{13}C); in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI and HR-EI-MS: *Jeol-JMS-SX102A* spectrophotometer; in *m/z* (rel. %).

Plant Material. The bark of *M. kobus* was collected from the experimental forest of the Southern Forest Research Center, Kyungnam, Korea, in June 2001, and identified by Dr. *Y. H. Kwon* (Korea National Arboretum, Pocheon, Korea). A voucher specimen was deposited with the Korea Forest Research Institute, Seoul, Korea.

Extraction and Isolation. Shade air-dried and powdered barks (12.0 kg) of *M. kobus* were extracted three times with 95% EtOH at r.t. for 72 h each. The combined EtOH extracts were concentrated under vacuum at 40° until EtOH was completely removed. The concentrated EtOH extract was dissolved in dist. H_2O and successively partitioned with petroleum ether, Et_2O, and AcOEt. The Et_2O-soluble fraction (85.0 g) was subjected to CC (*Sephadex LH-20*, MeOH/EtOH 3 : 7): *Fractions 1* and *2*. *Fr. 2* was subjected to CC (SiO_2, benzene/AcOEt 8 : 1): *Frs. 2.1–2.8*. *Fr. 2.2* gave pure **3** (500 mg). *Fr. 2.3* (2.52 g) was subjected to CC(SiO_2, $CHCl_3$/MeOH 20 : 1: *Fr. 2.3.1–2.3.5*. *Fr. 2.3.4* (758.9 mg) was subjected to two repeated CC (SiO_2, $CHCl_3$/MeOH 100 : 1): pure **2** (24 mg). *Frs. 2.4* and *2.5* were subjected separately to CC (SiO_2, hexane/AcOEt 2 : 1); *Sephadex*, MeOH: pure **5** (1.25 g) and **6** (120 mg), resp. *Fr. 2.6* (20.1 g)

was subjected to CC (SiO_2, hexane/AcOEt 2:1): *Frs. 2.6.1–2.6.3*. *Fr. 2.6.3* (15.3 g) was again subjected to CC (*Sephadex LH-20*, EtOH): *Frs. 2.6.3.1–2.6.3.3*. *Fr. 2.6.3.1* (1.0 g) gave, on CC (SiO_2, $CHCl_3$/MeOH 100:1), *Frs. 2.6.3.1.1–2.6.3.1.6*. *Frs. 2.6.3.1.4* (240 mg), *2.6.3.1.5* (250 mg), and *2.6.3.1.6* (200 mg) were separately subjected to CC (SiO_2, $CHCl_3$/MeOH 80:1): pure **7** (30 mg), **4** (25 mg), and **1** (16 mg), resp.

(+)-(7α,7′α,8α,8′α)-3′,4,4′,5,5′-Pentamethoxy-7,9′:7′,9-diepoxylignan-3-ol (=*2,3-Dimethoxy-5-{(1*S*,3a*R*,4*S*,6a*R*)-tetrahydro-4-(3,4,5-trimethoxyphenyl)-1*H*,3*H*-furo[3,4-*c*]furan-1-yl}phenol*; **1**): White crystals. M.p. 116–118°. $[\alpha]_D^{20.4} = +42.6$ ($c = 0.10$, $CHCl_3$). UV ($CHCl_3$): 235 (3.9), 273 (3.6). IR (KBr): 3417, 2927, 2359, 1599, 1515, 1465, 1412, 1264, 1235, 1141, 1056, 1025. ^{1}H- and ^{13}C-NMR: *Table.* EI-MS: 432 (M^+, 100), 207, 195, 181, 167, 161. HR-EI-MS: 432.1459 (M^+, $C_{23}H_{28}O_8^+$; calc. 432.1784).

(+)-(7α,7′α,8α,8′α)-4,5-Dimethoxy-3′,4′-(methylenedioxy)-7,9′:7′,9-diepoxylignan-3-ol (=*5-[(1*S*,3a*R*,4*S*,6a*R*)-4-(1,3-Benzodioxol-5-yl)tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1-yl]-2,3-dimethoxyphenol*; **2**): White crystals. M.p. 129–131°. $[\alpha]_D^{20.4} = +56.2$ ($c = 0.14$, $CHCl_3$). UV ($CHCl_3$): 248 (4.1), 276 (3.7). IR (KBr): 3414, 2924, 2356, 1594, 1508, 1463, 1440, 1245, 1236, 1138, 1045, 1026. ^{1}H- and ^{13}C-NMR: *Table.* EI-MS: 386 (M^+, 100), 195, 181, 169, 161, 149, 135, 122, 83. HR-EI-MS: 386.1374 (M^+, $C_{21}H_{22}O_7^+$; calc. 386.1366).

(+)-Sesamin (**3**): White crystals. $[\alpha]_D^{20.4} = +62.0$ ($c = 0.58$, CH_2Cl_2) ([24]: $[\alpha]_D = +63.2$). EI-MS: 354 (M^+). UV, IR, ^{1}H- and ^{13}C-NMR: in agreement with [5][24].

(+)-Yangambin (**4**): White solid. $[\alpha]_D^{20.4} = +43.2$ ($c = 0.42$, $CHCl_3$) ([25]: $[\alpha]_D = +45.1$). EI-MS: 446 (M^+). UV, IR, ^{1}H- and ^{13}C-NMR: in agreement with [23][25].

(+)-Kobusin (**5**): Colorless oil. $[\alpha]_D^{20.4} = +56.8$ ($c = 0.54$, CH_2Cl_2) ([19]: $[\alpha]_D = +58.0$). EI-MS: 370 (M^+). UV, IR, ^{1}H- and ^{13}C-NMR: in agreement with [5][19].

(+)-Eudesmin (**6**): Amorphous powder. $[\alpha]_D^{20.4} = +59.9$ ($c = 0.59$, acetone) ([19]: $[\alpha]_D = +61.0$). EI-MS: 386 (M^+). UV, IR, ^{1}H- and ^{13}C-NMR: in agreement with [5][19].

(+)-Magnolin (**7**): White solid. $[\alpha]_D^{20.4} = +55.1$ ($c = 0.07$, MeOH) ([26]: $[\alpha]_D = +55.7$). EI-MS: 386 (M^+). UV, IR, ^{1}H- and ^{13}C-NMR: in agreement with [17][26].

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