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Structures of Two Natural Hypotensive Diels–Alder Type Adducts, Mulberrofurans F and G, from the Cultivated Mulberry Tree (*Morus lhou* KOIDZ.)[1,2]

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Two novel 2-arylbenzofuran derivatives named mulberrofurans F and G (=albanol A), as well as albanol B (**3**), were isolated from the ethyl acetate extract of the root bark of cultivated mulberry tree (Japanese name "Rosō," a cultivated variety of *Morus lhou* KOIDZ.). The structures of mulberrofurans F and G were shown to be **1** and **2**, respectively, on the basis of spectral and chemical evidence. Mulberrofurans F (**1**) and G (**2**) were derived from chalcomoracin (**4**) and mulberrofuran C (**5**), respectively, by photocyclization in acidic solution. The compounds (**1**, **2**, and **3**) are optically active and can be regarded biogenetically as variations of Diels–Alder type adducts of chalcone derivatives and a dehydroprenyl-2-arylbenzofuran derivative. Intravenous injection of mulberrofuran F (**1**), as well as G (**2**), caused a marked depressor effect in rabbit.

Keywords——*Morus lhou*; Moraceae; mulberry tree; mulberrofuran F; mulberrofuran G; albanol B; Diels–Alder type adduct; 2-arylbenzofuran; depressor effect

In the previous papers,[1,3–5] we reported the structure determination of a series of natural Diels–Alder type adducts and geranylated 2-arylbenzofuran derivatives from the extract of the root bark of the cultivated mulberry tree (Japanese name "Rosō"; a cultivated variety of *Morus lhou* KOIDZ.[6]). Further extensive fractionation of the extract of the root bark led to the isolation of two novel 2-arylbenzofuran derivatives, mulberrofurans F (**1**) and G (**2**=albanol A[7]), along with albanol B[7] (**3**). We report here the structure determination of these compounds.

The dried root bark of the cultivated mulberry tree was extracted successively with *n*-hexane, benzene, and ethyl acetate. The ethyl acetate extract was fractionated sequentially by silica gel column chromatography, and then by preparative thin-layer chromatography (preparative TLC), resulting in the isolation of mulberrofurans F (**1**) and G (**2**), and compound **3**. Single intravenous injection of **1** or **2** (both 0.1 mg/kg) caused a marked depressor effect in rabbits (26 and 16 mmHg, respectively).[8]

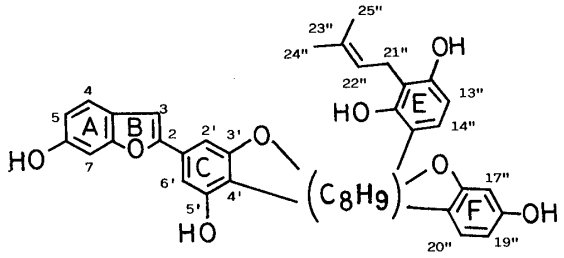
Mulberrofuran F (**1**), is a colorless amorphous powder. The field desorption mass spectrum (FD-MS) showed the molecular ion peak at *m/z* 630. The ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum indicated the presence of thirty-nine carbons: fifteen aliphatic carbons ($CH_3-\times 3$, $-CH_2-\times 2$, $>CH-\times 3$, $>C=CH-\times 2$, $-HC=C<_{O-}\times 1$, $-O-\overset{|}{C}-O-\times 1$), and twenty-four aromatic carbons (CH×10, C×6, C–O×8) (Table I). Treatment of **1** with dimethyl sulfate in acetone gave a pentamethyl ether (**1a**, M^+ 700) as an amorphous powder, the molecular formula of which was determined to be $C_{44}H_{44}O_8$ by high-resolution MS. Work-up of **1** with acetic anhydride in pyridine gave the pentaacetate (**1b**),

which showed a molecular ion peak at *m/z* 840 in its FD-MS. These results indicated the composition of mulberrofuran F to be $C_{39}H_{34}O_8$. Compound **1** was negative to the methanolic ferric chloride test, and its infrared (IR) spectrum showed absorption bands due to hydroxyl, conjugated double bond and benzene ring moieties, and indicated the absence of a carbonyl function. The ultraviolet (UV) spectrum of **1** exhibited maxima at 230, 285, 296 (sh), 306 (infl.), 321, and 335 nm, and was similar to those of chalcomoracin (**4**)[9] and mulberrofuran C (**5**),[10] suggesting that **1** is a 4′-substituted 6,3′,5′-trihydroxy-2-arylbenzofuran derivative. This was supported by a comparative examination of the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** with those of **4**,[9] **5**,[10] and other 2-arylbenzofuran

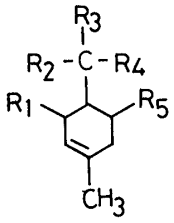
TABLE I. ^{13}C-NMR Chemical Shifts (ppm) of **1**, **2**, **3**, **4**, and **5**

Carbon No.	1	2	3	4[9]	5[10]
C-2	155.9[a]	156.7[a]	155.0	155.8[a]	155.9[a]
C-3	101.9	102.2	103.2	102.9	102.7
C-3a	121.8	122.5	122.5	121.2	121.3
C-4	121.4	122.0	122.3	121.6	121.5
C-5	112.7	113.4	113.5	112.5	112.6
C-6	157.0[a]	157.5[a]	157.4[a]	157.0[a]	157.1[a]
C-7	97.9	98.4	98.5	97.7	97.7
C-7a	154.0[a]	153.3[a]	153.6[a]	153.8[a]	153.9[a]
C-1′	130.4	131.1	129.8	129.2	129.2
C-2′	104.7	105.0	106.1	103.2	103.0
C-3′	154.6[a]	155.0[a]	157.1[a]	155.2[a]	155.3[a]
C-4′	116.6[b]	117.5[b]	123.0[c]	112.8	112.8
C-5′	156.8[a]	156.7[a]	160.8[a]	155.2[a]	155.3[a]
C-6′	105.5	105.4	105.4	103.2	103.0
C-1″	133.3	133.7	140.8	133.2	133.4
C-2″	121.8	122.9	125.3	127.9	128.1
C-3″	37.1[c]	37.2[c]	130.1[b]	33.1	33.6
C-4″	28.5	28.5	116.0[c]	46.9	47.1
C-5″	35.3[c]	35.1[c]	132.7[b]	33.9	33.3
C-6″	35.7	36.2	121.3	33.9	34.5
C-7″	23.7	23.9	22.3	23.2	23.4
C-8″	103.3	102.6	106.7	207.7	207.5
C-9″	115.7[b]	113.4	111.6	115.0	113.4
C-10″	155.9[a]	159.9[a]	160.2[a]	162.4[a]	164.6[a]
C-11″	112.6	103.9	105.0	114.4	102.7
C-12″	151.8[a]	157.7[a]	158.2[a]	162.0[a]	164.6[a]
C-13″	106.8	107.1	111.6	106.2	106.4
C-14″	127.3	130.3	131.6	131.2	128.5
C-15″	116.6[b]	116.8[b]	115.7[c]	122.0	122.3
C-16″	152.8[a]	154.5[a]	152.7[a]	155.4[a]	155.3[a]
C-17″	103.4	104.6	106.5	102.6	101.5
C-18″	156.8[a]	157.9[a]	157.4[a]	157.0[a]	157.1[a]
C-19″	109.8	109.9	107.4	107.2	108.1
C-20″	125.5	127.9	122.3	131.2	133.4
C-21″	22.9			21.0	
C-22″	123.1			122.0	
C-23″	130.7			130.4	
C-24″	25.7			25.4	
C-25″	17.8			17.6	
Solvent	A	A	B	C	C

A: Acetone-d_6, B: CD_3OD, C: DMSO-d_6. *a—c*) Assignments may be interchanged in each column.

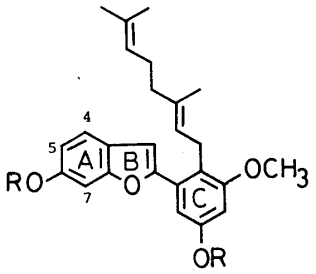


1′

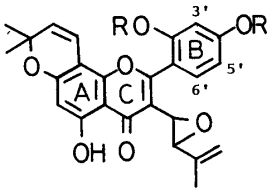


1″

Fig. 1



6: R=H
6a: R=CH_3CO



7: R=H
7a: R=CH_3CO

Fig. 2

TABLE II. Acetylation Shifts (ppm) of **1**, **6**, and **7**

Compd. No.	17″-H	19″-H	20″-H	Compd. No.	7-H	5-H	4-H	Compd. No.	3′-H	5′-H	6′-H
1	6.42	6.55	7.15	**6**[11]	6.99	6.78	7.40	**7**[15]	6.53	6.45	7.15
1b	6.63	6.83	7.41	**6a**	7.28	6.99	7.55	**7a**	7.16	7.18	7.58
Δ	−0.21	−0.28	−0.26	Δ	−0.29	−0.21	−0.15	Δ	−0.63	−0.73	−0.43
Solvent	Acetone-d_6				$CDCl_3$				Acetone-d_6		

derivatives.[11,12] The chemical shifts and coupling constants of the 2-arylbenzofuran moiety were as follows: δ 6.82 (1H, dd, J=2.2 and 8.5 Hz, C_5-H), 6.97 (1H, dd, J=0.9 and 2.2 Hz, C_7-H), 6.98 and 7.03 (each 1H, d, J=1.5 Hz, $C_{2'}$- and $C_{6'}$-H), 7.05 (1H, d, J=0.9 Hz, C_3-H), 7.40 (1H, d, J=8.5 Hz, C_4-H). As the chemical shift values of the protons at the C-2′ and -6′ positions appeared to be nonequivalent, it was suggested that one of the hydroxyl groups in the C-ring formed an ether linkage.[13] This assumption was further supported by a comparison of the ^{13}C-NMR spectrum of **1** with those of **4** and **5**. The chemical shifts of the carbon atoms of the 2-arylbenzofuran skeleton, except those of the carbon atoms at C-4′ and -6′ positions, were similar to those of the corresponding carbon atoms of **4** and **5** (Table I). The presence of the following moieties and the substitution pattern on the F-ring of **1** were supported by comparing the ^{1}H-NMR spectrum of **1** with those of prenylflavonoids[14] and Diels–Alder type adducts[14] obtained from Morus species, and by considering the following acetylation shifts in the ^{1}H-NMR spectra of **1** and **1b**. The signals of protons of a 2,4-dihydroxy-3-prenylphenyl moiety were observed at δ 1.57 and 1.73 (each 3H, br s, $C_{23''}$-CH_3), 3.36 (2H, d, J=6.8 Hz, $C_{21''}$-H×2), 5.23 (1H, m, $C_{22''}$-H), 6.38 (1H, d, J=8.5 Hz, $C_{13''}$-H), 7.17 (1H, d, J=8.5 Hz, $C_{14''}$-H), and those of aromatic protons of a 2,4-dioxygenated phenyl moiety were observed at δ 6.42 (1H, d, J=2.5 Hz, $C_{17''}$-H), 6.55 (1H, dd, J=2.5 and 8.5 Hz, $C_{19''}$-H), 7.15 (1H, d, J=8.5 Hz, $C_{20''}$-H). Comparison of the ^{1}H-NMR spectra of **1** and **1b**

indicates that the acetylation of the hydroxyl group in the 2,4-dioxygenated phenyl moiety caused downfield shifts (0.21—0.28 ppm) of the protons in the moiety. Similar shifts were observed in the case of the A-ring protons of mulberrofuran A (**6**) and its acetate (**6a**).[11] On the other hand, the acetylation of the 2′ and 4′ hydroxyl groups of **7**[15] caused larger downfield shifts (0.43—0.73 ppm) of the protons in the B-ring (Table II). These results suggest that **1** has a hydroxyl group in the 2,4-dioxygenated phenyl moiety and that the other oxygen atom formed the ether linkage. On the basis of the above results, the partial structure **1′** was proposed.

Several Diels–Alder type adducts with 4′-dehydroprenyl-2-arylbenzofuran and chalcone have been isolated from *Morus* root bark.[14b,c] The biogenetic analogy to these Diels–Alder type adducts led us to assume that the carbon skeleton of the C_8H_9 moiety has the structure **1″**. The presence of a trisubstituted methylcyclohexene ring in the C_8H_9 moiety was suggested based on an examination of the ^{1}H-NMR spectrum of **1a**. The spectrum was analyzed with the aid of sequential decoupling experiments, and the deduced structure is shown in Fig. 3 along with chemical shift values and the coupling constants of the protons of the C_8H_9 moiety. The location of the methylcyclohexene ring on the C-ring was also supported by the acetylation shift of the C-2″ olefinic proton signal as follows: the C-2″ proton signal of **1b** was shifted 0.47 ppm toward upper field from the corresponding proton of **1**. In the ^{13}C-NMR spectrum of **1**, the singlet signal at 103.3 ppm suggested the presence of an –O–C–O– type moiety in the structure.[16] All these results indicate that the structure of mulberrofuran F may be represented by **1** (except for the stereochemistry at the C-8″ position).

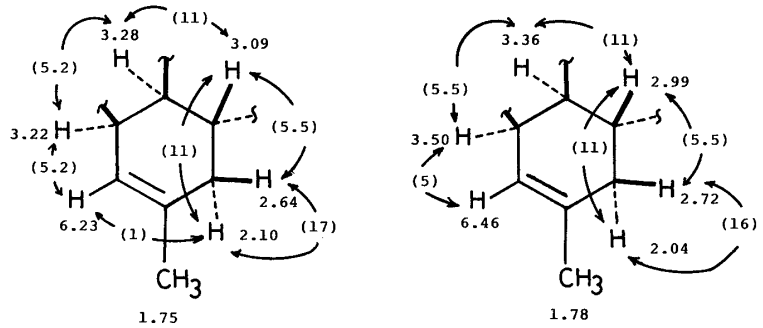


Fig. 3. ^{1}H-NMR Chemical Shifts (ppm) and Coupling Constants (Hz) of D-Ring Protons of Mulberrofuran F Pentamethyl Ether (**1a**) and Mulberrofuran G (**2**)

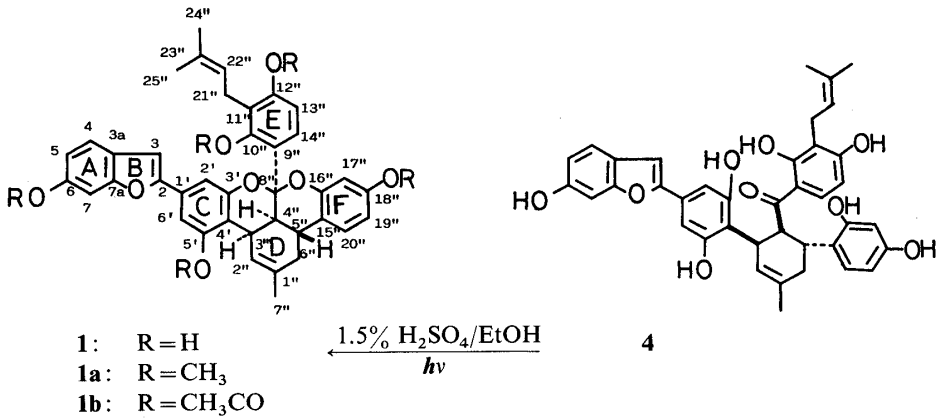
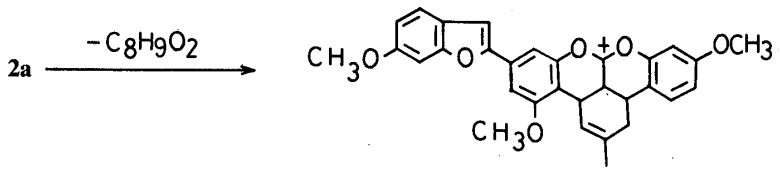


Fig. 4

In order to corroborate the structure, mulberrofuran F (**1**) was derived from chalcomoracin (**4**) by means of the following reaction. A solution of **4** in ethanol containing 1.5% sulfuric acid was externally irradiated in a glass vessel with a 100 W high-pressure mercury lamp. The products were purified by preparative TLC to give **1**. The IR and ^{1}H-NMR spectra of the product as well as the optical rotation value are in fair agreement with those of mulberrofuran F (**1**). The relative configuration of the E-ring with the methine protons on the methylcyclohexene ring was suggested by the coupling constants of the methylcyclohexene ring protons. The coupling constants of the ring protons were in good agreement with those expected for the relevant protons on the basis of the Dreiding model.[17] From the above results, we propose the formula **1** for the structure of mulberrofuran F.

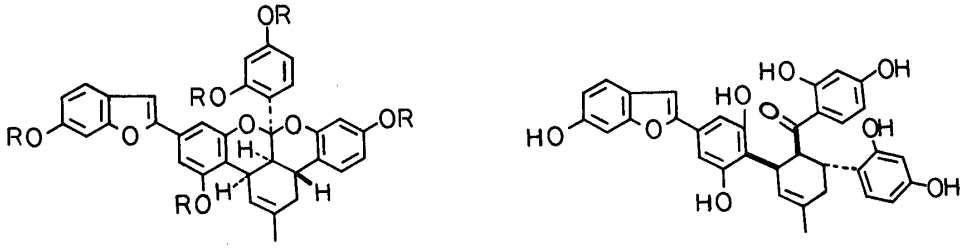
Mulberrofuran G (**2**), is a colorless amorphous powder. The FD-MS showed the molecular ion peak at *m/z* 562. The ^{13}C-NMR spectrum indicated the presence of thirty-four carbons: ten aliphatic carbons ($CH_3-\times 1$, $-CH_2-\times 1$, $>CH-\times 3$, $>C=CH-\times 1$, $-HC=C<_{O-}\times 1$, $-O-\overset{|}{C}-O-\times 1$), and twenty-four aromatic carbons ($CH\times 11$, $C\times 5$, $C-O\times 8$) (Table I). Treatment of **2** with dimethyl sulfate gave a pentamethyl ether (**2a**) as colorless needles, mp 182—183 °C; the molecular formula was determined to be $C_{39}H_{36}O_8$ by high-resolution MS. Work-up of **2** with acetic anhydride in pyridine gave the pentaacetate (**2b**) which showed a molecular ion peak at *m/z* 772 in its FD-MS. These results indicate the composition of mulberrofuran G to be $C_{34}H_{26}O_8$. The IR spectrum of **2** showed absorption bands due to hydroxyl, conjugated double bond and benzene ring moieties, and indicated the absence of a carbonyl function. The UV spectrum of **2** exhibited maxima at 223, 285, 295 (sh), 306 (infl.), 321 and 335 nm. The UV spectrum and the MS of **2** were similar to those of **1**. The MS of **2a** showed a significant fragment ion at *m/z* 495 ($M^+ - C_8H_9O_2$, **8**) corresponding to the loss of a dimethoxyphenyl moiety. The MS of **1a** showed the same fragment ion ($M^+ - C_{13}H_{17}O_2$, **8**). These results suggest that **2** is a deprenylmulberrofuran F. In the ^{13}C-NMR spectrum of **2**, all the carbon atoms except those of the E-ring has essentially the same chemical shift values as the corresponding carbon atoms of **1** (Table I). The ^{1}H-NMR spectrum of **2** was analyzed by comparing it with that of **1**.

The chemical shifts and coupling constants of the 2-arylbenzofuran moiety were as follows: δ 6.81 (1H, dd, $J=2$ and 8.6 Hz, C_5-H), 6.94 and 6.98 (each 1H, d, $J=1.5$ Hz, $C_{2'}$-



8: *m/z* 495

Fig. 5



2: R=H
2a: R=CH_3
2b: R=CH_3CO

$\xleftarrow[(h\nu)]{1.5\%\ H_2SO_4/EtOH}$

5

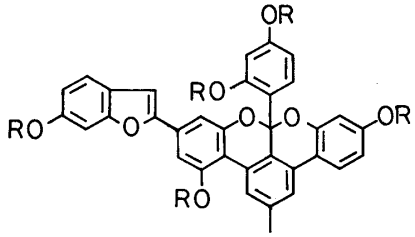
Fig. 6

and $C_{6'}$-H), 6.97 (1H, br d, J=2 Hz, C_7-H), 7.05 (1H, d, J=0.7 Hz, C_3-H), 7.41 (1H, d, J=8.6 Hz, C_4-H). The signals of protons of two 2,4-dioxygenated phenyl moieties were observed at δ 6.23 (1H, dd, J=2.4 and 8.8 Hz, $C_{13''}$-H), 6.38 (1H, d, J=2.5 Hz, $C_{17''}$-H), 6.42 (1H, d, J=2.4 Hz, $C_{11''}$-H), 6.51 (1H, dd, J=2.5 and 8.3 Hz, $C_{19''}$-H), 7.14 (1H, d, J=8.3 Hz, $C_{20''}$-H), 7.24 (1H, d, J=8.8 Hz, $C_{14''}$-H). The proton signals of a methylcyclohexene ring moiety are shown in Fig. 3. The coupling constants of the protons of the methylcyclohexene ring of **2** were similar to those of the corresponding protons of **1a**. All these results indicate that the structure of mulberrofuran G may be represented by **2**. To confirm the structure of **2**, the compound was derived from **5** as follows: a solution of **5** was treated as described in the case of **4** to give the product. The IR and ^{1}H-NMR spectra of the product as well as the optical rotation value were in fair agreement with those of **2**. On the other hand, **2** was also obtained by treatment of **5** in ethanol solution containing sulfuric acid without irradiation with the high-pressure mercury lamp. The yield of the compound was poor in this case. From these results, the structure of mulberrofuran G is concluded to be represented by the formula **2**.

Compound **3** was obtained as colorless needles, mp 240 °C (dec.). The FD-MS showed the molecular ion peak at m/z 558. The ^{13}C-NMR spectrum indicated the presence of thirty-four carbons: four aliphatic carbons (CH_3– × 1, –HC=C< × 1, –O–C–O– × 1), and thirty aromatic carbons (CH × 13, C × 9, C–O × 8) (Table I). Treatment of **3** with dimethyl sulfate in acetone gave a pentamethyl ether (**3a**, M^+ 628) as colorless prisms, mp 164—166 °C (dec.), and the molecular formula was determined to be $C_{39}H_{32}O_8$ by high-resolution MS. These results indicated the composition of **3** to be $C_{34}H_{22}O_8$. The ^{1}H-NMR spectrum of **3** was examined by comparing it with those of **1** and **2**, and showed the presence of the following moieties in **3**: protons in a 2-arylbenzofuran moiety, δ 6.99 and 7.01 (each 1H, d, J=1.5 Hz, $C_{2'}$ and $C_{6'}$-H), 6.74 (1H, dd, J=2.5 and 9 Hz, C_5-H), 6.97 (1H, d, J=0.5 Hz, C_3-H), 6.90 (1H, br d, J=2.5 Hz, C_7-H), 7.61 (1H, d, J=9 Hz, C_4-H); protons in two 2,4-dioxygenated phenyl moieties, δ 5.85 (1H, dd, J=2.5 and 9 Hz, $C_{13''}$-H), 6.13 (1H, d, J=9 Hz, $C_{14''}$-H), 6.26 (1H, d, J=2.5 Hz, $C_{11''}$-H), 6.47 (1H, d, J=2.5 Hz, $C_{17''}$-H), 6.52 (1H, dd, J=2.5 and 9 Hz, $C_{19''}$-H), 7.35 (1H, d, J=9 Hz, $C_{20''}$-H); protons in a 1-methyl-3,4,5-trisubstituted phenyl moiety, δ 2.51 (3H, s, $C_{1''}$-CH_3), 7.52 (1H, br s, $C_{6''}$-H),[18] 8.39 (1H, br s, $C_{2''}$-H).[18] The chemical shift values and coupling pattern of the $C_{2''}$-proton are similar to those of the C_6-proton of cannabinol.[18] All these results and the biogenetic analogy between **1** and **2** indicate that the structure of this compound is represented by the formula **3**.

On the other hand, Rama Rao *et al.* reported the isolation of albanols A and B from *Morus alba*, and assigned the formulae **2** and **3** for the compounds, respectively, on the basis of an X-ray study of albanol A pentamethyl ether.[7] Direct comparisons were carried out between mulberrofuran G and albanol A, as well as between the pentamethyl ether of **3** and albanol B pentamethyl ether. Mulberrofuran G and compound **3** were proved to be identical with albanols A and B, respectively. The structures of chalcomoracin (**4**) and mulberrofuran C (**5**), except for the absolute configurations, were also confirmed by the above chemical correlations.

From a biogenetic point of view, mulberrofurans F (**1**) and G (**2**) seem to be Diels–Alder



3: R=H
3a: R=CH_3

Fig. 7

type adducts derived from chalcomoracin (**4**) and mulberrofuran C (**5**), respectively, by the intramolecular ketalization reaction of the carbonyl group with the two adjoining hydroxyl groups. As albanol B (**3**) obtained by our group[19] is optically active, these compounds (**1**—**3**) seem to be formed by an enzymatic ketalization reaction process.

Experimental

All melting points are uncorrected. The ^{1}H- and ^{13}C-NMR spectra were measured with tetramethylsilane as an internal reference. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS), and coupling constants (J) in Hz. Abbreviations: s=singlet, d=doublet, t=triplet, m=multiplet, dd=double doublet, dt=doublet of triplet, ddd=doublet of double doublet, br=broad, sh=shoulder, infl.=inflection. The following instruments were used to obtain the physical data: melting points, Yazawa micromelting point apparatus (a hot-stage type), UV spectra, Hitachi 340 UV spectrometer; IR spectra, Hitachi 260-30 IR spectrometer; ^{1}H-NMR spectra, JEOL GX-400 and GX-270 NMR spectrometers and a JEOL JNM 4H-100 NMR spectrometer; ^{13}C-NMR spectra, JEOL GX-270 and GX-400, and Hitachi R-900 FT NMR spectrometers; optical rotation, JASCO DPI-4; mass spectra, JEOL JMS 01SG-2 and Hitachi RUM-7M mass spectrometers. For photochemical reactions, a 100 W high-pressure mercury lamp UVL-100 HA (Riko Kagaku) was used. Wakogel B-5FM was used for TLC, Wakogel B-5F for preparative TLC, and Wakogel C-200 for column chromatography.

Isolation of Mulberrofurans F (1) and G (2), and Albanol B (3)——The dried root bark of the cultivated mulberry tree (26 kg, Japanese name "Rosō," a cultivated variety of *Morus lhou* KOIDZ.), collected in the neighborhood of Takasaki, Gunma Prefecture, Japan, in December 1981, was extracted successively with *n*-hexane, benzene, and ethyl acetate. Evaporation of the *n*-hexane, benzene, and ethyl acetate solutions to dryness yielded 330, 200, and 1200 g of residue, respectively. The ethyl acetate extract (300 g) was chromatographed on silica gel (1600 g) with benzene–MeOH as an eluent, each fraction being monitored by TLC. The fractions eluted with benzene containing 1% MeOH were evaporated to give the residue (12 g), which was rechromatographed on silica gel (100 g) with *n*-hexane–acetone as an eluent. The fractions eluted with *n*-hexane containing 25% acetone were evaporated to give the residue (1 g), which was fractionated by preparative TLC (solvent system, $CHCl_3$: AcOEt=2:1; $CHCl_3$: $(CH_3)_2CO$=3:1) to give mulberrofuran F (**1**, 217 mg, 3×10^{-3}% yield from the root bark).

The fractions eluted with benzene containing 5% MeOH in the above column chromatography were evaporated to give the residue (24 g), which was rechromatographed on silica gel (150 g) with chloroform–ethyl acetate as an eluent. The fractions eluted with chloroform containing 7% ethyl acetate were evaporated to give the residue (10 g), which was fractionated by preparative TLC (*n*-hexane : $(CH_3)_2CO$)=1:1, $CHCl_3$: $(CH_3)_2CO$=3:2) to give mulberrofuran G (**2**, 5.2 g, 8×10^{-2}% yield from the root bark).

The fractions eluted with benzene containing 5% MeOH in the above column chromatography, which showed on the TLC plate a characteristic spot with light blue fluorescence and the spot of kuwanon H,[20] were evaporated to give the residue (29 g). To isolate the fluorescent compound, the residue (29 g) was rechromatographed on silica gel (200 g) with *n*-hexane–acetone as an eluent. The fluorescent compound (=albanol B, **3**, 930 mg, 1.4×10^{-2}% from the root bark) was obtained as a colorless precipitate from the fraction eluted with 100% acetone.

Mulberrofuran F (1)——Compound **1** was obtained as an amorphous powder. One spot was detected on TLC ($CHCl_3$: AcOEt=2:1; $CHCl_3$: $(CH_3)_2CO$=3:1). $[\alpha]_D^{23}$ +513° (c=0.024, MeOH). FD-MS m/z: 630 (M^+). $FeCl_3$ test: negative. *Anal.* Calcd for $C_{39}H_{34}O_8\cdot3/2H_2O$: C, 71.22; H, 5.67. Found: C, 71.42; H, 5.59. UV λ_{max}^{EtOH} nm (log ε): 230 (infl. 4.51), 285 (4.15), 296 (sh 4.12), 306 (infl. 4.26), 321 (4.46), 335 (4.39). IR ν_{max}^{KBr} cm^{-1}: 3380, 1615, 1610, 1600. EI-MS m/z: 293, 242. ^{1}H-NMR ($(CD_3)_2CO$, 400 MHz) δ: 1.57, 1.73 (each 3H, br s, $C_{23''}$-CH_3), 1.80 (3H, br s, $C_{1''}$-CH_3), 2.05—2.15 (1H, m, $C_{6''}$-H), 2.75 (1H, br d, J=15, $C_{6''}$-H), 3.00—3.05 (1H, m, $C_{5''}$-H), 3.30—3.50 (2H, br, $C_{3''}$ and $C_{4''}$-H, combined with the signal of $C_{21''}$-H), 3.36 (2H, d, J=6.8, $C_{21''}$-H×2), 5.23 (1H, m, $C_{22''}$-H), 6.38 (1H, d, J=8.5, $C_{13''}$-H), 6.42 (1H, d, J=2.5, $C_{17''}$-H), 6.47 (1H, br d, J=4, $C_{2''}$-H), 6.55 (1H, dd, J=2.5 and 8.5, $C_{19''}$-H), 6.82 (1H, dd, J=2.2 and 8.5, C_5-H), 6.97 (1H, dd, J=0.9 and 2.2, C_7-H), 6.98 and 7.03 (each 1H, d, J=1.5, $C_{2'}$ and $C_{6'}$-H), 7.05 (1H, d, J=0.9, C_3-H), 7.15 (1H, d, J=8.5, $C_{20''}$-H), 7.17 (1H, d, J=8.5, $C_{14''}$-H), 7.40 (1H, d, J=8.5, C_4-H), 7.84, 8.44, 8.47, 8.60, 8.84 (each 1H, br s, OH). The ^{13}C-NMR chemical shifts are shown in Table I.

Mulberrofuran F Pentamethyl Ether (1a)——A mixture of mulberrofuran F (17 mg), $(CH_3)_2SO_4$ (0.05 ml), and K_2CO_3 (5 g) in dry $(CH_3)_2CO$ (30 ml) was refluxed for 4.5 h, and treated as usual. The product was purified by preparative TLC (Et_2O : *n*-hexane=2:1) to give an amorphous powder (**1a**, 17 mg). UV λ_{max}^{EtOH} nm (log ε): 230 (infl. 4.68), 283 (sh 4.23), 286 (4.25), 296 (sh 4.26), 307 (infl. 4.46), 321 (4.65), 336 (4.56). IR ν_{max}^{KBr} cm^{-1}: 2900, 1610, 1480. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.68 and 1.73 (each 3H, br s, $C_{23''}$-CH_3), 1.75 (3H, br s, $C_{1''}$-CH_3), 2.10 (1H, ddd, $J_{2'',6''}$=1, $J_{5'',6''}$=11, $J_{6'',6''}$=17, $C_{6''}$-H), 2.64 (1H, dd, J=5.5 and 17, $C_{6''}$-H), 3.09 (1H, dt, $J_{5'',6''}$=5.5, $J_{4'',5''}$=$J_{5'',6''}$=11, $C_{5''}$-H), 3.22 (2H, m, $C_{3''}$ and $C_{21''}$-H), 3.28 (1H, dd, J=5.2 and 11, $C_{4''}$-H), 3.45 (1H, dd, J=7.7 and 15.4, $C_{21''}$-H), 3.73, 3.74, 3.76, 3.83, 3.86 (each 3H, s, OCH_3), 5.17 (1H, br t, J=7.7, $C_{22''}$-H), 6.23 (1H, dd, J=1 and 5.2, $C_{2''}$-H), 6.48 (1H, d, J=8.5, $C_{13''}$-H), 6.53 (1H, d, J=2.5, $C_{17''}$-H), 6.60 (1H, dd, J=2.5 and 8.5, $C_{19''}$-H), 6.86 (1H, dd, J=2 and 8.5, C_5-H), 6.87 (1H, br s, C_3-H), 6.88 (1H, d, J=1.5, $C_{6'}$-H), 7.05 (1H, d, J=2, C_7-H), 7.13 (1H, d, J=

1.5, $C_{2'}$-H), 7.17 (1H, d, J=8.5, $C_{20''}$-H), 7.24 (1H, d, J=8.5, $C_{14''}$-H), 7.43 (1H, d, J=8.5, C_4-H). High-resolution MS, Calcd for $C_{44}H_{44}O_8$ (M^+), m/z 700.3032. Found: m/z 700.3023; Calcd for $C_{43}H_{42}O_8$, m/z 686.2877. Found: m/z 686.2890; Calcd for $C_{37}H_{36}O_6$, m/z 576.2510. Found: m/z 576.2524; Calcd for $C_{36}H_{33}O_6$, m/z 561.2275. Found: m/z 561.2264; Calcd for $C_{33}H_{28}O_6$, m/z 520.1885. Found: m/z 520.1905; Calcd for $C_{31}H_{27}O_6$, m/z 495.1805. Found: m/z 495.1762; Calcd for $C_{30}H_{25}O_6$, m/z 481.1650. Found: m/z 481.1660; Calcd for $C_{20}H_{18}O_4$, m/z 322.1204. Found: 322.1182.

Mulberrofuran F Pentaacetate (1b)——A mixture of **1** (22 mg), acetic anhydride (0.52 ml) and pyridine (0.17 ml) was kept at room temperature for 3.5 h, and then poured into ice water. The solid was collected and purified by preparative TLC (n-hexane : $(CH_3)_2CO$ = 3 : 2) to give an amorphous powder (**1b**, 17 mg). FD-MS m/z: 840 (M^+). UV λ_{max}^{EtOH} nm (log ε): 283 (sh 4.14), 290 (infl. 4.20), 313 (4.47), 329 (4.41). IR ν_{max}^{KBr} cm^{-1}: 1770, 1620, 1600. ^{1}H-NMR ($(CD_3)_2CO$, 400 MHz, 55 °C) δ: 1.65, 1.69 (each 3H, br s, $C_{23''}$-CH_3), 1.80 (3H, br s, $C_{1''}$-CH_3), 2.16 (1H, dd, J=11 and 16, $C_{6''}$-H), 1.94, 2.23, 2.26, 2.28, 2.32 (each 3H, s, OAc), 2.86 (1H, dd, J=5 and 16, $C_{6''}$-H), 2.96—3.03 (1H, br, $C_{4''}$-H), 3.07 (1H, dt, $J_{5'',6''}$=5, $J_{4'',5''}$=$J_{5'',6''}$=11, $C_{5''}$-H), 3.12 (1H, dd, J=7 and 15, $C_{21''}$-H), 3.20 (1H, m, $C_{3''}$-H), 3.21 (1H, dd, J=7 and 15, $C_{21''}$-H), 5.05 (1H, br t, J=7, $C_{22''}$-H), 6.00 (1H, br d, J=6, $C_{2''}$-H), 6.63 (1H, d, J=2, $C_{17''}$-H), 6.83 (1H, dd, J=2 and 8, $C_{19''}$-H), 6.95 (1H, d, J=8, $C_{13''}$-H), 7.03 (1H, dd, J=2 and 8, C_5-H), 7.27 (1H, d, J=8, $C_{14''}$-H), 7.28 (1H, d, J=1.8, $C_{6'}$-H), 7.32 (1H, br s, C_3-H), 7.37 (1H, br d, J=2, C_7-H), 7.41 (1H, d, J=8, $C_{20''}$-H), 7.43 (1H, d, J=1.8, $C_{2'}$-H), 7.62 (1H, d, J=8, C_4-H).

Formation of Mulberrofuran F (1) from Chalcomoracin (4)——A solution of **4** (40 mg) in EtOH (2.3 ml) containing 1.5% H_2SO_4 was externally irradiated in a glass vessel with a 100 W high-pressure mercury lamp for 9 h. The reaction mixture was purified by preparative TLC (Et_2O) to give an amorphous powder (**1**, 4 mg). The compound **1** thus obtained was identical with mulberrofuran F on the basis of the IR, UV, and ^{1}H-NMR spectral comparisons and optical rotation measurement.

Mulberrofuran G (2)——Compound **2** was obtained as an amorphous powder. One spot was detected on TLC (n-hexane: $(CH_3)_2CO$ = 1 : 1, $CHCl_3$: $(CH_3)_2CO$ = 3 : 2). $[\alpha]_D^{22}$ +546° (c=0.0326, MeOH). FD-MS m/z: 562 (M^+). $FeCl_3$ test: negative. UV λ_{max}^{EtOH} nm (log ε): 223 (4.63), 285 (4.29), 295 (sh 4.24), 306 (infl. 4.37), 321 (4.57), 335 (4.50). IR ν_{max}^{KBr} cm^{-1}: 3400 (br), 1620, 1600. ^{1}H-NMR ($(CD_3)_2CO$, 400 MHz) δ: 1.78 (3H, br s, $C_{1''}$-CH_3), 2.04 (1H, dd, J= 11 and 16, $C_{6''}$-H), 2.72 (1H, dd, J=5.5 and 16, $C_{6''}$-H), 2.99 (1H, dt, $J_{5'',6''}$=5.5, $J_{4'',5''}$=$J_{5'',6''}$=11, $C_{5''}$-H), 3.36 (1H, dd, J=5.5 and 11, $C_{4''}$-H), 3.50 (1H, dd, J=5 and 5.5, $C_{3''}$-H), 6.23 (1H, dd, J=2.4 and 8.8, $C_{13''}$-H), 6.38 (1H, d, J=2.5, $C_{17''}$-H), 6.42 (1H, d, J=2.4, $C_{11''}$-H), 6.46 (1H, br d, J=5, $C_{2''}$-H), 6.51 (1H, dd, J=2.5 and 8.3, $C_{19''}$-H), 6.81 (1H, dd, J=2 and 8.6, C_5-H), 6.94 and 6.98 (each 1H, d, J=1.5, $C_{2'}$- and $_{6'}$-H), 6.97 (1H, br d, J=2, C_7-H), 7.05 (1H, d, J=0.7, C_3-H), 7.14 (1H, d, J=8.3, $C_{20''}$-H), 7.24 (1H, d, J=8.8, $C_{14''}$-H), 7.41 (1H, d, J=8.6, C_4-H), 8.33, 8.45, 8.53, 8.55, 8.70 (each 1H, br s, OH). The ^{13}C-NMR chemical shifts are shown in Table I. Mulberrofuran G (**2**) was shown to be identical with albanol A by IR and ^{1}H-NMR spectral comparisons. Although the specific optical rotation value of albanol A was reported to be +137.17° (ref. 7), the specimen which was sent by Dr. Rama Rao showed $[\alpha]_D^{20}$ +515° (c=0.043, MeOH) when measured by us.

Mulberrofuran G Pentamethyl Ether (2a)——A mixture of mulberrofuran G (58 mg), $(CH_3)_2SO_4$ (0.08 ml), and K_2CO_3 (5 g) in dry $(CH_3)_2CO$ (30 ml) was refluxed for 5 h, and treated as usual. The product was purified by preparative TLC (C_6H_6) to give the pentamethyl ether (**2a**, 54 mg). The compound **2a** was obtained as colorless needles, mp 182—183 °C (from C_6H_6 containing 50% $(CH_3)_2CO$). *Anal.* Calcd for $C_{39}H_{36}O_8$: C, 74.04; H, 5.73. Found: C, 74.36; H, 6.04. UV λ_{max}^{EtOH} nm (log ε): 244 (4.54), 279 (infl. 4.05), 284 (4.10), 287 (sh 4.09), 297 (sh 4.08), 308 (infl. 4.26), 322 (4.45), 337 (4.37). IR ν_{max}^{KBr} cm^{-1}: 1620 (sh), 1610, 1585, 1560. EI-MS m/z: 632 (M^+), 617, 508, 493. ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.79 (3H, br s, $C_{1''}$-CH_3), 2.10 (1H, m, $C_{6''}$-H), 2.65 (1H, dd, J=5 and 16, $C_{6''}$-H), 3.00—3.20 (1H, m, $C_{5''}$-H), 3.30—3.40 (2H, m, $C_{3''}$ and $C_{4''}$-H), 3.74, 3.77, 3.78, 3.86, 3.87 (each 3H, s, OCH_3), 6.24 (1H, br d, J=5, $C_{2''}$-H), 6.32 (1H, dd, J=2.4 and 7.8, $C_{13''}$-H), 6.48 (1H, d, J=2.4, $C_{17''}$-H), 6.57 (1H, d, J=2.4, $C_{11''}$-H), 6.58 (1H, dd, J=2.4 and 8.8, $C_{19''}$-H), 6.86 (1H, dd, J=2.5 and 8.8, C_5-H), 6.87 (1H, br s, C_3-H), 6.89 (1H, d, J=1.5, $C_{6'}$-H), 7.05 (1H, br d, J=2.5, C_7-H), 7.13 (1H, d, J=1.5, $C_{2'}$-H), 7.14 (1H, d, J=8.8, $C_{20''}$-H), 7.33 (1H, d, J=7.8, $C_{14''}$-H), 7.42 (1H, d, J=8.8, C_4-H). High-resolution MS, Calcd for $C_{39}H_{36}O_8$, m/z 632.2407. Found: m/z 632.2372; Calcd for $C_{38}H_{33}O_8$, m/z 617.2173. Found: m/z 617.2173; Calcd for $C_{38}H_{33}O_7$, m/z 601.2224. Found: 601.2197; Calcd for $C_{31}H_{27}O_6$, m/z 495.1805. Found: m/z 495.1799; Calcd for $C_{31}H_{25}O_6$, m/z 493.1642. Found: m/z 493.1645; Calcd for $C_{30}H_{25}O_6$ m/z 481.1648. Found: m/z 481.1618; Calcd for $C_8H_9O_2$, m/z 137.0602. Found: m/z 137.0612.

Mulberrofuran G Pentaacetate (2b)——A mixture of **2** (43 mg), acetic anhydride (0.64 ml) and pyridine (0.21 ml) was kept at room temperature for 30 min, and treated as usual. The reaction product was purified by preparative TLC (Et_2O : n-hexane = 2 : 1) to give an amorphous powder (**2b**, 39 mg). FD-MS m/z: 772 (M^+). UV λ_{max}^{EtOH} nm (log ε): 282 (sh 4.24), 291 (infl. 4.31), 312 (4.57), 328 (4.51). IR ν_{max}^{KBr} cm^{-1}: 1770, 1620, 1590. ^{1}H-NMR ($(CD_3)_2CO$, 100 MHz) δ: 1.75 (3H, br s, $C_{1''}$-H), 1.99—2.10 (overlapping with the signals of solvent, $C_{6''}$-H), 1.93, 2.22, 2.24, 2.26, 2.31 (each 3H, s, OAc), 2.83 (1H, dd, J=5 and 16, $C_{6''}$-H), 2.94 (1H, m, $C_{5''}$-H), 3.15 (1H, dd, J=5 and 11, $C_{4''}$-H), 3.20 (1H, m, $C_{3''}$-H), 6.00 (1H, br d, J=5, $C_{2''}$-H), 6.62 (1H, d, J=2, $C_{17''}$-H), 6.78 (1H, dd, J=2 and 8, $C_{19''}$-H), 6.92 (1H, dd, J= 2 and 8, $C_{13''}$-H), 7.00 (1H, dd, J=2 and 8, C_5-H), 7.04 (1H, d, J=2, $C_{11''}$-H), 7.29 (1H, d, J=2, $C_{6'}$-H), 7.31 (1H, br s, C_3-H), 7.36 (1H, d, J=2, C_7-H), 7.37 (2H, d, J=8, $C_{14''}$ and $C_{20''}$-H), 7.41 (1H, d, J=2, $C_{2'}$-H), 7.59 (1H, d, J= 8, C_4-H).

Formation of Mulberrofuran G (2) from Mulberrofuran C (5)——1) A solution of **5** (30 mg) in EtOH (2 ml) containing 1.5% H_2SO_4 was externally irradiated in a glass vessel with a 100 W high-pressure mercury lamp for 9 h. The reaction product was purified by preparative TLC ($CHCl_3$: $(CH_3)_2CO$ = 1 : 1) to give an amorphous powder (**2**, 19 mg). The compound **2** thus obtained was identical with mulberrofuran G on the basis of IR and ^{1}H-NMR spectral comparisons, and optical rotation measurement. The compound **2** derived from **5** was methylated as described in the case of mulberrofuran G to give the pentamethyl ether, which was shown to be identical with mulberrofuran G pentamethyl ether by mixed melting point determination.

2) A solution of **5** (28 mg) in EtOH (2.6 ml) containing 1.5% H_2SO_4 was kept in the dark for 9 h. The reaction mixture was purified by preparative TLC ($CHCl_3$: $(CH_3)_2CO$ = 3 : 2) to give an amorphous powder (**2**, 9 mg).

Albanol B (3)——Compound **3** was obtained as colorless needles, mp 240 °C (dec. from $(CH_3)_2CO$). $[\alpha]_D^{20}$ −15° (c = 0.02, MeOH). FD-MS m/z: 558 (M^+), 449. $FeCl_3$ test: negative. UV λ_{max}^{EtOH} nm (log ε): 222 (4.71), 275 (sh 4.12), 285 (4.18), 318 (sh 4.34), 335 (sh 4.54), 350 (4.68), 365 (4.65). ^{1}H-NMR (CD_3OD, 400 MHz) δ: 2.51 (3H, s, $C_{1''}$-CH_3), 5.85 (1H, dd, J=2.5 and 9, $C_{13''}$-H), 6.13 (1H, d, J=9, $C_{14''}$-H), 6.26 (1H, d, J=2.5, $C_{11''}$-H), 6.47 (1H, d, J=2.5, $C_{17''}$-H), 6.52 (1H, dd, J=2.5 and 9, $C_{19''}$-H), 6.74 (1H, dd, J=2.5 and 9, C_5-H), 6.90 (1H, br d, J=2.5, C_7-H), 6.97 (1H, d, J=0.5, C_3-H), 6.99 and 7.01 (each 1H, d, J=1.5, $C_{2'}$ and $C_{6'}$-H), 7.35 (1H, d, J=9, $C_{20''}$-H), 7.52 (1H, br s, $C_{6''}$-H), 7.61 (1H, d, J=9, C_4-H), 8.39 (1H, br s, $C_{2''}$-H). The ^{13}C-NMR chemical shifts are shown in Table I.

Albanol B Pentamethyl Ether (3a)——A mixture of **3** (31 mg), $(CH_3)_2SO_4$ (0.08 ml), and $(CH_3)_2CO$ (30 ml) was refluxed for 2.5 h, and treated as usual to give the pentamethyl ether (**3a**, 30 mg). This compound **3a** was obtained as colorless prisms, mp 164—166 °C (dec. from $CHCl_3$ containing 50% MeOH. UV λ_{max}^{EtOH} nm (log ε): 210 (4.69), 221 (sh 4.60), 278 (sh 4.04), 285 (4.04), 318 (sh 4.21), 337 (sh 4.39), 350 (4.54), 369 (4.49). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1610, 1590, 1150. ^{1}H-NMR ($CDCl_3$, 100 MHz) δ: 2.49 (3H, s, $C_{1''}$-CH_3), 3.57, 3.74, 3.83, 3.98, 4.01 (each 3H, s, OCH_3), 5.98 (1H, dd, J=2 and 8, $C_{13''}$-H), 6.41 (1H, d, J=2, $C_{11''}$-H), 6.46 (1H, d, J=8, $C_{14''}$-H, combined with a part of the $C_{11''}$-H signal), 6.55 (1H, dd, J=2 and 8, $C_{19''}$-H), 6.63 (1H, d, J=2, $C_{17''}$-H, combined with a part of the $C_{19''}$-H signal), 6.85 (1H, dd, J=2 and 8, C_5-H), 6.91 (1H, br s, C_3-H, combined with a part of the C_5-H signal), 7.00 (1H, d, J=2, $C_{6'}$-H), 7.05 (1H, br d, J=2, C_7-H), 7.18 (1H, d, J=2, $C_{2'}$-H), 7.42 (1H, d, J=8, C_5-H), 7.46 (1H, br s, $C_{6''}$-H), 7.60 (1H, d, J=8, $C_{20''}$-H), 8.23 (1H, br s, $C_{2''}$-H). High-resolution MS, Calcd for $C_{39}H_{32}O_8$ (M^+), m/z 628.2095. Found: m/z 628.2074; Calcd for $C_{38}H_{29}O_8$, m/z 613.1860. Found: m/z: 613.1843; Calcd for $C_{31}H_{23}O_6$, m/z 491.1493. Found: m/z 491.1494; Calcd for $C_{15}H_{10}O_3$, m/z 238.0629. Found: m/z: 238.0641. The pentamethyl ether (**3a**) was identical with albanol B pentamethyl ether on the basis of IR spectral comparison (in $CHCl_3$ solution).

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References and Notes

1) Part XXV on "Constituents of the Cultivated Mulberry Tree" (Part V on "Constituents of Root Bark of *Morus lhou* KOIDZ.). Part XXIV: T. Fujimoto and T. Nomura, *Planta Med.*, in press. Part IV on Constituents of Root Bark of *Morus lhou* KOIDZ.: T. Fukai, T. Fujimoto, Y. Hano, T. Nomura, and J. Uzawa, *Heterocycles*, **22**, 2805 (1984).
2) A part of this work was described in the preliminary communication: T. Fukai, Y. Hano, K. Hirakura, T. Nomura, J. Uzawa, and K. Fukushima, *Heterocycles*, **22**, 473 (1984).
3) K. Hirakura, Y. Hano, T. Fukai, T. Nomura, J. Uzawa, and K. Fukushima, *Chem. Pharm. Bull.*, **33**, 1088 (1985).
4) K. Hirakura, T. Fukai, Y. Hano, and T. Nomura, *Phytochemistry*, **24**, 159 (1985).
5) Y. Hano, K. Hirakura, T. Nomura, S. Terada, and K. Fukushima, *Planta Med.*, **50**, 127 (1984).
6) K. Takagi, "Saisogaku," Nihon Gakujutsu Shinkokai, Tokyo, 1952, p. 45.
7) A. V. Rama Rao, V. H. Deshpande, R. K. Shastri, S. S. Tavale, and N. N. Dhaneshwar, *Tetrahedron Lett.*, **24**, 3013 (1983).
8) The details of the pharmacological experiments will be described in another paper.
9) M. Takasugi, S. Nagao, T. Masamune, A. Shirata, and K. Takahashi, *Chem. Lett.*, **1980**, 1573.
10) T. Nomura, T. Fukai, J. Matsumoto, and T. Ohmori, *Planta Med.*, **46**, 28 (1982).
11) T. Nomura, T. Fukai, J. Uno, and T. Arai, *Heterocycles*, **9**, 1593 (1978).
12) T. Nomura, T. Fukai, T. Shimada, and I.-S. Chen, *Planta Med.*, **49**, 90 (1983).
13) M. Takasugi, S. Nagao, and T. Masamune, *Chem. Lett.*, **1982**, 1217.
14) *a*) T. Nomura and T. Fukai, *Heterocycles*, **15**, 1531 (1981) and references cited therein; *b*) T. Nomura, *Kagaku No Ryoiki*, **36**, 596 (1982) and references cited therein; *c*) T. Nomura, Abstracts of Papers, the 20th Symposium on Phytochemistry, Tokyo, January 1984, p. 1 and references cited therein.

15) *a*) T. Nomura, T. Fukai, and J. Matsumoto, *J. Heterocycl. Chem.*, **17**, 641 (1980); *b*) T. Nomura and T. Fukai, *Heterocycles*, **9**, 635 (1978).
16) H. Hikino, N. Shimoyama, Y. Kasahara, M. Takahashi, and C. Konno, *Heterocycles*, **19**, 1381 (1982).
17) L. M. Jackman and S. Sternhall, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, Inc., New York, 1969, p. 280.
18) R. Mechoulam and Y. Gaoni, *Tetrahedron*, **21**, 1223 (1965).
19) The optical rotation value of albanol B was not given in reference 7.
20) T. Nomura, T. Fukai, and T. Narita, *Heterocycles*, **14**, 1943 (1980).