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Structures of a Novel 2-Arylbenzofuran Derivative and Two Flavone Derivatives from the Cultivated Mulberry Tree (*Morus lhou* KOIDZ.)[1,2]

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A new 2-arylbenzofuran derivative, mulberrofuran H and two isoprenylated flavones, kuwanons S and T, 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 mulberrofuran H and kuwanons S and T were shown to be **1**, **2**, and **3**, respectively, on the basis of spectral evidence. Mulberrofuran H can be regarded biogenetically as a variation of a Diels–Alder type adduct of a chalcone derivative and a dehydroprenyl-2-arylbenzofuran derivative.

Keywords——*Morus lhou*; Moraceae; mulberry; mulberrofuran H; Diels–Alder type adduct; kuwanon S; kuwanon T; prenylfavone

In the previous papers,[1,3] we reported the structure determination of a series of natural Diels–Alder type adducts and geranylated 2-arylbenzofuran derivatives isolated from the extract of the cultivated mulberry tree (Japanese name "Rosō," a cultivated variety of *Morus lhou* KOIDZ.[4]). Further extensive fractionation of the extract of the root bark led us to the isolation of a novel 2-arylbenzofuran derivative, mulberrofuran H (**1**), along with kuwanons S (**2**) and T (**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 mulberrofuran H (**1**), and kuwanons S (**2**) and T (**3**).

Mulberrofuran H (**1**), is colorless amorphous powder, $[\alpha]_D^{22}$ +25°, which was negative to the methanolic ferric chloride test. The molecular formula of **1** was determined to be $C_{27}H_{22}O_6$ from the high-resolution mass spectrum (MS). The ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum indicated the presence of twenty-seven carbons: nine aliphatic carbons ($CH_3 \times 1$, $-CH_2- \times 2$, $>CH- \times 1$, $>C=C<^{H} \times 1$, $-\overset{|}{C}-O- \times 1$, $^{H}>C=C<_{O-} \times 1$) and eighteen aromatic carbons (CH × 8, C × 4, C–O × 6) (Table I). Work-up of **1** with acetic anhydride in pyridine gave the tetraacetate (**1a**) which showed a molecular ion peak at *m/z* 610 in its MS. The infrared (IR) spectrum of **1** disclosed absorption bands due to hydroxyl, conjugated double bond, and benzene ring moieties, but no band due to a carbonyl function. The ultraviolet (UV) spectrum of **1** exhibited maxima at 220, 285, 321, and 333 nm and was similar to those of moracin C (**4**),[5] and mulberrofurans F (**5**) and G (**6**),[1,6] suggesting that **1** is a 4′-substituted 6,3′,5′-trioxygenated-2-arylbenzofuran derivative. This suggestion was supported through a comparative examination of the ^{1}H-NMR spectra of **1** and some 2-arylbenzofuran

TABLE I. ^{13}C-NMR Chemical Shifts of Mulberrofurans H (**1**) and C (**8**), and Kuwanons T (**3**) and N (**17**)[3d]

C	**1**[a]	**8**[a]	C	**3**[b]	**17**[b]
2	156.7[c]	156.5[c]	2	161.6[d]	161.0[c]
3	102.2	103.6	3	120.2	120.3
3a	122.4	121.9	4	181.8	181.8
4	121.9	121.9	4a	103.7	103.6, 103.8
5	113.2	113.1	5	161.5[d]	161.5[c]
6	156.7[c]	157.8[c]	6	98.3	98.0
7	98.4	98.4	7	164.0	163.7
7a	155.3[c]	155.4[c]	8	93.4	93.2, 93.4
1′	131.5	130.9	8a	157.9[e]	157.4
2′	103.7	104.8	1′	111.8	112.9
3′	155.7	156.5	2′	153.3	154.5
4′	117.4	113.6	3′	115.8	116.6
5′	155.7	156.5	4′	157.8[e]	158.0
6′	103.7	104.8	5′	106.9	105.8
1″	132.4		6′	127.5	128.2
2″	135.6		9	23.6	24.1
3″	39.8		10	121.4	121.3
4″	31.8		11	130.0[f]	129.8
5″	34.6		12	25.4[g]	25.3
6″	71.8		13	17.2[h]	17.5
7″	27.5		14	22.2	
8″	119.0		15	123.0	
9″	155.2[c]		16	131.1[f]	
10″	103.9		17	25.5[g]	
11″	157.8[c]		18	17.7[h]	
12″	108.8				
13″	130.6				

a) In acetone-d_6. *b*) In DMSO-d_6. *c*—*h*) Assignments may be interchanged in each column.

derivatives.[6-11] The chemical shifts and coupling constants of the 2-arylbenzofuran moiety are as follows: δ 6.81 (1H, dd, J=2 and 9 Hz, C_5-H), 6.85 (2H, s, $C_{2'}$- and $C_{6'}$-H), 6.97 (1H, d, J=2 Hz, C_7-H), 6.99 (1H, br s, C_3-H), 7.39 (1H, d, J=9 Hz, C_4-H). Comparison of the proton nuclear magnetic resonance (^{1}H-NMR) spectra of **1** and **1a** indicates that the protons at $C_{2'}$ and $C_{6'}$ positions seem to be equivalent in terms of the chemical shift values, and that the acetylation of the hydroxyl groups on the C-ring caused a downfield shift (0.52 ppm) of the signals of protons in the ring. In the case of the C-ring protons of moracin C (**4**) and its acetate (**4a**), acetylation of the relevant hydroxyl groups caused a downfield shift (0.44 ppm).[5,12] On the other hand, the acetylation of the 3′-hydroxyl group of moracin D (**7**) caused a smaller downfield shift (0.30 ppm) of the protons on the C-ring (Table II).[5,12] These results suggest that the C-ring of **1** has a 4′-substituted 3′,5′-dihydroxyphenyl structure. The acetylation of the 6-hydroxyl group of **1** caused downfield shifts of the A-ring protons. Similar shifts were observed upon acetylation of **4** (Table II).[5,12] In the ^{13}C-NMR spectrum of **1**, the chemical shifts of the carbon atoms of the 2-arylbenzofuran skeleton, except for that of the carbon atom at the $C_{4'}$ position, were similar to those of the relevant carbon atoms of mulberrofuran C (**8**)[8] (Table I). These results suggest that **1** is a 4′-substituted 6,3′,5′-trihydroxy-2-arylbenzofuran derivative.

The MS of **1** gave fragment ions at m/z 332 (**9**) and 110 (**10**). The formulae of these fragment ions were supported by high-resolution MS. This result suggests the presence of a dioxygenated phenyl moiety in **1**. The ^{1}H-NMR spectrum of **1** supported the presence of a

2,4-dioxygenated phenyl moiety as follows: δ 6.27 (1H, d, $J=2$ Hz, $C_{10''}$-H), 6.37 (1H, dd, $J=$ 2 and 8 Hz, $C_{12''}$-H), 6.97 (1H, d, $J=8$ Hz, $C_{13''}$-H). Comparison of the ^{1}H-NMR spectra of **1** and **1a** indicates that acetylation of the hydroxyl group on the 2,4-dioxygenated phenyl moiety caused downfield shifts (0.26—0.30 ppm) of the protons at the $C_{10''}$ and $C_{12''}$ positions. On the other hand, acetylation of the 2′- and 4′-hydroxyl groups of morusin (**11**)[13] caused larger downfield shifts (0.53—0.56 ppm) of the relevant protons (Table II). These results suggest that **1** has a hydroxyl group in the 2,4-dioxygenated phenyl moiety, and that the other oxygen atom forms the ether linkage. From the above results, the partial structure (**1′**) was proposed. The remaining part of the $C_{4'}$-side chain composed of C_7H_9 was indicated by the ^{13}C-NMR spectrum to contain seven aliphatic carbon atoms: $-CH_3\times1$, $-CH_2-\times2$, $>CH-\times1$, $>C<_{O-}\times1$, $_H>C=C<\times1$ (Table I). In order to clarify the nature of the $C_{4'}$-side chain, the ^{1}H-NMR spectrum of **1** was analyzed with the aid of sequential decoupling

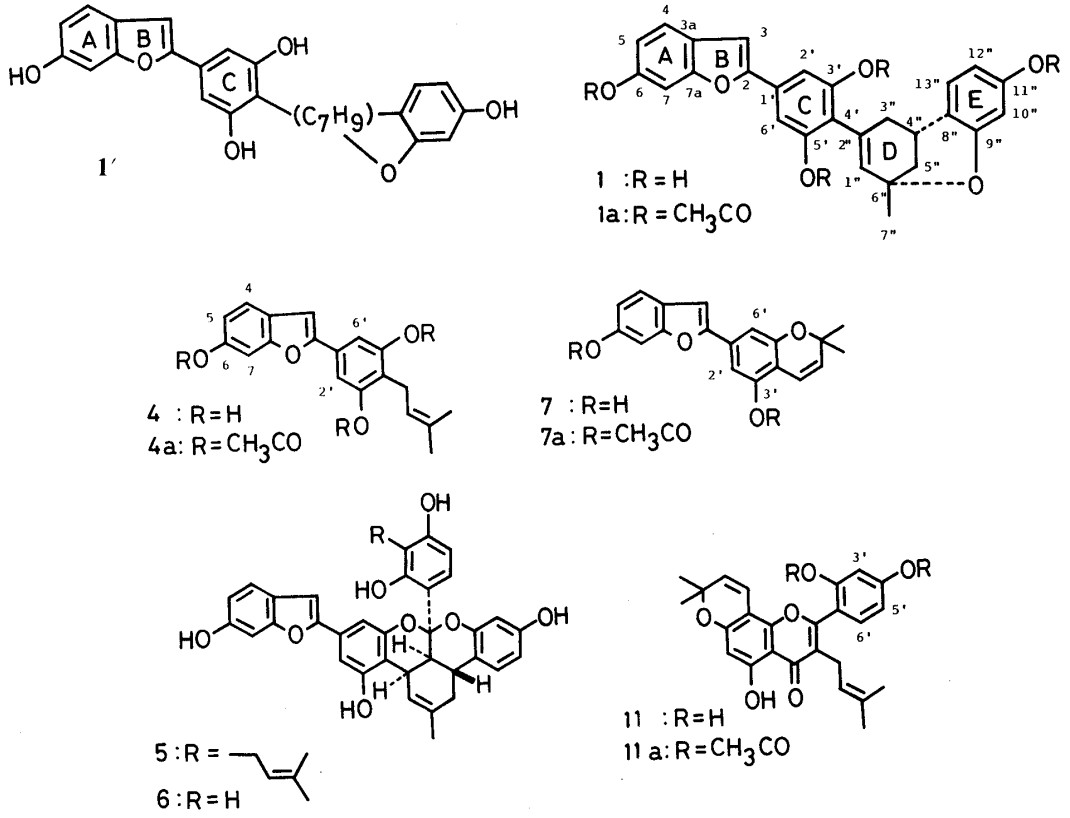
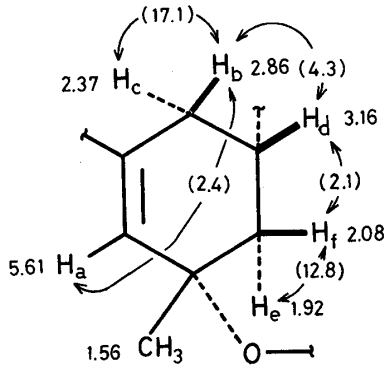


Fig. 1



$J_{a,c}=>0$ Hz
$J_{a,e}=>0$ Hz
$J_{c,d}=2.1$ Hz
$J_{c,e}=1.5$ Hz
$J_{d,e}=4.3$ Hz

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

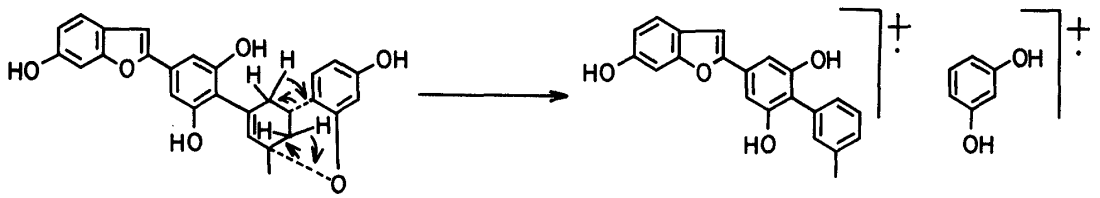
TABLE II. ^{1}H-NMR Acetylation Shifts of **1**, **4**, **7**, and **11**

	2′- and 6′-H		2′ and 6′-H		2′-H	6′-H
1	6.85[a]	**4**[5]	6.97[a]	**7**[5]	6.82	6.96[a]
1a	7.37[b]	**4a**[12]	7.41[b]	**7a**[12]	7.12	7.26[b]
Δ	−0.52	*Δ*	−0.44	*Δ*	−0.30	−0.30

	10″-H	12″-H	13″-H		7-H	5-H	4-H
1	6.27	6.37	6.97[a]	**1**	6.97	6.81	7.39[a]
1a	6.57	6.63	7.14[b]	**1a**	7.25	6.98	7.53[b]
Δ	−0.30	−0.26	−0.17	*Δ*	−0.28	−0.17	−0.14

	7-H	5-H	4-H		3′-H	5′-H	6′-H
4[5]	7.01	6.85	7.43[a]	**11**	6.55	6.59	7.23[a]
4a[12]	7.24	6.95	7.50[b]	**11a**[13]	7.11	7.12	7.46[b]
Δ	−0.23	−0.10	−0.07	*Δ*	−0.56	−0.53	−0.23

a) In Acetone-d_6. *b*) In $CDCl_3$.



1 **9**: *m/z* 332 **10**: *m/z* 110

Chart 1

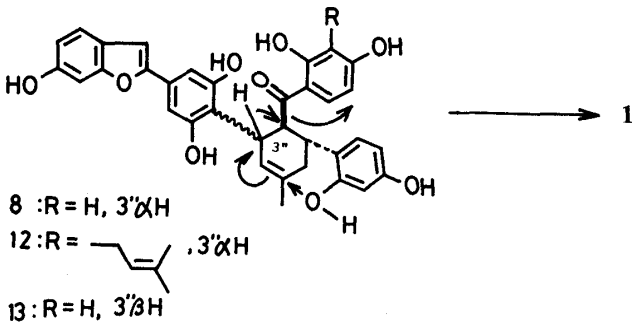
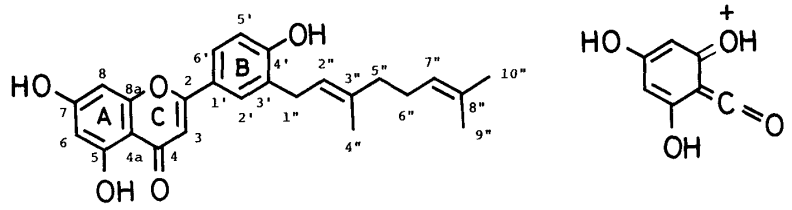


Chart 2

experiments. The deduced structure of the $C_{4''}$-side chain is shown in Fig. 2 along with the chemical shift values (δ) and the coupling constants (Hz) of the protons of the C_7H_9 moiety.

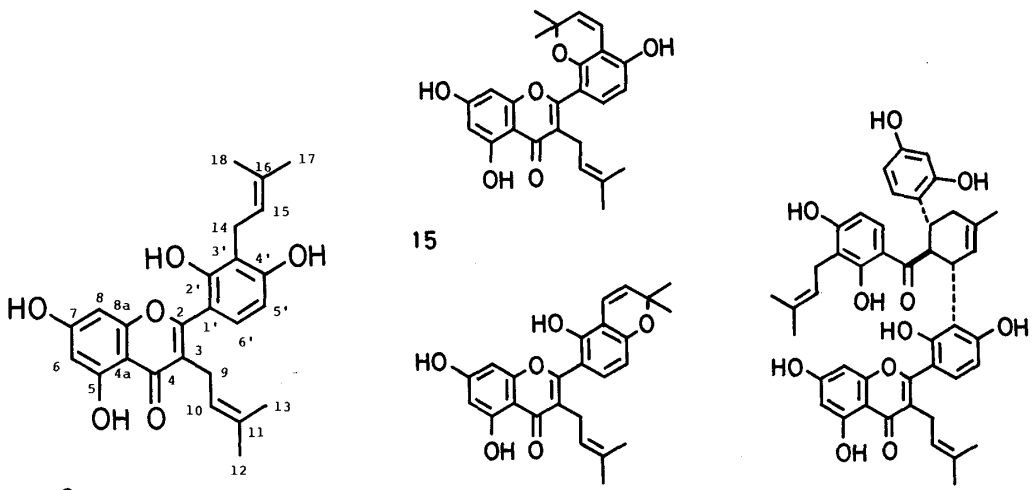
Further supporting data for the structure were obtained by the following long-range selective ^{1}H decoupling (LSPD) technique:[14] when the proton signal at δ 1.56 ($C_{6''}$-CH_3) was weakly irradiated, the carbon signal at δ 71.8 (C-6″) increased in area (*ca.* +70%). Irradiation of the signal at δ 3.16 ($C_{4''}$-H) increased the area (*ca.* +15%) of the C-6″ signal, and irradiation of the signal at δ 5.61 ($C_{1''}$-H) also increased the area (*ca.* +30%) of the same carbon signal. On the other hand, the MS of **1** showed the characteristic fragment ion at *m/z* 332 (**9**), which may be formed as shown in Chart 1. From these results, we propose the formula (**1**) for the structure (except the absolute configuration) of mulberrofuran H.

Biogenetically, mulberrofuran H seems to be a derivative of the Diels–Alder type



2 14: *m/z* 153

Fig. 3



3 15 16 17

Fig. 4

adducts, such as chalcomoracin (**12**)[7] and mulberrofurans C (**8**)[8] and J (**13**),[3b] possibly through the mechanism illustrated in Chart 2.

Kuwanon S (**2**) was obtained as yellow prisms, mp 78—80 °C, exhibiting a positive ferric chloride test and magnesium–hydrochloric acid test. The molecular formula of **2** was determined to be $C_{25}H_{26}O_5$ by high-resolution MS. The IR spectrum of **2** disclosed hydroxyl, aromatic ring, and conjugated carbonyl group absorption bands. The UV spectrum of **2** showed absorption maxima at 269, 300, and 342 nm, which shifted to 278, 304, 351, and 386 nm in the presence of aluminum chloride. When sodium methoxide was added,[15] the spectrum showed a large bathochromic shift of band I of about 50 nm, without a decrease in intensity. Based on the UV spectra and the results of the color reaction tests, **2** seems to be a flavone derivative having hydroxyl groups at the C-5 and C-4′ positions.[15] The ^{1}H-NMR spectrum of **2** showed the characteristic signal of the proton at the C-3 position [δ 6.60 (1H, s)], and revealed the presence of *meta*-coupled aromatic protons [δ 6.26 (1H, d, J=2.1 Hz, C_6-H), 6.51 (1H, d, J=2.1 Hz, C_8-H)], ABC-type aromatic protons [δ 7.02 (1H, d, J=8.5 Hz, $C_{5'}$-H), 7.76 (1H, dd, J=2.4 and 8.5 Hz, $C_{6'}$-H), 7.81 (1H, d, J=2.4 Hz, $C_{2'}$-H)], a hydrogen-bonded hydroxyl group [δ 13.04 (1H, s)], and one alkenyl ($C_{10}H_{17}$) group. The alkenyl group was assigned a geranyl structure by comparing the ^{1}H-NMR spectrum with those of 2-geranyl- and 2-nerylresorcinol[16] as well as other geranylphenols[3a,10,11,16,17] as follows: δ 1.59, 1.62 (each 3H, s, $C_{8''}$-CH_3), 1.78 (3H, s, $C_{3''}$-CH_3), *ca.* 2.12 (4H, m, $C_{5''}$-H × 2 and $C_{6''}$-H × 2), 3.43 (2H, d, J=7 Hz, $C_{1''}$-H × 2), 5.13 (1H, m, $C_{7''}$-H), 5.43 (1H, m, $C_{2''}$-H). In order to corroborate the structure of kuwanon S, the ^{13}C-NMR spectrum was analyzed, as described in the experimental section, by comparing the spectrum with that of a model compound, apigenin,[18] taking into account the substituent effect of the alkyl group on the B-ring.[19] The

presence of a geranyl group was suggested by comparing the chemical shifts of the signals of C-4'' and C-5'' of **2** with the shifts of the relevant carbon atoms of geraniol and nerol[20] as well as of geranylphenols.[3a,10,11,17] The MS of **2** gave a significant peak at *m/z* 153 (**14**)[13,17,21] arising from the A-ring by a retro Diels–Alder fragmentation.[13,17] All these data indicate that kuwanon S can be represented by formula **2**.

Kuwanon T (**3**) was obtained as yellow prisms, mp 191—193 °C, exhibiting a positive ferric chloride test and magnesium–hydrochloric acid test. The molecular formula of **3** was determined to be $C_{25}H_{26}O_6$ by high-resolution MS. The IR spectrum of **3** disclosed hydroxyl, aromatic ring, and conjugated carbonyl group absorption bands. The UV spectrum of **3** showed absorption maxima at 230 (sh), 254 (sh), 259, 295 (sh), 326 nm, and was similar to those of kuwanons A (**15**) and B (**16**).[21] The ^{1}H-NMR spectrum of **3** showed the characteristic signals of two γ,γ-dimethylallyl groups [δ 1.39, 1.57, 1.66, and 1.77 (each 3H, br s or br d), 3.08 and 3.45 (each 2H, br d, $J=7$ Hz), 5.10 and 5.31 (each, 1H, br t, $J=7$ Hz)]. Based on the UV and the ^{1}H-NMR spectrum as well as the results of color reaction tests, **3** seems to be a flavone derivative having a γ,γ-dimethylallyl group at the C-3 position.[13] The ^{1}H-NMR spectrum also revealed the presence of *meta*-coupled aromatic protons [δ 6.24 (1H, d, $J=1.8$ Hz, C_6-H), 6.31 (1H, d, $J=1.8$ Hz, C_8-H)], *ortho*-coupled aromatic protons [δ 6.58 (1H, d, $J=8.4$ Hz, $C_{5'}$-H), 7.01 (1H, d, $J=8.4$ Hz, $C_{6'}$-H)], and a hydrogen-bonded hydroxyl group [δ 13.12 (1H, s)]. A 2′,4′-dioxygenated B-ring pattern is suggested on the basis of the biogenetic analogy to the other prenylflavonoids isolated from *Morus* sp. and of the chemical shift values of the B-ring protons as well as the coupling pattern.[21,22] The MS of **3** gave a significant peak at *m/z* 153 (**14**). From these results, the structure of kuwanon T seems to be **3**. In order to corroborate this structure, the ^{13}C-NMR spectrum was analyzed by comparing the signals with those of model compounds, apigenin,[18] morusin (**11**),[22a] and kuwanon C,[22a] taking into account the substituent effect of the alkyl group[19] and that of kuwanon N (**17**).[3d] In the ^{13}C-NMR spectrum of **3**, the chemical shift values of the flavone skeleton were similar to those of the relevant carbon atoms of **17** (Table I). All these results indicate that kuwanon T can be represented by the formula **3**.

Experimental

All melting points are uncorrected. The ^{1}H- and ^{13}C-NMR spectra were measured with tetramethylsilane (TMS) as an internal reference. Chemical shifts are expressed in ppm downfield from TMS, and coupling constants (J) in Hz. abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, ddd = doublet of double doublets, m = multiplet, 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 NMR spectrometer; ^{13}C-NMR spectra, Hitachi R-900 FT-NMR, JEOL GX-270 and JEOL FX-100 NMR spectrometers; optical rotation, JASCO DIP-4; MS, JEOL JMS 01SG-2; high-resolution MS, Hitachi RMU-7M mass spectrometer. Wakogel B-5FM was used for TLC, Wakogel B-5F for preparative TLC, and Wakogel C-200 for column chromatography.

Isolation of Mulberrofuran H (1)——The ethyl acetate extract (300 g) of the root bark of the cultivated mulberry tree (Japanese name "Rosō," a cultivated variety of *Morus lhou* Koidz.), described in the previous paper,[3d] was chromatographed on silica gel (1.6 kg) with benzene (1.5 l) and benzene–MeOH (128 l) as successive eluents, each fraction (fr.) (500 ml) being monitored by TLC. The fractions (fr. 200—286) eluted with benzene containing 1% MeOH, which showed a characteristic spot with light blue fluorescence under UV light on the TLC plate, were evaporated to give the residue (12 g). To isolate the fluorescent compound, the residue (12 g) was rechromatographed on silica gel (100 g) with *n*-hexane–acetone as an eluent. The fractions eluted with *n*-hexane containing 20% acetone were evaporated to give the residue (0.8 g), which was fractionated by preparative TLC (solvent system, $CHCl_3:(CH_3)_2CO=3:1$, $CHCl_3:MeOH=12:1$, $C_6H_6:MeOH=4:1$) to give mulberrofuran H (**1**, 43 mg, 7×10^{-4}% from the root bark).

Isolation of Kuwanons S (2) and T (3)——The ethyl acetate extract (300 g) of the root bark, described in the previous paper,[3d] was chromatographed on silica gel (1.6 kg) with benzene (34 l) and benzene–MeOH (40 l) successively, each fraction (500 ml) being monitored by TLC. The fractions (fr. 118—119) eluted with benzene

containing 1% MeOH was evaporated to give the residue (5.4 g), which was rechromatographed on silica gel (60 g) with *n*-hexane–acetone as an eluent. The fractions eluted with *n*-hexane containing 30% acetone were evaporated to give the residue (1.2 g), which was fractionated by preparative TLC ($CHCl_3$: Et_2O = 4 : 1, C_6H_6 : MeOH = 10 : 1, $CHCl_3$: $(CH_3)_2CO$ = 6 : 1, *n*-hexane : AcOEt = 2 : 1) to give kuwanons S (2 mg) and T (20 mg).

Mulberrofuran H (1)——Compound **1** was obtained as an amorphous powder. One spot was detected on TLC ($CHCl_3$: $(CH_3)_2CO$ = 3 : 1, $CHCl_3$: MeOH = 12 : 1, C_6H_6 : Et_2O = 4 : 1). $[\alpha]_D^{22}$ +25° (*c* = 0.103, MeOH). MS *m/z*: 442 (M^+), 332, 110. High-resolution MS, Calcd for $C_{27}H_{22}O_6$ (M^+), *m/z* 442.1415. Found: *m/z* 442.1400; Calcd for $C_{21}H_{16}O_4$, *m/z* 332.1048. Found: *m/z* 332.1058; Calcd for $C_6H_6O_2$, *m/z* 110.0367. Found: *m/z* 110.0368. $FeCl_3$ test: negative. UV λ_{max}^{EtOH} nm (log ε): 220 (sh 4.48), 285 (sh 4.15), 321 (4.52), 333 (sh 4.45). IR ν_{max}^{KBr} cm^{-1}: 3400 (br), 1640 (sh), 1620, 1600 (sh). ^{1}H-NMR ($(CD_3)_2CO$, digital resolution: 0.31 Hz) δ: 1.56 (3H, s, $C_{6''}$-CH_3), 1.92 (1H, br dd, *J* = 4.3, 12.8, $C_{5''}$-H), 2.08 (1H, dd, *J* = 2.1, 12.8, $C_{5''}$-H), 2.37 (1H, br d, *J* = 17.1, $C_{3''}$-H), 2.86 (1H, ddd, $J_{1'',3''}$ = 2.4, $J_{3'',4''}$ = 4.3, $J_{3'',3''}$ = 17.1, $C_{3''}$-H), 3.16 (1H, m, $C_{4''}$-H), 5.61 (1H, br s, $C_{1''}$-H), 6.27 (1H, d, *J* = 2, $C_{10''}$-H), 6.37 (1H, dd, *J* = 2, 8, $C_{12''}$-H), 6.81 (1H, dd, *J* = 2, 9, C_5-H), 6.85 (2H, s, $C_{2'}$- and $C_{6'}$-H), 6.97 (1H, br d, *J* = 2, C_7-H), 6.97 (1H, d, *J* = 8, $C_{13''}$-H), 6.99 (1H, br s, C_3-H), 7.39 (1H, d, *J* = 9, C_4-H).

Mulberrofuran H Tetraacetate (1a)——A mixture of **1** (7 mg), acetic anhydride (0.5 ml) and pyridine (0.2 ml) was kept at room temperature overnight, and then poured into ice water. The solid was collected and purified by preparative TLC (Et_2O : *n*-hexane = 2 : 5) to give an amorphous powder (**1a**, 4 mg). MS *m/z*: 610 (M^+), 525, 123. UV λ_{max}^{EtOH} nm (log ε): 230 (sh 3.94), 285 (sh 3.95), 300 (infl. 4.14), 311 (4.28), 325 (4.19). IR ν_{max}^{KBr} cm^{-1}: 1760, 1610, 1585, 1200. ^{1}H-NMR ($CDCl_3$, digital resolution: 0.31 Hz) δ: 1.56 (3H, s, $C_{6''}$-CH_3), 1.78 (1H, dd, *J* = 2, 12, $C_{5''}$-H), 1.97 (1H, br dd, *J* = 4, 12, $C_{5''}$-H), 2.27, 2.34 (each 6H, s, CH_3CO–), 2.38 (1H, br d, *J* = 17, $C_{3''}$-H), 2.68 (1H, ddd, $J_{1'',3''}$ = 2, $J_{3'',4''}$ = 4, $J_{3'',3''}$ = 17, $C_{3''}$-H), 3.23 (1H, m, $C_{4''}$-H), 5.56 (1H, br s, $C_{1''}$-H), 6.57 (1H, d, *J* = 2, $C_{10''}$-H), 6.63 (1H, dd, *J* = 2, 8, $C_{12''}$-H), 6.97 (1H, d, *J* = 0.7, C_3-H, combined with a part of the C_5-H signal), 6.98 (1H, dd, *J* = 2, 8, C_5-H), 7.14 (1H, d, *J* = 8, $C_{13''}$-H), 7.25 (1H, dd, *J* = 0.7, 2, C_7-H), 7.37 (2H, s, $C_{2'}$- and $C_{6'}$-H), 7.53 (1H, d, *J* = 8, C_4-H).

Kuwanon S (2)——Compound **2** was crystallized from MeOH to give pale yellow prisms, mp 78—80 °C (mp 144—146 °C from C_6H_6–$(CH_3)_2CO$), $FeCl_3$ test: dark brown, Mg–HCl test: positive. UV λ_{max}^{EtOH} nm (log ε): 210 (4.40), 235 (sh 4.06), 269 (4.03), 300 (infl. 3.94), 342 (4.14); $\lambda_{max}^{EtOH+AlCl_3}$: 210 (4.41), 230 (infl. 4.18), 255 (sh 3.81), 278 (4.01), 304 (3.94), 351 (4.09), 386 (4.04); $\lambda_{max}^{EtOH+NaOMe}$: 265 (infl. 4.06), 277 (4.07), 325 (3.91), 400 (4.20). IR ν_{max}^{KBr} cm^{-1}: 3530 (br), 1665, 1620, 1600, 1570. High-resolution MS, Calcd for $C_{25}H_{26}O_5$ (M^+), *m/z* 406.1779. Found: *m/z* 406.1784; Calcd for $C_{24}H_{23}O_5$, *m/z* 391.1546. Found: *m/z* 391.1568; Calcd for $C_{20}H_{18}O_5$, *m/z* 338.1155. Found: *m/z* 338.1166; Calcd for $C_{19}H_{15}O_5$, *m/z* 323.0920. Found: *m/z* 323.0943; Calcd for $C_7H_5O_4$, *m/z* 153.0186. Found: *m/z* 153.0164. ^{1}H-NMR ($(CD_3)_2CO$, digital resolution: 0.18 Hz) δ: 1.59, 1.62, 1.78 (each 3H, br s, $C_{3''}$- or $C_{8''}$-CH_3), 2.05—2.18 (4H, m, $C_{5''}$- and $C_{6''}$-H), 3.43 (2H, br d, *J* = 7.3, $C_{1''}$-H × 2), 5.13 (1H, multiplet of triplet, *J* = 7.0, $C_{7''}$-H), 5.43 (1H, quartet of triplet, *J* = 1.1, 7.3, $C_{2''}$-H), 6.26 (1H, d, *J* = 2.1, C_6-H), 6.51 (1H, d, *J* = 2.1, C_8-H), 6.60 (1H, s, C_3-H), 7.02 (1H, d, *J* = 8.5, $C_{5'}$-H), 7.76 (1H, dd, *J* = 2.4, 8.5, $C_{6'}$-H), 7.81 (1H, d, *J* = 2.4, $C_{2'}$-H), 9.46 (2H, br, OH × 2), 13.04 (1H, s, C_5-OH). ^{13}C-NMR ($(CD_3)_2CO$, 67.8 MHz) δ: 16.3 (q, C-4″), 17.8 (q, C-9″), 25.8 (q, C-10″), 27.5 (t, C-6″), 28.9 (t, C-1″), 40.5 (t, C-5″), 94.7 (d, C-8), 99.7 (d, C-6), 104.0 (d, C-3), 105.3 (s, C-4a), 116.3 (d, C-5′), 122.9 (d, C-2″), 123.2 (s, C-1′), 125.0 (d, C-6′), 126.6 (d, C-7″), 128.8 (d, C-2′), 129.9 (s, C-8″), 131.8 (s, C-3″), 137.2 (s, C-3′), 158.8 (s, C-8a), 159.6 (s, C-5), 163.4 (s, C-4′), 164.9 (s, C-7), 165. 4 (s, C-2), 183.0 (s, C-4).

Kuwanon T (3)——Compound **3** was crystallized from MeOH to give pale yellow prisms, mp 191—193 °C, $FeCl_3$ test: dark purple, Mg–HCl test: positive. UV λ_{max}^{EtOH} nm (log ε): 230 (sh 4.69), 254 (sh 4.60), 259 (4.61), 295 (sh 4.23), 326 (4.27); $\lambda_{max}^{EtOH+AlCl_3}$: 328 (infl. 4.65), 265 (infl. 4.64), 268 (4.65), 314 (sh 4.12), 333 (4.15), 372 (4.17). IR ν_{max}^{KBr} cm^{-1}: 3350 (br), 1650, 1620 (sh), 1615, 1570. High-resolution MS, Calcd for $C_{25}H_{26}O_6$ (M^+), *m/z* 422.1729. Found: *m/z* 422.1729. MS *m/z*: 422 (M^+), 379, 311, 213, 187, 153. ^{1}H-NMR ($(CD_3)_2CO$, digital resolution: 0.18 Hz) δ: 1.39 and 1.77 (each 3H, br s, C_{11}- or C_{16}-CH_3), 1.57 (3H, br d, *J* = 1.1, C_{11}- or C_{16}-CH_3), 1.66 (3H, br d, *J* = 0.9, C_{11}- or C_{16}-CH_3), 3.08 (2H, br d, *J* = 7.2, C_9- or C_{14}-H × 2), 3.45 (2H, br d, *J* = 7.3, C_9- or C_{14}-H × 2), 5.10 and 5.31 (each 1H, br t, *J* = 7, C_{10}- or C_{15}-H), 6.24 (1H, d, *J* = 1.8, C_6-H), 6.31 (1H, d, *J* = 1.8, C_8-H), 6.58 (1H, d, *J* = 8.4, $C_{5'}$-H), 7.01 (1H, d, *J* = 8.4, $C_{6'}$-H), 13.12 (1H, s, C_5-OH).

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References and Notes

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