STRUCTURES OF MULBERROFURANS B AND L, 2-ARYLBENZOFURAN DERIVATIVES FROM THE ROOT BARK OF THE CULTIVATED MULBERRY TREE (MORUS LHOU (SER.) KOIDZ.)[1,2]

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Abstract ——— Mulberrofuran L, a new 2-arylbenzofuran derivative, was isolated from benzene extract of the cultivated mulberry tree (Japanese name "Rosô", a cultivated variety of Morus lhou (SER.) KOIDZ), and the structure was shown to be 3 on the basis of the spectral and chemical data. The structure of mulberrofuran B was reversed from the structure (2) to 2' on the basis of the formation of 3 from 2'.

In the previous papers,[3,4] we reported a series of 2-arylbenzofuran derivatives obtained from the root barks of mulberry tree and the callus culture of Morus alba L. In this paper, we report the structure of a new 2-arylbenzofuran derivative, mulberrofuran L obtained from the cultivated mulberry tree (Japanese name "Rosô", a cultivated variety of Morus lhou (SER.) KOIDZ),[5] as well as the revised structure of mulberrofuran B.[6]

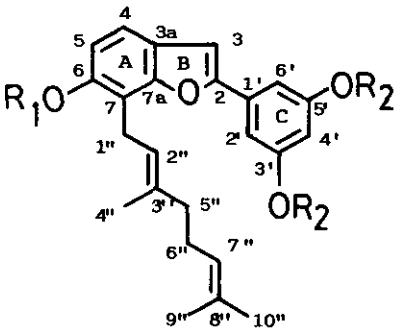
The dried root bark of the cultivated mulberry tree (Japanese name "Rosô") was extracted successively with hexane and benzene. From the benzene extract, mulberrofurans A (1),[7] B (2),[6] and a new compound, mulberrofuran L (3) were isolated. The known compounds (1 and 2) were identical with authentic specimens. Mulberrofuran L (3) was obtained as colorless needles, mp 148-152 °C, M^+ = 378.1861, $C_{24}H_{26}O_4$, exhibiting a negative ferric chloride test. The ir spectrum disclosed absorption bands for hydroxyl and benzene ring, and showed the absence

of carbonyl function as follows: $\nu_{max}^{CHCl_3}$ cm^{-1}, 3600, 3350 (br), 1620, 1610, 1580, 1490. The uv spectrum exhibited maxima at 244(sh), 254 (sh), 280 (infl.), 315, and 330 (sh) nm, and resembled those of mulberrofurans A (1),[7] D (4),[3c] and other 6,3',5'-trioxygenated 2-arylbenzofuran derivatives[8] suggesting that 3 possesses a 6,3',5'-trioxygenated 2-arylbenzofuran skeleton.

Treatment of 3 with dimethyl sulfate and potassium carbonate in acetone effected exhaustive methylation to give trimethyl ether (3a), m/z 420 (M^+) as an oily substance. The ^1H nmr spectrum of 3 (100 MHz, acetone-d_6) showed the signals corresponding to six protons in the aromatic region. A sharp singlet at δ 7.02 probably due to C-3-H suggests that C-7 position of the benzofuran ring is occupied by a substituent, since a small long-range coupling was observed between protons on C-3 and C-7 in C-7 unsubstituted 2-arylbenzofuran.[3c,7,9] An AB system, e.g. two doublets at δ 6.85 (1H, d, J = 8, C-5-H) and δ 7.25 (1H, d, J = 8, C-4-H) indicates that the hydrogen atoms in the A-ring were replaced by the substituents in the 4- and 7-positions or in the 6- and 7-positions and the chemical shift values were similar to those of 6-oxygenated benzofurans.[3c] In the ^{13}C nmr spectrum of 3, all the carbon atoms were assigned by the insensitive nuclear enhanced by population transfer (INEPT) technique as well as by comparison of the ^{13}C nmr spectrum of 3 with those of the model compounds, mulberrofurans D (4),[3c] G (5)[3d] and the benzofuran derivatives.[10] The chemical shift values of the carbon atoms of the A-ring were similar to those of the relevant carbon atoms of 4[3c] (Table 1). These results suggest that mulberrofuran L has a 6-oxygenated-7-alkenyl substituted-benzofuran partial structure.

The ^1H nmr spectrum of 3 showed the meta-coupled two proton doublet (J = 2 Hz) at δ 6.91 (C-2' and C-6'-H) and the meta-coupled triplet (J = 2) at δ 6.38 (C-4'-H), and also showed the presence of geranyl (or neryl) group as follows: δ 1.53, 1.57, 1.91 (each 3H, br s, C-3"-CH_3 and C-8"-CH_3 x 2), 2.01 (4H, br s, C-5" and C-6"-H x 2, overlapping with the solvent), 3.65 (2H, br d, J = 7, C-1"-H x2), 5.05 (1H, m, C-7"-H), 5.48 (1H, br t, J = 7, C-2"-H). The possibility of geranyl group was supported by comparing the chemical shifts of the signals of the C-4" and C-5" of 3 with the shifts of the relevant carbon atoms of geraniol and nerol.[11]

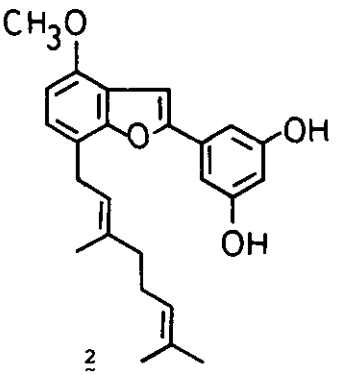
The substituent pattern of the A-ring was confirmed by the following results. After the mixture of 3 and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was kept in dry benzene at room temperature, the reaction mixture was purified by preparative thin layer chromatography to give compound (6).[3c,12] The presence of 2-methyl-2-



3:$R_1 = R_2 = H$ (= 2'a)

3a : $R_1 = R_2 = CH_3$ (= 2'b)

2':$R_1 = CH_3$, $R_2 = H$



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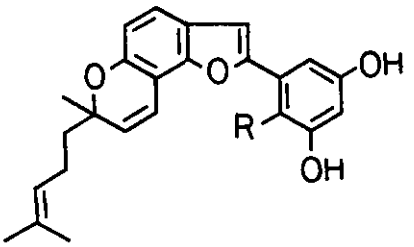
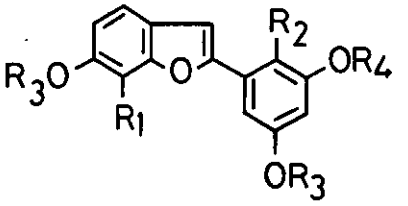
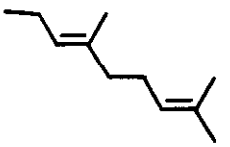


6: R = H

8: R = 3,3-dimethylallyl

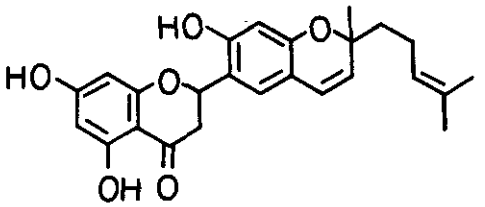


1:$R_1 = R_3 = H$, $R_4 = CH_3$

R_2 =  (geranyl)

4:R_1 = geranyl, R_2 = 3,3-dimethylallyl, $R_3 = R_4 = H$

4a:R_1 = geranyl, R_2 = 3,3-dimethylallyl, $R_3 = R_4 = CH_3$



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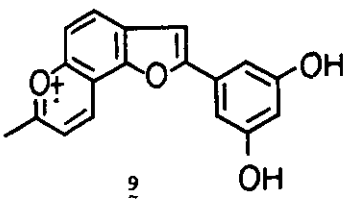

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Fig. 1

(4-methylpent-3-enyl)chromene ring as a partial structure of 6 was supported by comparison of the ^1H nmr spectrum and mass spectrum of 6 with those of kuwanon F (7)[12] and compound (8)[3c] as follows: 6, δ 1.43 (3H, s, C-3"-CH_3), 1.57, 1.64 (each 3H, br s, C-8"-CH_3), ~ 1.76 (2H, m, C-5"-H x 2), ~ 2.17 (2H, m, C-6"-H x

Table 1 ^{13}C nmr chemical shifts (ppm) of 2 - 5

carbon	3	2'*	2'	4	4a	5
2	155.4	155.9	155.2	156.1	155.1	157.7**
3	102.6	102.5	102.9	103.9	105.4	102.2
3a	122.6	123.7	122.9	122.3	123.0	122.5
4	118.9	118.9	118.0	118.7	117.8	122.0
5	113.1	108.9	108.4	112.8	108.1	113.4
6	153.5	155.6	154.5	154.5	154.9	155.0**
7	112.2	114.0	114.0	110.6	113.9	98.4
7a	153.5	154.5	154.3	152.2	154.1	156.7**
1'	135.7	135.7	135.5	139.0	135.2	
2'	103.8	104.0	104.4	118.1	121.5	
3'	159.8	159.8	157.1	154.0	158.5	
4'	103.5	103.7	102.2	105.7	99.2	
5'	159.9	159.8	157.1	154.5	159.0	
6'	103.8	104.0	104.4	108.6	104.5	
1"(1'")	23.3	23.3	22.9	23.1	22.9	
2"(2'")	123.0	122.9	122.0	121.1	122.1	
3"(3'")	133.6	133.3	133.3	134.4	131.8	
4"(4'")	16.4	16.4	16.2	16.3	16.2	
5"(5'")	40.5	40.4	39.8	39.7	39.8	
6"(6'")	27.4	27.3	26.7	26.4	26.7	
7"(7'")	125.0	125.0	124.4	123.9	124.4	
8"(8'")	131.6	131.6	131.4	132.1	131.3	
9"(9'")	17.7	17.6	17.6	17.7	17.6	
10"(10'")	25.7	25.7	25.6	25.7	25.6	
OCH_3		56.9	56.8		55.4	
					55.8	
					56.8	
solvent	A	A	B	B	B	A

solvent; A : acetone-d_6, B : $CDCl_3$

• : The carbon shift assignment is based on the use of selective ^1H decoupling and LSPD technique; ** : Assignments may be reversed.

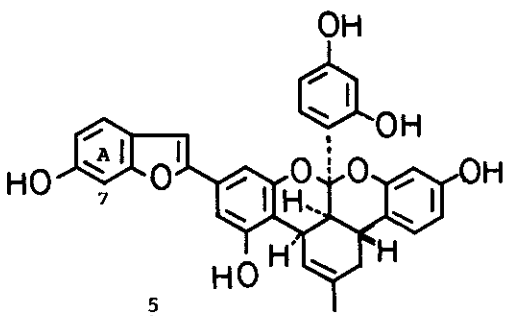

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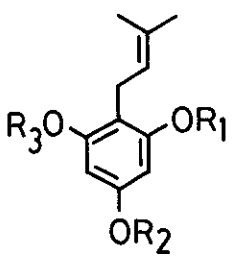
Table 2 Mass spectral data of 10 - 13

compound	$M^+ - C_3H_7$	$M^+ - C_4H_7$
10	m/z 151 (10%)	139 (100)
11	none	181 (20)
12	179 (28)	167 (83)
13	none	167 (23)



10 : $R_1 = R_2 = R_3 = H$

11 : $R_1 = R_2 = R_3 = CH_3$

12 : $R_1 = R_2 = CH_3$, $R_3 = H$

13 : $R_1 = R_3 = CH_3$, $R_2 = H$

2), 5.13 (1H, br t, J = 6, C-7"-H), 5.85 (1H, d, J = 10, C-2"-H), 6.92 (1H, d, J = 10, C-1"-H); m/z 376 (M^+), 293 (**9**, base peak), 83. From these results, we propose the formula (**3**) for the structure of mulberrofuran L.

We proposed the formula (**2**) for the structure of mulberrofuran B on the basis of spectral data.[6] In the paper, two possible structures (**2** and **2'**) were suggested, and the formula (**2**) was proposed on the basis of the following examination of the mass spectrum of mulberrofuran B. If a geranyl side chain was adjacent to a methoxyl group, the mass spectrum would exhibit fragment ions at m/z 281 ($M^+ - C_8H_{15}$) and m/z 269 ($M^+ - C_9H_{15}$).[7,13] As a fragment ion at m/z 281 was not observed, the formula (**2'**) was excluded. Recently, the mass spectrum of prenylphloroglucinol derivatives (**10**[14], **11**[15], **12**[16], and **13**) were examined (Table 2). The compounds (**11** and **13**), having a prenyl side chain adjacent to methoxyl groups on both sides, showed no fragment ions at m/z 193 ($M^+ - C_3H_7$) and m/z 179 ($M^+ - C_3H_7$), respectively. These results suggest that the formula (**2**) for mulberrofuran B should be reinvestigated. In the ^{13}C nmr spectrum of mulberrofuran B, the chemical shift values of the carbon atoms of the A-ring were similar to those of the relevant carbon atoms of mulberrofuran D trimethyl ether (**4a**)[3c] (Table 1). This result suggests that mulberrofuran B has the substituent pattern on A-ring as **4a**. Further supporting data for the structure were obtained by the following long-range selective ^1H decoupling (LSPD) technique[17] and nuclear Overhauser effect (NOE) measurements: When the signal at δ 3.62 (C-1"-H x 2) and δ 7.34 (C-4-H) were weakly irradiated, the signals at δ 154.5 (C-7a) and δ 155.6 (C-6) were altered. The irradiation of the signals at δ 7.34 (C-4-H) and δ 3.86 (C-6-OCH_3) altered the signals of the carbon atoms at C-6 and C-7a positions (Fig. 2). The NOE experiment was carried out as follows: Irradiation of the methoxyl hydrogens at δ 3.86 (C-6-OCH_3) produced 20% enhancement of the signal at δ 6.92 (C-5-H), while irradiation of the signal at δ 3.62 (C-1"-H x 2) produced no observable enhancement on the aromatic proton signals. From these results, the 7-oxygenated-6-geranyl substituted benzofuran partial structure was excluded. Final proofs for the structure (**2'**) were obtained by the following results. When mulberrofuran B was treated with pyridine-hydrochloride,[18] demethylmulberrofuran B (**2'a**) was obtained, which was identical with mulberrofuran L (**3**) by the thin layer chromatography and the ir spectroscopy. Mulberrofuran B dimethyl ether (**2'b**), obtained by treatment of **2'** with dimethyl sulfate and potassium carbonate in acetone, was identical with mulberrofuran L trimethyl ether (**3a**) by the thin layer chromatography and the ir spectroscopy. From above

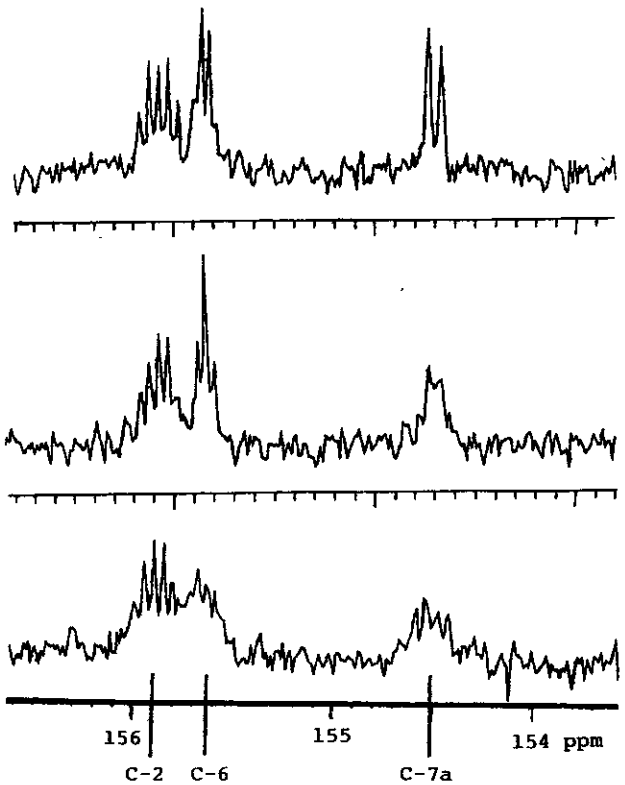


Fig. 2 LSPD spectra of mulberrofuran B (2')
The sample (20 mg) was dissolved in acetone-d_6. The conditions for (b) and (c) were as follows, flip angle 45°, repetition time 1 sec, 10000 accumulations, data points 32K, spectral width 2 KHz, power level for LSPD ($\gamma H_2/2\pi$) 80 Hz.

results, we propose the revised formula (2') for the structure of mulberrofuran B.

EXPERIMENTAL

All melting points were uncorrected. The nmr spectra were measured with tetramethylsilane as the internal reference. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, br = broad, sh = shoulder, infl. = inflection. The following instruments were used: uv spectra; Hitachi 340 UV Spectrometer, ir spectra; Hitachi 295 IR Spectrometer, mass spectra (ms); JEOL JMS OISG-2 Mass Spectrometer, ^{1}H nmr spectra; JEOL GX-400, FX-100 FT NMR Spectrometers, JEOL JNM 4H-100 NMR Spectrometer, and Varian XL-200 NMR Spectrometer. ^{13}C nmr spectra; JEOL FX-100 and FX-270 NMR Spectrometers, and Hitachi R-900 FT NMR Spectrometer. Long-range selective ^{1}H decoupling technique (LSPD); JEOL GX-400 FT NMR Spectrometer, nuclear Overhauser effect (NOE) measurement: JEOL GX-400 FT NMR Spectrometer. For thin layer chromatography (TLC), Wakogel B-5F and Merck Kieselgel 60 PF_{254} were used. For column chromatography, Wakogel C-200 was used.

Isolation of mulberrofurans A (1), B (2'), and L(3)

The dried root bark of the cultivated mulberry tree (4 Kg, Japanese name "Rosô", a cultivated variety of Morus lhou (SER.) KOIDZ.), collected in the neighbourhood of Takasaki, Gunma Prefecture, Japan, in December 1981, was extracted successively with n-hexane and benzene. Evaporation of the benzene solution to dryness yielded 27 g of the residue. This benzene extract was dissolved in methanol and the methanol solution was evaporated to give residue (15 g). The methanol extract (15 g) was chromatographed on deactivated silica gel[19] (4.5 x 40 cm) with benzene (saturated with water) as an eluent, each fraction (500 ml) being monitored by TLC. The fractions (No. 13 - 15) were evaporated to give the residue (2.7 g), which was fractionated by preparative TLC (benzene:methyl ethyl ketone = 7:1, benzene:acetone:ammonia water = 100:20:0.2) to give mulberrofurans A (1, 94 mg) and B (2', 107 mg). The fractions (No. 23 - 28) were evaporated to give the residue (0.35 g), which were fractionated by preparatie TLC (acetone:n-hexane:benzene = 2:1:1) to give mulberrofuran L (3, 20 mg). The known compounds (1 and 2') were identical with authentic specimens by comparison of TLC and ^{1}H nmr spectra.

Mulberrofuran L (3)

The compound (3) was obtained as colorless needles, mp 148 - 152 °C (from benzene-n-hexane). High-resolution ms : Calcd. for $C_{24}H_{26}O_4$ (M^+, m/z) : 378.1836. Found: 378.1861. uv λ_{max}^{MeOH} nm (log ε): 244 (sh 3.85), 254 (sh 3.79), 280 (infl. 3.81), 315 (4.30), 330 (sh 4.19). ir $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3350 (br), 1620, 1610, 1580, 1490. ^{1}H nmr (100 MHz, acetone-d_6): δ 1.53, 1.57, 1.91 (each 3H, br s, C-3"-CH_3 and C-8"-CH_3 x 2), 2.01 (4H, br s, C-5"-H x 2 and C-6"-H x 2, overlapping with the solvent), 3.65 (2H,br d, J = 7, C-1"-H x 2), 5.05 (1H, m, C-7"-H), 5.48 (1H, br t, J = 7, C-2"-H), 6.38 (1H, t, J = 2, C-4'-H), 6.85 (1H, d, J = 8, C-5-H), 6.91 (2H, d, J = 2, C-2'-H and C-6'-H), 7.02 (1H, s, C-3-H), 7.25 (1H, d, J = 8, C-4-H), 8.37 (1H, s, OH), 8.48 (2H, s, OH). ms (75 eV) m/z (relative intensity): 379 (M^+ + 1, 20), 378 (M^+, 78), 293 (29), 256 (22), 255 (84), 254 (100), 239 (10), 225 (10), 137 (50), 123 (29), 109 (13), 81 (11), 69 (58), 41 (77).

Treatment of mulberrofuran L (3) with DDQ

A mixture of 3 (4 mg) and DDQ (5 mg) in dry benzene was allowed to stand for 3.5 h at room temperature and the solvent was removed under reduced pressure. The product was purified by preparative TLC (n-hexane:acetone = 2:1) to give the amorphous powder (6, 2 mg). ir $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3300 (br), 1640, 1610, 1580, 1480. ^{1}H nmr (400 MHz, acetone-d_6): δ 1.43 (3H, s, C-3"-CH_3), 1.57, 1.64 (each 3H, br s, C-8"-CH_3), ~ 1.76 (2H, m, C-5"-H x 2), ~ 2.17 (2H, m, C-6"-H x 2), 5.13 (1H, br t, J = 6, C-7"-H), 5.85 (1H, d, J = 10, C-2"-H), 6.38 (1H, t, J = 2, C-4'-H), 6.72 (1H, d, J = 8, C-5-H), 6.89 (2H, d, J = 2, C-2'-H and C-6'-H), 6.92 (1H, d, J = 10, C-1"-H), 7.06 (1H, s, C-3-H), 7.33 (1H, d, J = 8, C-4-H), 8.49 (2H, s, OH x 2). ms (75 eV) m/z (relative intensity): 376 (M^+, 26), 294 (20), 293 (100), 123 (13), 111 (13), 109 (15), 98 (19), 97 (27), 95 (28), 93 (16), 85 (22), 84 (13), 83 (33), 82 (14), 81 (25), 79 (14), 71 (41), 70 (12), 69 (48), 68 (13), 67 (27), 59 (20), 56 (15). 57 (67), 55 (60), 45 (26), 44 (47), 43 (76), 41 (68).

Mulberrofuran L trimethyl ether (3a)

A mixture of 3 (6 mg), dimethyl sulfate (0.1 ml), and potassium carbonate (5 g) in acetone (30 ml) was refluxed for 40 min, and treated as usual. The product was purified by preparative TLC (benzene:n-hexane = 1:1) to give oily substance (3a, 3.5 mg). The compound (3a) was identical with mulberrofuran B dimethyl ether (2'a) by TLC (benzene:n-hexane = 1:1) and the ir spectroscopy. ir $\nu_{max}^{CHCl_3}$ cm^{-1}: 3010, 2960, 2850, 1610, 1600, 1580, 1500, 1340.

Demethylation of mulberrofuran B (2') (Formation of mulberrofuran L (3) from 2')

Mulberrofuran B (2', 40 mg) was added to pyridine-hydrochloride (190 mg) and the mixture was heated at 215 °C for 15 min.[18] After the tube was cooled, the reaction mixture was dissolved in ether and diluted with water. After extractions with ether, the combined extract was washed with

water. The solution was evaporated under reduced pressure and the residue was purified by preparative TLC (n-hexane:acetone = 2:1, benzene:acetone = 4:1) to give 2'a (2 mg). The compound (2'a) thus obtained was identical with 3 by TLC (n-hexane:acetone = 2:1, benzene:acetone = 4:1, chloroform:methanol = 10:1) and the ir spectoroscopy.

Mulberrofuran B dimethyl ether (2'b)

A mixture of 2' (28 mg), dimethyl sulfate (0.1 ml), and potassium carbonate (5 g) in acetone (25 ml) was refluxed for 40 min, and treated as usual. The product was purified by preparative TLC (benzene:n-hexane = 1:1) to give oily substance (2'b, 19 mg). ms (75 eV) m/z (relative intensity) : 421 (M^+ + 1, 42), 420 (M^+, 100), 352 (7), 351 (18), 334 (8), 333 (28), 321 (14), 298 (15), 297 (23), 165 (23), 151 (10), 123 (17), 69 (30), 41 (33). The compound (2'b) was identical with 3a by TLC (benzene:n-hexane= 1:1) and the ir spectroscopy.

Mulberrofuran D trimethyl ether (4a)[3c]

A mixture of 4 (12 mg), dimethyl sulfate (0.5 ml) and potassium carbonate (5 g) in acetone (30 ml) was refluxed for 30 min, and treated as usual. The product was purified by preparative TLC to give oily substance (4a, 5.5 mg). ms (75 eV) m/z (relative intensity): 489 (M^+ + 1, 37), 488 (M^+, 100), 473 (6), 445 (3), 419 (6), 377 (3), 366 (3), 365 (9), 364 (6), 216 (61), 123 (7), 69 (24), 58 (39), 43 (83). ^{1}H nmr (200 MHz, $CDCl_3$): δ 1.54, 1.62 (each 3H, br s, C-3" or C-8"-CH_3), 1.71 (6H, br s, C-3" or C-8"'-CH_3), 1.86 (3H, br s, C-3"'-CH_3), ~ 2.01 (4H, br, C-5"-H x 2 and C-6"-H x 2), 3.52, 3.66 (each 2H, br d, J = 7, C-1"-H x 2 and C-1"'-H x 2), 3.86 (6H, s, OCH_3 x 2), 3.92 (3H, s, OCH_3), 5.07, 5.22, 5.42 (each 1H, br t, J = 7, C-2"-H, C-2"'-H and C-7"'-H), 6.52 (1H, d, J = 2, C-4'-H), 6.79 (1H, s, C-3-H), 6.91 (1H, d, J = 2, C-6'-H), 6.91 (1H, d, J = 8, C-5-H), 7.37 (1H, d, J = 8, C-4-H).

Prenylphloroglucinol (10)[14]

A mixture of phloroglucinol (10 g), 2-methyl-3-butene-2-ol (8.3 ml), and boron trifluoride etherate (3 ml) in dioxane (70 ml) was allowed to stand for 22 h at room temperature, and treated as usual. The product was column chromatographed on silica gel with benzene as an eluent to give colorless needles (10, 1 g), mp 95 - 97 °C (from benzene). ^{1}H nmr (100 MHz, acetone-d_6): δ 1.58, 1.69 (each 3H, br s, C-3'-CH_3), 3.19 (2H, br d, J = 7, C-1'-H x 2), 5.18 (1H, br t, J = 7, C-2'-H), 5.87 (2H, s, C-4 and C-6-H). ms (75 eV) m/z (relative intensity): 195 (M^+ + 1, 8), 194 (M^+, 62), 179 (40), 151 (10), 139 (100), 138 (18), 126 (19), 123 (15), 110 (14), 69 (19), 58 (33), 43 (88).

Methylation of prenylphloroglucinol (10) (Formation of 11, 12, and 13)

A mixture of 10 (100 mg), dimethyl sulfate (0.2 ml), and potassium carbonate (5 g) in acetone (30 ml) was refluxed for 20 min, and treated as usual. The product was purified by preparative TLC (benzene:ether = 8:1, n-hexane:acetone = 6:1) to give 11 (52 mg), 12 (74 mg), and 13 (14 mg).

Trimethyl prenylphloroglucinol (11)[15] ——— ir ν_{max}^{KBr} cm^{-1}: 1610, 1590, 1490. ^{1}H nmr (100 MHz, $CDCl_3$): δ 1.63, 1.73 (each 3H, br s, C-3'-CH_3), 3.23 (2H, br d, J = 7.5, C-1'-H x 2), 3.74 (9H, s, OCH_3 x 3), 5.10 (1H, br t, J = 7.5, C-2'-H), 6.05 (2H, s, C-4 and C-6-H). ms (75 eV) m/z (relative intensity): 236 (M^+, 30), 222 (12), 221 (100), 207 (12), 205 (14), 191 (20). 181 (20), 179 (10), 168 (58), 167 (24), 69 (25).

3,5-dimethoxy-2-prenylphenol (12)[16]——— ir ν_{max}^{KBr} cm^{-1}: 3600, 3420, 1610, 1590, 1490. ^{1}H nmr (100 MHz, $CDCl_3$): δ 1.68, 1.76 (each 3H, br s, C-3'-CH_3), 3.28 (2H, br d, J = 7.5, C-1'-H x 2), 3.68, 3.72 (each 3H, s, OCH_3), 5.15 (1H, br t, J = 7.5, C-2'-H), 5.97, 6.01 (each 1H, d, J = 2, C-4 and C-6-H). ms (75 eV) m/z (rerative intensity): 222 (M^+, 47), 193 (25), 207 (100), 179 (28), 167 (83), 154 (34), 69 (36), 55 (23), 43 (18).

3,5-dimethoxy-4-prenylphenol (13) ——— High-resolution ms: Calcd. for $C_{13}H_{18}O_3$ (M^+, m/z): 222.1257. Found: 222.1223; Calcd. for $C_{12}H_{15}O_3$: 207.1022. Found 207.1025; Calcd. for $C_9H_{11}O_3$:

167.0709. Found: 167.0670. ir ν_{max}^{KBr} cm^{-1}: 3380, 1620, 1600, 1490. ^1H nmr (100 MHz, $CDCl_3$): δ 1.62, 1.71 (each 3H, br s, C-3'-CH_3), 3.19 (2H, br d, J = 7, C-1'-H x 2), 3.69 (6H, s, OCH_3 x 2), 5.08 (1H, br t, J = 7, C-2'-H), 5.97 (2H, s, C-2 and C-6-H). ms (75 eV) m/z (relative intensity): 222 (M^+, 46), 207 (100), 191 (15), 177 (15), 167 (23), 154 (33), 69 (44), 53 (17).

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