Isoflavan and Related Compounds from *Dalbergia odorifera*. II[1)]

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In a previous paper, we reported the isolation of the twenty-seven monomeric and dimeric isoflavonoid derivatives from the heartwood of *Dalbergia odorifera* T. CHEN (Leguminosae) and the structure elucidation of twelve monomeric and five dimeric isoflavonoids, which presented novel examples of naturally occurring biisoflavonoids. In a continuing study on this plant, we deal with the structure determination of four new dimeric flavonoids and a new arylbenzofuran among the uncharacterized compounds among the isolated ones.

Keywords *Dalbergia odorifera*; Leguminosae; biflavonoid; arylbenzofuran

In the preceding paper,[2)] we reported on the isolation and structure elucidation of twelve monomeric and five dimeric isoflavonoids (DO-1—DO-17) from the methanolic extract of *Dalbergia odorifera* T. CHEN. Our continuing study on this crude drug has led to the characterization of four new dimeric aromatic compounds and one arylbenzofuran derivative. This paper is concerned with the structure elucidation of these new aromatic compounds.

DO-18, white powder, $[\alpha]_D$ −198.0° (MeOH) showed $[M^+]$ at *m/z* 572 along with strong fragment peaks at *m/z* 300, 286, and 272 in the field desorption mass spectrum (FD-MS), which suggested DO-18 to be a dimeric flavonoid. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum exhibited signals due to a total of thirty two carbons, which were assigned to the C-2, C-3 and C-4 of the isoflavane (δ 71.1, 35.1 and 36.7), C-2, C-3 and C-4 of the flavanone (δ 78.2, 44.1 and 197.0), nine oxygenated sp^2 carbons (δ 136.1, 148.9, 151.7, 155.8, 156.5, 157.3, 161.7, 162.5 and 165.9), five quaternary sp^2 carbons (δ 97.2, 109.1, 118.7, 120.5 and 131.1), ten aromatic carbons (δ 95.6, 103.2, 103.6, 108.4, 115.6×2, 123.1, 127.1×2, 129.2) having aromatic proton and two methoxyl groups (δ 55.7 and 60.5). This indicated DO-18 to be a dimer constituted with each 1 mol of isoflavan and flavanone. Thus, a comparative study of the ^{13}C-NMR spectrum of DO-18 with those of vestitol[2)] and naringenin,[3)] and the interpretation of the fragments at *m/z*: 393, 300, 272 and 179 produced *via* retro Diels–Alder fission at the C-ring in the upper unit on the electron impacting mass spectrometry (EI-MS, Fig. 1) of DO-18 allowed to assign the structure of DO-18 to be 3′,7-dihydroxy-2′,4′-dimethoxyisoflavan as an upper unit and naringenin as a lower unit. As regards the bonding location, it was estimated to possess a linkage between C-4 in the isoflavan unit and C-6 or C-8 in the flavanone unit on the basis of the fact that the signal (δ 36.7) due to C-4 of the isoflavan unit shifted by +5.9 ppm by comparing that of vestitol, and the signal (δ 109.1, s) due to the C-6 or C-8 of the flavanone unit shifted by +11.3 ppm by comparing that of naringenin. In the case of the condensed tannin, when it posseses a 4—6 bonding, the proton

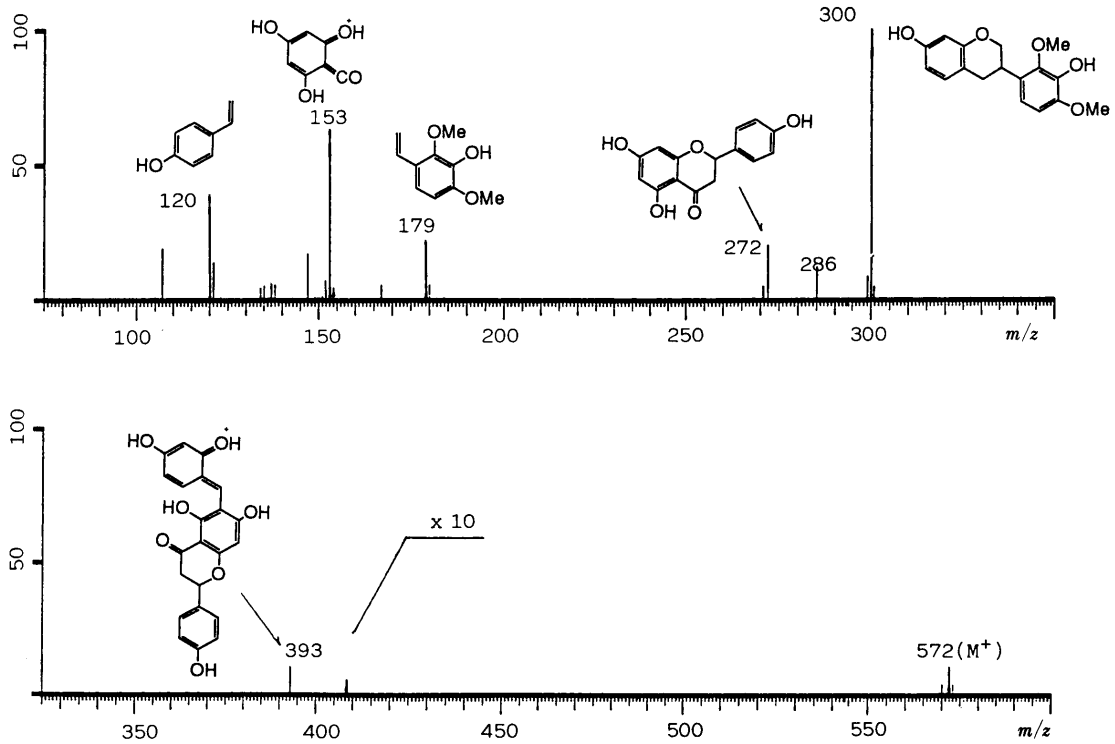
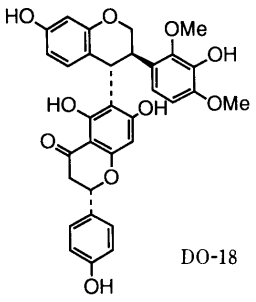
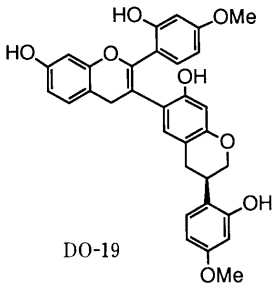


Fig. 1. EI-MS of DO-18

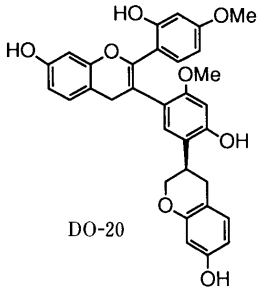
signal at H-2 does not shift in comparison with that of the monomer and when it has a 4—8 bonding, the proton signal due to H-2 shifts by +0.4 ppm in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum.[4] Therefore, the location of the bond was concluded to be between C-4 and C-6″ from the fact that the chemical shift of the H-2 signal [δ 5.51 (dd, J=11, 9 Hz)] in the lower unit (naringenin part) in DO-18 is approximate to that of (+)-naringenin [δ 5.47 (1H, dd, J=11, 9 Hz, H-2)] in the ^{1}H-NMR spectrum. Moreover, the carbon-13 NMR (^{13}C-NMR) spectrum of the DO-18 heptapermethyl ether showed three deshielded methoxyl signals at δ 60.7 (×2) and 61.0 (×1) supporting the above presumption. The configurations at C-3, C-4 and C-2″ were determined by the circular dichroism (CD) spectrum. It showed strong negative Cotton curves at 290 and 238 nm suggesting that the configurations at C-3 and C-4 in the upper unit were both *R* and the one at C-2 in the lower unit was *S*.[5] Consequently, the structure of DO-18 could be represented as (3*R*,4*R*)-3,4-*trans*-3′,7-dihydroxy-2′,4′-dimethoxy-4-[(2*S*)-4′,5,7-trihydroxyflavanone-6-yl] isoflavan.



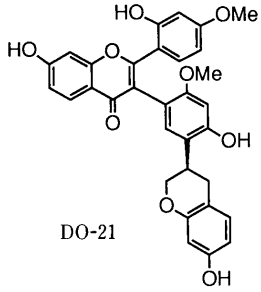
DO-18



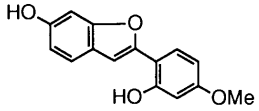
DO-19



DO-20



DO-21



DO-22

DO-18, an amorphous powder, $[\alpha]_D$ −19.6° (MeOH), showed a molecular ion peak *m/z* 540 in the fast atom bombardment mass spectrometry (FAB-MS), which suggested DO-19 to be a flavonoid dimer. The ^{1}H-NMR spectrum exhibited proton signals [1H, dd, J=15, 5 Hz, at δ 2.64 (H-4), 1H, dd, J=15, 10 Hz, at δ 2.72 (H′-4), 1H, m, at δ 3.36 (H-3), 1H, t, J=10 Hz, at δ 3.77 (H-2), 1H, m, at δ 4.11 (H′-2)] of the isoflavan moieties. Furthermore, signals due to a methylene (δ 3.91, 2H, s) and two methoxy groups (δ 3.73, 3.83, each 3H, s), and three protons on the ABX system and two singlet protons attached to the sp^2 carbon were also observed. Next, a comparative study of the ^{1}H-NMR spectra of the DO-18 acetate and the DO-14 acetate,[2] which constituted with 2 mol of vestitol molecule, was undertaken: in the DO-18 acetate, signals due to the H_2-2, H-3, H-4 at C-ring in the upper unit were not observed and the two proton signals at δ 4.0 newly occurred. In the other signals, both compounds did not exhibit so significant a difference. The EI-MS (Fig. 2) of DO-19 exhibited $[M]^+$

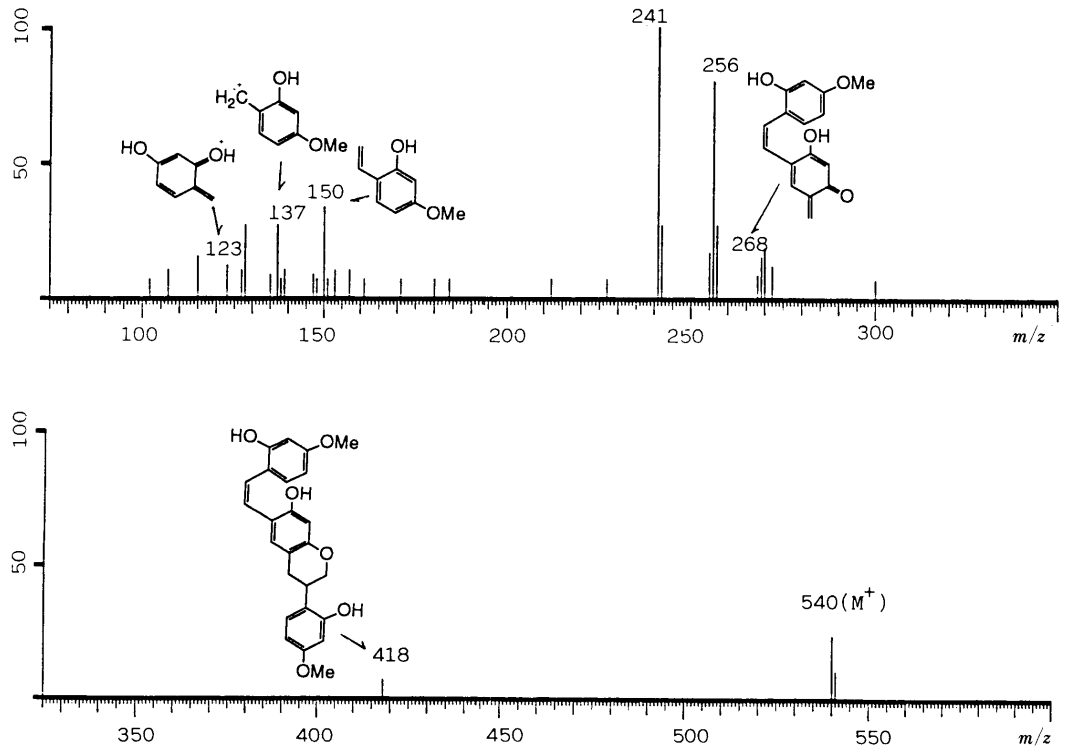


Fig. 2. EI-MS of DO-19

Table I. ^{13}C-NMR Data for DO-18, 19, 20, 21, Vestitol and Naringenin

(in Acetone-d_6)

	Vestitol	Naringenin	DO-18	DO-19	DO-20	DO-21
Upper unit						
C-2	70.3		71.1	151.0	150.4	156.2
C-3	32.4		35.1	111.1	112.4	122.1
C-4	30.8		36.7	24.5	24.5	179.6
C-4a	114.2		118.7	114.5	116.0	115.2
C-5	130.8		129.2	133.1	131.0	134.4
C-6	108.6		108.4	108.2	108.7	109.0
C-7	156.4		156.5	157.9	157.8	162.0
C-8	103.5		103.2	104.2	103.6	103.8
C-8a	155.8		155.8	157.9	155.9	157.3
C-1′	120.7		120.5	119.8	118.1	117.2
C-2′	157.1		151.7	155.4	157.3	159.2
C-3′	102.4		136.1	96.7	96.2	99.9
C-4′	160.1		148.9	158.8	158.5	164.8
C-5′	105.5		103.6	111.8	111.5	116.1
C-6′	128.5		123.1	121.3	120.9	128.2
Lower unit						
C-2		79.9	78.2	70.8	70.3	70.3
C-3		43.4	44.1	32.3	32.6	32.5
C-4		197.2	197.0	31.3	30.8	31.4
C-4a		103.0	97.2	116.4	114.1	114.7
C-5		164.9	162.5	129.5	130.8	131.1
C-6		96.7	109.1	124.6	107.2	106.2
C-7		167.7	165.5	157.7	157.7	159.7
C-8		95.9	95.6	100.1	100.3	103.2
C-8a		164.3	161.7	156.4	156.4	157.8
C-1′		130.5	131.1	120.1	120.3	120.6
C-2′		128.9	127.1	156.2	155.9	158.5
C-3′		116.1	115.6	103.9	103.1	102.5
C-4′		158.8	157.3	160.7	158.5	164.2
C-5′		116.1	115.6	109.2	130.8	131.0
C-6′		128.9	127.1	131.3	124.4	130.9
OMe	55.2		55.7	55.7	55.7	55.7
			60.5	56.0	55.8	56.2

at m/z 540, which was 2 mass units smaller than that of DO-14,[2] hence DO-19 was supposed to have a new one double bond. It also showed fragment ions at m/z 418, 268 and 123 produced *via* retro Diels–Alder fission. On the basis of the EI-MS evidence and the coupling pattern of the aromatic proton, the structure of DO-19 could be assumed to be a dimer having a C–C linkage between C-3 and C-6 of the two vestitol molecules, in which a double bond was introduced in the C-2 and C-3 on the participated side to the bonding. The ^{13}C-NMR spectrum of DO-19 (Table I) indicated a total of thirty two carbon signals, which were composed of signals due to the methylene (δ 24.5), the C-2, C-3 and C-4 of the isoflavone unit [δ 31.3 (t), 32.3 (d) and 70.8 (d)] and two methoxyl groups (δ 55.7 and 56.0) and the remaining twenty-six sp^2 carbon signals (benzene ring × 4 and double bond × 1). In comparing this ^{13}C-NMR spectrum with that of vestitol, it was revealed that DO-19 was constituted with one vestitol unit and one Δ^2-vestitol unit bonding through C-3 and C-6 to each other. The configuration at C-3 was determined to be *R* by the CD spectrum showing a positive Cotton at 292 nm and a negative Cotton at 235 nm. However, two possible structures of **1a** and **1b** for DO-19 were also conceivable. Measurement of the ^{1}H–^{13}C shift correlation spectrum (COSY) followed by an examination of the long range selective proton decoupling (LSPD) method were undertaken. That is, when the H-4 [δ 3.91 (s)] was irradiated, the carbon signal (δ 124.6) due to C-6″ turned a little sharper than under nonirradiated, suggesting DO-19 to be expressed as the formula **1a**. Next, as shown in Chart 1, DO-19 was permethylated with CH_3I and K_2CO_3 in acetone, oxidized with OsO_4, $NaIO_4$ in ether and water, reduced with $NaBH_4$, saponified with NaOH–MeOH and acetylated to give a product (**1d**), whose EI-MS showed $[M]^+$ peak at m/z 550,

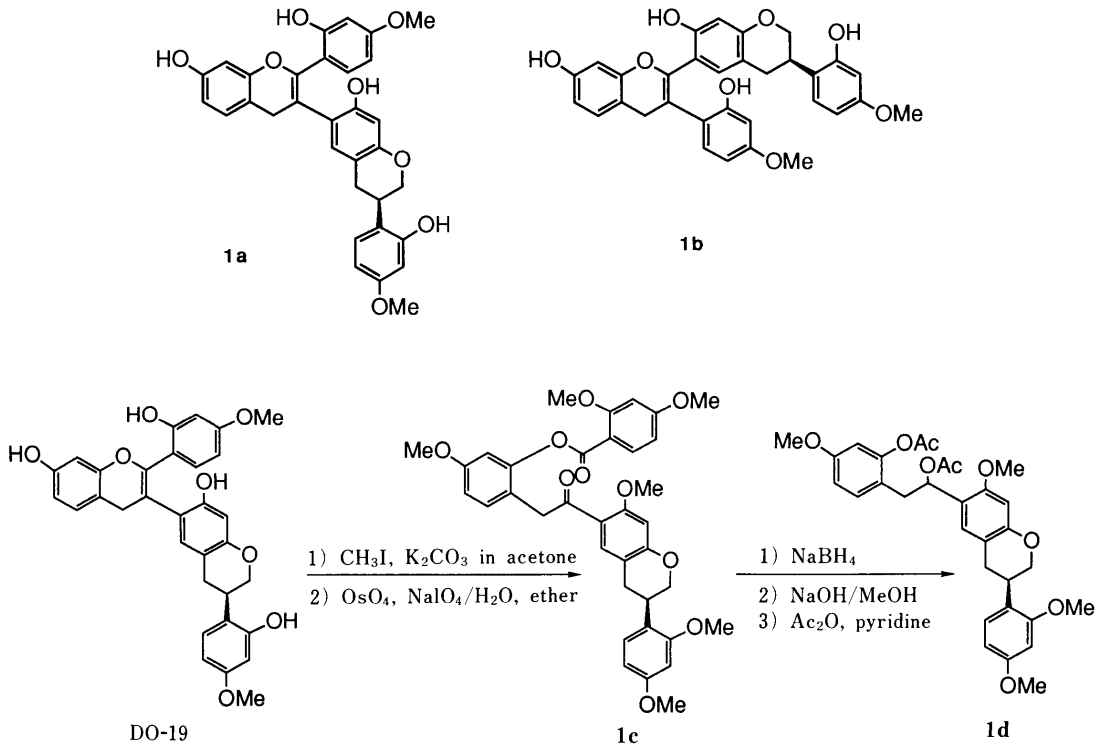


Chart 1. Degradation of DO-19

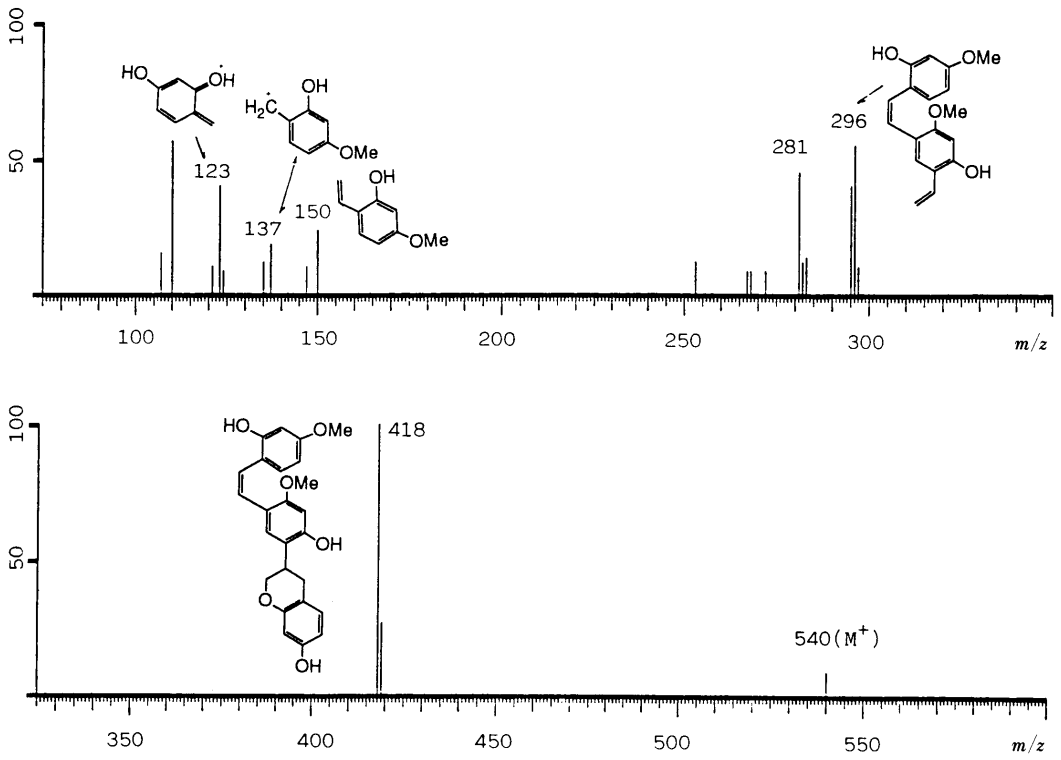


Fig. 3. EI-MS of DO-20

together with fragment peaks at m/z 490 $[M-AcOH]^+$, 448 $[m/z\ 490-Ac]^+$, 313 and 299. The ^{1}H-NMR spectrum of **1d** displayed signals due to two pairs of methylene at δ 2.70—2.85 (2H, m) and 2.95—3.11 (2H, m), one methine at δ 3.49 (1H, m), an oxygenated methylene at δ 3.86 (1H, t, $J=10$ Hz) and 4.22 (1H, dd, $J=10$, 6 Hz), two acetyl groups at δ 1.91 and 2.32 (each 3H, s), and four methoxyl groups at δ 3.76, 3.77, 3.82 and 3.83 (each 3H, s), eight aromatic protons at δ 6.40—7.23, which supported the structure **1d**. Consequently, the structure of DO-19 was elucidated as shown in the formula.

DO-20, an amorphous powder, $[\alpha]_D$ $-12.9°$ (MeOH), showed a peak due to $[M]^+$ at m/z 540 in the EI-MS. The DO-20 acetate showed a peak due to $[M]^+$ at m/z 708 the same as that of the DO-19 acetate in the EI-MS. The ^{1}H-NMR spectrum displayed three ABX-type signals and two singlet signals, which were analogous to those of DO-19 though their chemical shifts were different. Moreover, it showed signals ascribable to the H-4 [δ 2.79 (1H, dd, $J=15$, 5 Hz)], H-3 [δ 3.50 (1H, m)], H_2-2 [δ 3.94 (1H, t, $J=10$ Hz) and 4.31 (1H, ddd, $J=10$, 3, 2 Hz)] of vestitol, and a singlet signal due to 2H at δ 3.84 as like as those of H_2-4 in DO-19, indicating DO-20 to be an isomer with a different bonding site from DO-19. When the EI-MS spectrum (Fig. 3) of DO-20 was compared with that of DO-19, a fragment ion at m/z 418 produced *via* fission of the C-ring was observed in both compounds, but a fragment at m/z 268 observed in DO-19 banished and a fragment at m/z 296 newly appeared. Therefore, it was indicated that DO-20 was linked between C-3 of the flavene and C-5′ of the isoflavan. By the ^{1}H–^{1}H COSY measurement of DO-20, the correlation of three ABX-type signals and two singlet signals was revealed and the long range correlations of the methoxyl group and the C-4 methylene protons were also observed respectively with H-3′ and H-3‴ and H-5, thus they were respectively

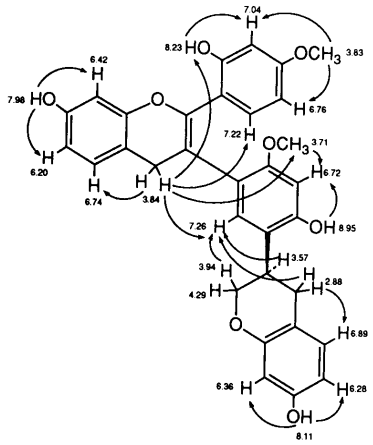


Fig. 4. NOE of DO-20

ascribable to the upper unit and the lower unit. The nuclear Overhauser effect experiment (NOE) in the ^{1}H-NMR of DO-20 resulted as shown in Fig. 4. Moreover, in connection with the ^{1}H-NMR assignments, the signals of the respective carbons could be attributed by the ^{1}H–^{13}C COSY. Singlet signals were assigned by comparing those of vestitol. Thus, when comparing its ^{13}C-NMR spectrum (Table I) with that of DO-19, signals assignable to C-6″, C-4‴ and C-6‴ showed upfield shifts by 17.4, 2.2 and 6.0 ppm, and signals assignable to C-5″ and C-5‴ showed lower-field shifts by 1.3 and 21.6 ppm, respectively, in comparing with those of DO-19. Other signals remained unchanged. This fact supported the deduced structure with the bonding between C-3 and C-5‴ constructed from the ^{1}H-NMR and MS. The configuration of this lower unit was determined to be 3(R) by showing a negative Cotton at 235 nm in CD spectrum. This accumulated evidence could assign the structure as shown in the formula for DO-20.

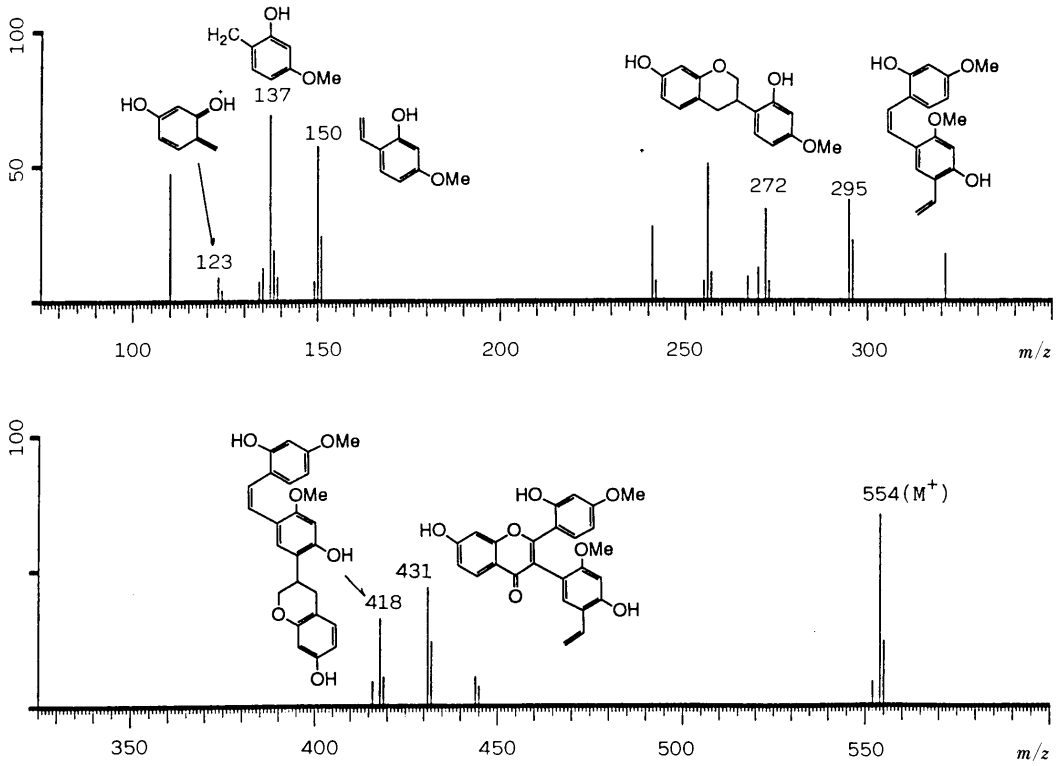


Fig. 5. EI-MS of DO-21

DO-21, an amorphous powder, showed a molecular ion at *m/z* 554, which is larger by a 14 mass unit than that of DO-20, in the EI-MS. In the ^{13}C-NMR spectrum (Table I), there appeared three sp^3 carbons at δ 31.4, 32.5 and 70.3, two methoxyl at δ 55.7 and 56.2, nine carbons attached to oxygen, six quaternary sp^2 carbons, eleven carbons bearing aromatic proton, and a carbonyl carbon at δ 179.6, totaling up to thirty two carbons, indicating DO-21 to consist of four benzene rings and another double bond. Thus, in comparing the ^{13}C-NMR signals of DO-21 with those of DO-20, a signal at δ 24.5 in DO-20 disappeared and a new signal at δ 179.6 attributable to a carbonyl group appeared, and the respective signals around C-4 shifted lower by 3—10 ppm, suggesting that the structure of DO-21 could be replaced by the carbonyl group at C-4 in DO-20. In the EI-MS (Fig. 5) of DO-21, the molecular weight is larger by a 14 mass unit than that of DO-20, indicating that the methylene group in DO-20 was oxydized to the carbonyl function in DO-21. Furthermore, fragment ion peaks at *m/z* 418, 431, 295, 137 and 123 derived from retro Diels–Alder fission supported the presence of the carbonyl group at C-4. The configuration of the vestitol unit was determined to be 3(*R*) by showing that the CD spectrum exhibited a positve Cotton at 288 nm and a negative one at 240 nm the same as that of 3(*R*)-vestitol. From the above facts, the structure of DO-21 could be represented as shown in the formula.

DO-22, an amorphous powder, showed a molecular ion at *m/z* 256 and fragment peaks at *m/z* 171, 157, 137, 128 and 115, suggesting the molecular formula $C_{15}H_{12}O_4$. The ^{13}C-NMR spectrum of DO-22 exhibited only one signal of a methoxyl group at δ 56.0 in the sp^3 carbon range. On the other hand, in the range of sp^2 carbon range, it showed signals due to five carbons attached to the oxygen atom, three quaternary carbons and six carbons having aromatic proton, totaling up to fifteen carbon signals. The ^{1}H-NMR spectrum of the DO-22 acetate showed signals due to two acetyl groups at δ 2.31 and 2.42 and a methoxyl group at δ 3.87, and two ABX type signals [δ 7.04 (1H, d, J=2 Hz), 6.88 (1H, dd, J=9, 2 Hz), 7.45 (1H, d, J=9 Hz), 7.26 (1H, d, J=2 Hz), 7.12 (1H, dd, J=9, 2 Hz), 7.96 (1H, d, J=9 Hz)] and a signal at δ 6.96 (1H, d, J=1 Hz), indicating that DO-22 is a 2-arylbenzofuran derivative. Moreover, on the basis of the appearance of two ABX type signals in the ^{1}H-NMR spectrum of the DO-22 acetate, it was substantiated that DO-22 has a structure of 2-arylbenzofuran with two hydroxyl groups and one methoxyl group at C-6, 2′ and 4′ and methoxyl group, whose location was estimated to be at the B-ring by the appearance of a fragment peak with a strong intensity at *m/z* 137 in the EI-MS. Furthermore, by exhibiting a good accordance in the chemical shifts of DO-22 with those of the B-ring of vestitol in the ^{13}C-NMR spectrum, it was determined to be at C-4′. Therefore, the structure of DO-22 was concluded to be 2′,6-dihydroxy-4′-methoxy-2-arylbenzofuran.

Experimental

The optical rotations were measured with a JASCO DIP-360 digital polarimater. The ultraviolet (UV) spectra were recorded with a Hitachi 556 digital polarimeter. The EI-MS were measured with a JMS-01SG (ionizing voltage, 70—75 eV; ionizing current, 200—300 μA; ion source temperature, 130—180 °C) and FD- and FAB-MS were obtained with a JEOL JMS-DX-300. The ^{1}H-NMR spectra were recorded with JEOL JNM-FX-100 (100 MHz) and JNM-GX-400 (400 MHz), and the ^{13}C-NMR spectra with JEOL JNM-GX-270 (67.5 MHz) and JNM-GX-400 (100 MHz) spectrometers; chemical shifts were given on a δ (ppm) scale with tetramethylsilane as an internal standard. DO-18—DO-22 were obtained according to the separation procedure as shown in Chart 1 in the preceding paper.[2] Thin layer chromatography (TLC) was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) and detection was achieved by spraying 10% H_2SO_4 reagent followed by heating, or by

irradiating with a UV-lamp (254 nm). Purity was checked by HPLC (TOSOH HPLC 803D, UV-8 system (280 nm); column, TOSOH TSK-gel-80TM (ODS, 4.6 mm × 150); solvent, 70% MeOH).

DO-18 *Rf* 0.45 (solvent: $CHCl_3$: MeOH = 10 : 1), a white powder. $[\alpha]_D^{25}$ −198.0° (c = 0.50, MeOH). CD ($c = 4.08 \times 10^{-4}$, MeOH) [θ] (nm): -1.21×10^5 (290), -7.88×10^4 (238). FD-MS m/z: 572 $[M]^+$, 542, 300, 286, 272. FAB-MS m/z: 572 $[M]^+$. ^{1}H-NMR (acetone-d_6) δ: 2.71 [2H, m, lower unit (l)-3], 3.67, 3.76 (each 3H, s, OMe), 3.96—4.21 [2H, m, upper unit (u)-2], 4.37 (1H, m, u-3), 5.03 (1H, d, J = 9 Hz, u-4), 5.51 (1H, dd, J = 11, 9 Hz, l-2), 5.93 (1H, s, l-8), 6.23—7.41 (total 9H, m, u-5, 6, 8, 5′, 6′, l-2′, 3′, 5′, 6′), 12.08 (1H, br s, ArOH).

DO-18 Pentaacetate DO-18 (10 mg) was acetylated with pyridine (2 ml) and acetic anhydride (1 ml) in the usual manner to afford the product, which was purified by using silica gel column chromatography with n-hexane : acetone = 3 : 1 as a solvent to give the acetate (11 mg), a white powder, EI-MS m/z: 782 $[M]^+$, ^{1}H-NMR ($CDCl_3$) δ: 2.26, 2.31, 2.34 × 2, 2.35 (each 3H, s, OAc).

DO-18 Heptamethyl Ether After a solution of DO-18 (32 mg) in MeOH was added with diazomethane in ether and left to stand overnight, the solvent was removed to give a residue, which was dissolved in anhydrous acetone, added with dimethyl sufuric acid (1 ml) and anhydrous potassium carbonate (4 g) and refluxed for 3 h. The reaction products were purified over silica gel (solvent: n-hexane : AcOEt = 3 : 1) to provide the permethyl ether (18 mg) as a white powder. ^{13}C-NMR ($CDCl_3$) δ 55.4, 55.7, 56.2 × 2, 60.7 × 2, 61.0.

DO-19 *Rf* 0.46 (solvent: $CHCl_3$: MeOH = 10 : 1), a white powder. $[\alpha]_D^{18}$ −19.6° (c = 0.49, MeOH). UV ν_{max}^{EtOH} nm (log ε): 305.6 (4.45), 289.2 (4.52), 285.6 (4.52), 217.2 (4.82). CD ($c = 4.08 \times 10^{-5}$, MeOH) [θ] (nm): 1.96×10^3 (292), 0 (277), -1.52×10^4 (235). FAB-MS m/z: 540 $[M]^+$, 285, 269, 256, 137, 123. ^{1}H-NMR (acetone-d_6) δ: 2.64 (1H, dd, J = 15, 5 Hz, l-4), 2.72 (1H, dd, J = 15, 10 Hz, l-4), 3.36 (1H, m, l-3), 3.73, 3.83 (each 3H, s, OMe), 3.77 (1H, t, J = 10 Hz, l-2), 3.91 (2H, s, u-4), 4.11 (1H, m, l-2), 6.25 (1H, d, J = 2 Hz, u-8), 6.35 (1H, dd, J = 8, 2 Hz, u-6), 6.47 (1H, dd, J = 8, 2 Hz, l-5′), 6.55 (1H, s, l-8), 6.56 (1H, d, J = 2 Hz, l-3′), 6.78 (1H, dd, J = 8, 2 Hz, u-5′), 6.81 (1H, d, J = 8 Hz, u-5), 6.83 (1H, s, l-5), 7.02 (1H, d, J = 2 Hz, u-3′), 7.20 (1H, d, J = 8 Hz, l-6′), 7.23 (1H, d, J = 8 Hz, u-6′).

DO-19 Tetraacetate DO-18 (9 mg) was acetylated with pyridine (2 ml) and acetic anhydride (1 ml) in the usual manner to afford the product which was purified by using silica gel column chromatography with n-hexane : AcOEt = 2 : 1 as a solvent to give the acetate (5 mg), a white powder. EI-MS m/z: 708 $[M]^+$. ^{1}H-NMR ($CDCl_3$) δ: 2.10, 2.27 (each 3H, s, OAc), 2.30 (6H, s, OAc × 2), 2.67 (2H, m, l-4), 3.12 (1H, m, l-3), 3.68 (1H, t, J = 10 Hz, l-2), 3.77, 3.86 (each 3H, s, OMe), 4.00 (2H, s, u-4), 4.07 (1H, dd, J = 2, 10 Hz, l-2), 6.50 (1H, d, J = 2 Hz, u-8), 6.54 (1H, dd, J = 8, 2 Hz, u-6), 6.57 (1H, s, l-8), 6.75 (1H, s, l-5), 6.80 (1H, dd, J = 8, 2 Hz, l-5′), 6.94 (1H, d, J = 8 Hz, u-5), 6.97 (1H, dd, J = 8, 2 Hz, u-5′), 7.03 (1H, d, J = 2 Hz, l-3′), 7.08 (1H, d, J = 2 Hz, u-3′), 7.19 (1H, d, J = 8 Hz, l-6′), 7.44 (1H, d, J = 8 Hz, u = 6′).

DO-19 Hexamethyl Ether A mixture of DO-19 (150 mg), CH_3I (1 ml) and anhydrous potassium carbonate (3 g) was refluxed for 3 h with stirring. After removal of inorganic salts by filtration, the filtrate was concentrated to a syrup, which was chromatographed over silica gel (solvent: n-hexane : EtOAc = 1 : 1) to provide the hexamethyl ether (102 mg) as a white powder. $[\alpha]_D^{28}$ −17.6° (c = 0.50, $CHCl_3$). FAB-MS m/z: 596 $[M]^+$, 460, 230, 165, 151, 137, 123. ^{1}H-NMR ($CDCl_3$) δ: 2.64 (2H, d, J = 8 Hz, l-4), 3.40 (1H, m, l-3), 3.69, 3.72, 3.81 × 3, 3.84 (each 3H, s, OMe), 3.76 (1H, t, J = 10 Hz, l-2), 3.89 (2H, s, u-4), 4.12 (1H, dd, J = 10, 3 Hz, l-2), 6.33 (1H, d, J = 2 Hz, u-8), 6.40 (1H, dd, J = 8, 2 Hz, u-6), 6.43 (1H, s, l-8), 6.51 (1H, d, J = 2 Hz, l-3′), 6.53 (1H, dd, J = 8, 2 Hz, l-5′), 6.69 (1H, s, l-5), 6.75 (1H, dd, J = 8, 2 Hz, u-5′), 6.82 (1H, d, J = 8 Hz, u-5), 7.01 (1H, d, J = 2 Hz, u-3′), 7.17 (1H, d, J = 8 Hz, l-6′), 7.29 (1H, d, J = 8 Hz, u-6′).

OsO_4 Oxidation of DO-19 Hexamethyl Ether To a solution of DO-19 hexamethyl ether (10 mg) in ether (10 ml), water (10 ml), OsO_4 (10 mg) and $NaIO_4$ (20 mg) were added under stirring and then the mixture was left to stand for 48 h. The reaction mixture was partitioned between ether and water, and the residue was obtained after removal of the solvent of the organic layer. It was then chromatographed over silica gel (solvent: n-hexane : AcOEt = 3 : 1) to give the crude keto-ester compound, **1c** (3 mg). A solution of **1c** (3 mg) in ether (10 ml) was reduced with $NaBH_4$ (5 mg) under stirring and was kept standing for 24 h with 1 N NaOH–MeOH (2 ml) was added and decomposition was by heating on a hot bath. The reaction mixture was acidified with 1 N HCl–MeOH and partitioned between ether and water to provide the organic residue, which was then acetylated with Ac_2O (1 ml) and pyridine (2 ml) to give the acetate after silica gel chromatographic purification with benzene and AcOEt = 15 : 1. A white powder, EI-MS m/z: 550 $[M]^+$, 490 $[M-AcOH]^+$, 448 [m/z 490 − Ac]$^+$, 313, 299. ^{1}H-NMR ($CDCl_3$) δ: 1.91, 2.32 (each 3H, s, OAc), 2.70—2.85 (2H, m), 2.95—3.11 (2H, m), 3.49 (1H, m), 3.49 (1H, m), 3.76, 3.77, 3.77, 3.82, 3.83 (each 3H, s, OMe), 3.86 (1H, t, J = 10 Hz), 4.22 (1H, dd, J = 10, 6 Hz), 6.40—7.23 (total 8H, Ar-H).

DO-20 *Rf* 0.41 (solvent: $CHCl_3$: MeOH = 10 : 1), a white powder. $[\alpha]_D^{28}$ −12.9° (c = 0.55, MeOH). UV ν_{max}^{EtOH} nm (log ε): 308.8 (4.07), 280.4 (4.08), 206.4 (4.74). CD ($c = 2.96 \times 10^{-5}$, MeOH) [θ] (nm): 1.43×10^3 (294), 0 (272), -4.18×10^4 (235).

DO-20 Tetraacetate A solution of DO-20 (10 mg) in acetic anhydride (1 ml) and pyridine (2 ml) was kept at room temperature overnight and as usual worked up to provide the corresponding crude acetate which was further purified over silica gel column chromatography with n-hexane : AcOEt = 3 : 1 to give the DO-20 tetraacetate (8 mg). A white powder, $[\alpha]_D^{25}$ −14.0° (c = 0.78, $CHCl_3$). EI-MS m/z: 708 $[M]^+$, 695, 666, 653, 624, 612, 582, 570, 540, 418, 296, 165, 150, 137, 123. ^{1}H-NMR ($CDCl_3$) δ: 2.23, 2.25, 2.29, 2.35 (each 3H, s, OAc), 2.89—2.95 (2H, m, l-4), 3.25—3.29 (1H, m, l-3), 3.52, 3.85 (each 3H, s, OMe), 3.83 (2H, s, u-4), 3.94 (1H, t, J = 11 Hz, l-2), 4.25—4.30 (1H, m, l-2), 6.59 (1H, s, l-3′), 6.61 (1H, dd, J = 7, 2 Hz, u-6), 6.67 (1H, d, J = 2 Hz, l-8), 6.81 (1H, dd, J = 8, 2 Hz, l-6), 6.83 (1H, dd, J = 8, 2 Hz, u-5′), 6.90 (1H, d, J = 2 Hz, u-3′), 7.04 (1H, d, J = 8 Hz, u-5), 7.05 (1H, d, J = 2 Hz, u-8), 7.10 (1H, d, J = 8 Hz, l-5), 7.15 (1H, d, J = 8 Hz, u-6′), 7.33 (1H, s, l-6′).

DO-21 *Rf* 0.43 (solvent: $CHCl_3$: MeOH = 10 : 1), a white powder. CD ($c = 3.96 \times 10^{-4}$, MeOH) [θ] (nm): 3.32×10^3 (288), 0 (260), -1.33×10^{-4} (240). FD-MS m/z: 554 $[M]^+$, 293, 277. ^{1}H-NMR (acetone-d_6) δ: 2.63 (2H, m, l-4), 3.43 (1H, m, l-3), 3.66, 3.67 (each 3H, s, OMe), 4.02 (2H, m, l-2), 6.20—7.08 (total 11H, m, u-5, 6, 8, 5′, 6′, 8′, l-5, 6, 8, 3′, 6′).

DO-22 *Rf* 0.63 (solvent: $CHCl_3$: MeOH = 10 : 1), a white powder. $[\alpha]_D^{28}$ ±0° (c = 0.51, MeOH). EI-MS m/z: 256 $[M]^+$, 241, 171, 157, 137, 128, 115. ^{13}C-NMR (acetone-d_6) δ: 159.4, 103.8, 128.2, 111.0, 108.4, 155.4, 104.0, 156.4 (C-2—C-7a), 124.2, 153.5, 96.3, 158.7, 112.2, 121.5 (C-1′—C-6′), 56.0 (OMe).

DO-22 Diacetate A solution of DO-22 (9 mg) in acetic anhydride (1 ml) and pyridine (2 ml) was kept at room temperature overnight and as usual worked up to provide the corresponding crude acetate which was further purified over silica gel column chromatography with n-hexane : AcOEt = 3 : 1 to give the DO-22 diacetate (7 mg). A white powder, $[\alpha]_D^{27}$ ±0° (c = 0.45, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.31, 2.42 (each 3H, s, OAc), 3.87 (3H, s, OMe), 6.88 (1H, dd, J = 9, 2 Hz, H-5), 6.96 (1H, d, J = 1 Hz, H-3), 7.04 (1H, d, J = 2 Hz, H-7), 7.12 (1H, dd, J = 9, 2 Hz, H-5′), 7.26 (1H, d, J = 2 Hz, H-3′), 7.45 (1H, d, J = 9 Hz, H-4), 7.96 (1H, d, J = 9 Hz, H-6′).

Acknowledgements The authors are grateful to Prof. I. Nishioka, Kyushu University, Prof. T. Tomimatsu, Tokushima University, Prof. K. Mihashi, Fukuoka University, and Dr. M. Yamasaki and Mr. K. Takeda, Kumamoto University, for measurements of the NMR spectra and MS.

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