Isoflavan and Related Compounds from *Dalbergia odorifera*. I

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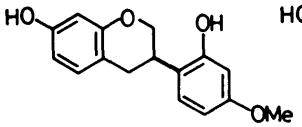
Twenty-seven isoflavonoid monomer and dimer derivatives were obtained from the heartwood of *Dalbergia odorifera* T. CHEN (Leguminosae). The structure elucidation of twelve monomeric and five dimeric isoflavonoids is dealt with in this paper, affording novel examples of naturally occurring biisoflavonoids.

Keywords *Dalbergia odorifera*; Leguminosae; isoflavonoid; biisoflavonoid; (3*R*)-vestitol; (3*R*)-claussequinone; formononetin; bowdichione; liquiritigenin; isoliquiritigenin; medicarpin; X-ray analysis

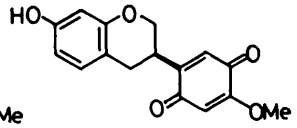
Hypercholesterolemia has been suggested to cause sclerosis of the artery in human adults. Cholesterol and neutral lipid play an important role in causing hypercholesterolemia. Thus, we started an investigation to identify substances effective against hypercholesterolemia among the oriental crude drugs. Since it is supposed that hypercholesterolemia is related to "Oketsu" (瘀血), we planned to screen a series of crude drugs traditionally regarded as effective againt Oketsu. The methanolic extractives of *Dalbergia odorifera* T. CHEN, *Caesalpinia sappan* L. and *Daemonorops draco* BLUME were shown to be effective. The constituents of *Caesalpinia sappan* L. have already been reported.[1] As a part of our studies on the constituents of the crude drugs effective against Oketsu, we describe here the characterization of the chemical structures of seventeen among twenty-seven compounds obtained from the methanolic extractive of *Dalbergia odorifera*.

Extraction and separation were undertaken as shown in Chart 1. The methanolic extractive obtained corresponded to about half the weight of the crude drug. Various column chromatographies using silica gel, Sephadex LH-20, MCI-gel CHP 20P and Bondapak C_{18}, gave twenty seven compounds, tentatively designated DO-1—DO-27, which were shown to be monomers and dimers related to the isoflavonoids.

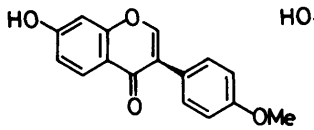
Monomers The monomers, DO-1, DO-2, DO-4, DO-5, DO-6, DO-7 and DO-3 were identified as (3*R*)-vestitol,[2] (3*R*)-claussequinone,[3] formononetin,[4] bowdichione,[5] liquiritigenin,[6] isoliquiritigenin,[7] and medicarpin,[8] respectively. The other monomers, DO-8, DO-9, DO-10, DO-11 and DO-12 were newly isolated compounds.



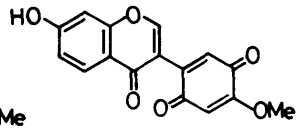
DO-1 ((3 *R*)-vestitol)



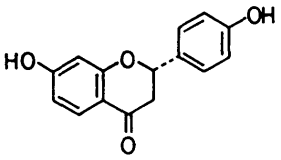
DO-2 ((3 *R*)-claussequinone)



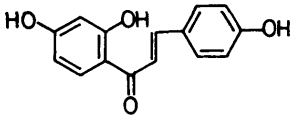
DO-4 (formononetin)



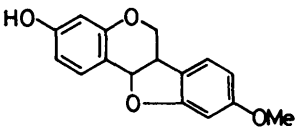
DO-5 (bowdichione)



DO-6 (liquiritigenin)



DO-7 (isoliquiritigenin)



DO-3 (medicarpin)

TABLE I. ^{13}C-NMR Data for DO-8, DO-9, DO-10 and Vestitol (in DMSO-d_6)

	DO-8	DO-9	DO-10	Vestitol
C-2	70.2	70.9	70.3	70.3
C-3	32.7	33.2	47.2	32.4
C-4	30.9	31.2	190.6	30.8
C-4a	114.1	115.5	115.9	114.2
C-5	130.8	120.0	128.9	130.8
C-6	108.7	108.8	110.5	108.6
C-7	157.2	144.4	147.8	155.8
C-8	103.6	134.6	103.0	103.5
C-8a	155.9	143.9	163.3	156.4
C-1′	119.4	121.9	114.1	120.7
C-2′	149.9	144.5	144.1	157.1
C-3′	102.2	133.9	133.9	102.4
C-4′	149.6	148.0	164.2	160.1
C-5′	143.6	103.9	102.3	105.5
C-6′	113.9	117.9	119.5	128.5
OMe	56.0 57.2	56.4	55.8	55.2

DO-8, a pale brown crystalline powder, $[\alpha]_D$ −26.2° (MeOH), showed M^+ at *m/z* 302 along with fragment ion peaks at *m/z* 180 and 123 in the electron impact mass spectrum (EI-MS). Its proton nuclear magnetic resonance (^{1}H-NMR) spectrum exhibited ABX-type signals [δ 6.30 (1H, d, J=2 Hz), 6.36 (1H, dd, J=2, 8 Hz), and 6.88 (1H, d, J=8 Hz)] and two singlet signals at δ 6.57 and 6.76 due to phenolic protons. Moreover, signals due to two methoxyls at δ 3.70 and 3.73, one oxygenated methylene at δ 3.80—4.40 and one methylene at δ 2.90 were observed. From the above evidence, DO-8 was deduced to possess one ad-

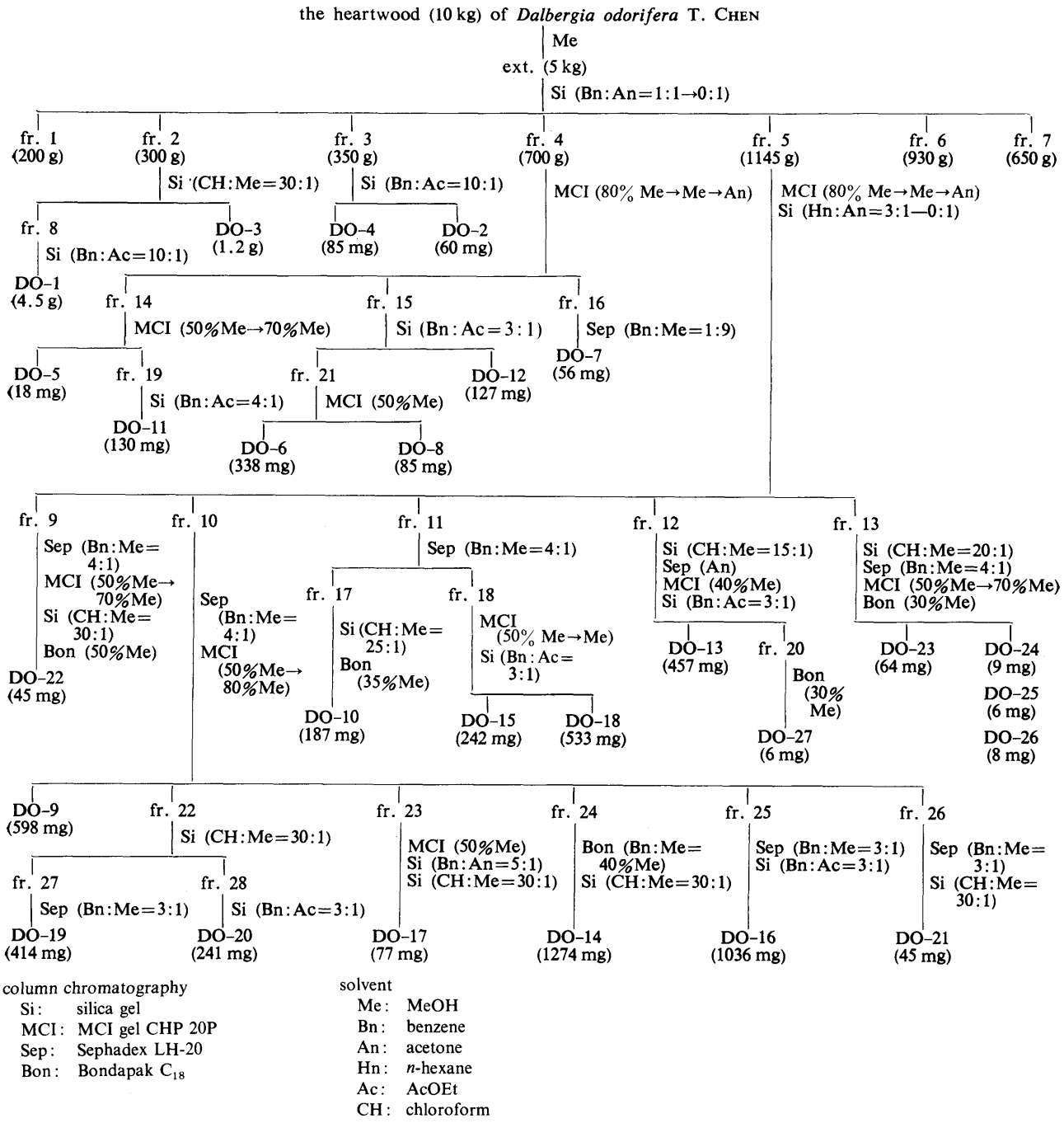


Chart 1. Extraction and Separation of Heartwood of *Dalbergia odorifera* T. CHEN

ditional methoxyl group linked to C-5′ of vestitol. Signals that originated from the A and C rings in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (Table I) of DO-8 were coincident with those of vestitol, except that the signal assignable to C-5′ was shifted +38.1 ppm, while signals of the *ortho* (C-4′ and C-6′) and *para* (C-2′) carbons were shifted to higher field by 10.5, 14.6 and 7.2 ppm, supporting the above presumptive structure. The configuration at C-3 was estimated as *R* from the circular dichroism (CD) spectrum,[9] which showed a negative Cotton effect at 237 nm. Therefore, DO-8 was determined to be (3*R*)-5′-methoxyvestitol.

DO-9, colorless needles, mp 224—226 °C, $[\alpha]_D$ −5.2° (MeOH), showed M^+ at *m/z* 304 together with fragment peaks at *m/z* 166, 153 and 139 in the EI-MS, suggesting that one additional oxygen atom had been introduced into each of the A and B rings of the vestitol molecule to form DO-9. The signals assignable to H-2, H-3 and H-4 of the isoflavan skeleton appeared at δ 4.13 (2H, m), 3.31 (1H, m), and 2.90 (2H, m), respectively, in the ^{1}H-NMR spectrum. Furthermore, observation in the ^{1}H-NMR spectrum of one methoxyl signal (δ 3.78), and two pairs of the AB-type aromatic proton signals at δ 6.34 (1H, d, J=8 Hz), 6.48 (1H, d, J=8 Hz), 6.53 (1H, d, J=8 Hz), 6.68 (1H, d, J=8 Hz) suggested that DO-9 has a hydroxyl group at C-8 and at C-3′. This presumptive structure was consistent with the ^{13}C-NMR spectrum as listed in Table I. The CD spectrum showed a negative Cotton curve (232 nm) suggesting the

configuration at C-3 to be *R*; thus, DO-9 could be represented as (3*R*)-3′,8-dihydroxyvestitol.

DO-10, pale brown powder, $[\alpha]_D$ −18.6° (DMSO), exhibited M^+ at *m/z* 302, providing a molecular formula of $C_{16}H_{14}O_6$, besides strong peaks at *m/z* 166, 153 and 137. The ^{13}C-NMR spectrum (Table I) showed sixteen signals due to two sp^3 carbons at δ 47.2 (d) and 70.3 (t), one methoxyl group at δ 55.8, five oxygenated aromatic carbons, two quaternary aromatic carbons, five aromatic carbons bearing a proton and one carbonyl carbon at δ 190.6. The ^{1}H-NMR spectrum exhibited signals ascribable to an ABX system at δ 6.36 (1H, d, *J*=2 Hz), 6.54 (1H, dd, *J*=2, 8 Hz) and 7.69 (1H, d, *J*=8 Hz), two protons with *ortho* coupling at δ 6.42 and 6.43 (each 1H, d, *J*=8 Hz), one methylene proton adjacent to oxygen at δ 4.42 (1H, dd, *J*=3, 11 Hz), 4.58 (1H, t, *J*=11 Hz), a methine proton at δ 4.08 (1H, dd, *J*=3, 11 Hz), one methoxyl group at δ 3.75 and three hydroxyl protons at δ 8.62 (2H, br s) and 10.70 (1H, br s). From the above evidence, DO-10 was assumed to be a trihydroxymonomethoxyisoflavanone derivative. The ^{1}H-NMR spectrum suggested that DO-10 has a hydroxyl group either at C-8 or C-3′ on a vestitol-type structure. The EI-MS showed fragment ion peaks at *m/z* 166 (B-ring) and 137 (A-ring) produced by retro Diels–Alder fission at the C-ring of the isoflavone, thus indicating the substitution of the hydroxyl group at the B-ring. Signals of C-2′, C-3′, C-4′ and C-6′ in the ^{13}C-NMR spectrum (Table I) of DO-10 were shifted by −13.0, +31.5, +4.1 and −9.0, respectively, from those of vestitol, thus indicating the presence of the hydroxyl group at C-3′ in DO-10. The configuration at C-3 was determined as *R* from the fact that the CD spectrum of DO-10 indicated a negative Cotton effect at 234 nm. Therefore, the structure of DO-10 was established as (3*R*)-2′,3′,7-trihydroxy-4′-methoxyisoflavanone.

DO-11, pale yellow plates, mp 250—252 °C, showed a molecular ion at *m/z* 284 in the EI-MS. Its ^{1}H-NMR spectrum showed signals due to six aromatic protons at δ 6.80—7.18 (5H, m), 8.00 (1H, d, *J*=8 Hz), a proton attached to the sp^2 carbon at δ 8.26 (1H, s) and a methoxyl group at δ 3.81, but no signal due to the proton attached to the sp^3 carbon. This means that DO-11 should be an isoflavone or a flavone derivative. In the ^{13}C-NMR spectrum (Table II), fifteen sp^2 carbon signals were observed due to five oxygenated carbons, three quaternary carbons, six carbons bearing an aromatic proton and one carbonyl carbon along with one methoxyl group. From the evidence of the ^{13}C-NMR spectrum, DO-11 was deduced to be an isoflavone derivative. In a comparison of the ^{13}C-NMR chemical shifts with those of daidzein,[10] a signal attributable to the C-3′ of daidzein was shifted downfield from δ 114.9 to 147.5 in DO-11, and the signals of C-2′, C-4′ and C-6′ located *ortho* and *para* to C-3′ were shifted to higher field by 18.1, 10.9 and 10.3 ppm. Therefore, DO-11 was characterized as 3′-methoxydaidzein.

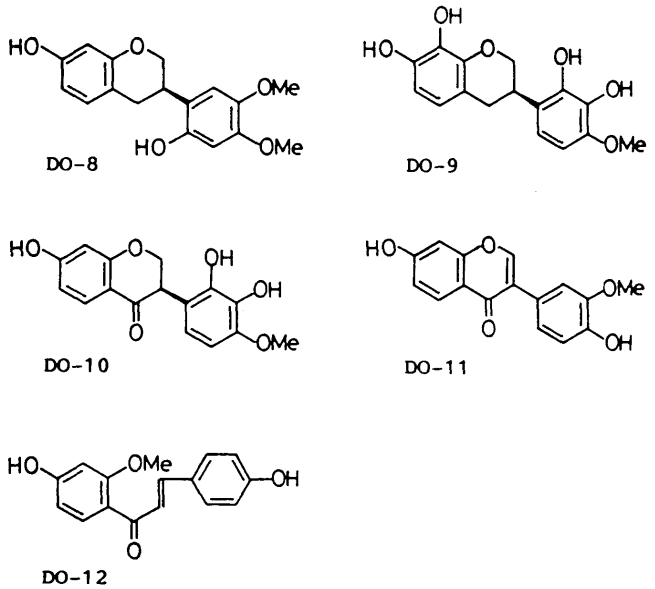
TABLE II. ^{13}C-NMR Data for DO-11 (in Acetone-d_6) and Daidzein (in DMSO-d_6)

	DO-11	Daidzein		DO-11	Daidzein
C-2	152.8	153.3	C-8a	157.4	156.9
C-3	124.7	123.7	C-1′	123.5	122.3
C-4	174.6	175.0	C-2′	111.9	130.0
C-4a	116.7	118.4	C-3′	147.5	114.9
C-5	127.2	127.0	C-4′	146.1	157.0
C-6	115.1	115.6	C-5′	116.5	114.9
C-7	162.5	161.3	C-6′	119.7	130.0
C-8	102.1	103.3	OMe	55.6	—

TABLE III. ^{13}C-NMR Data for DO-12 and Isoliquiritigenin (in DMSO-d_6)

	DO-12	Isoliquiritigenin		DO-12	Isoliquiritigenin
C-1	120.1	125.8	C-3′	99.2	102.6
C-2	130.2	130.6	C-4′	162.4	165.4
C-3	116.3	115.8	C-5′	107.9	107.9
C-4	159.6	159.9	C-6′	132.3	132.3
C-5	116.3	115.8	α	120.3	117.8
C-6	130.2	130.6	β	141.7	143.8
C-1′	124.0	113.2	C=O	189.0	191.4
C-2′	160.4	164.6	OMe	55.7	—

DO-12, pale yellow plates, mp 169—171 °C, showed a molecular ion at *m/z* 270 together with other fragment ions at *m/z* 176 and 163 in the EI-MS. Its ^{1}H-NMR spectrum showed, in the sp^2 region, the signals of nine protons consisting of a pair of ABX type signals [δ 6.51 (1H, d, *J*=2 Hz), 6.43 (1H, dd, *J*=2, 8 Hz), 7.53 (1H, d, *J*=8 Hz)], a pair of A_2B_2 type signals [δ 6.80 (2H, d, *J*=8 Hz), 7.53 (2H, d, *J*=8 Hz] and two proton signals [δ 7.42 (s)]. Besides the above signals, a methoxyl signal [δ 3.85 (3H, s)] and two hydroxyl signals (δ 10.10, br s) were observed. This signal pattern was similar to that of isoliquiritigenin, and the structure was estimated to have a methoxyl group instead of the hydroxyl group on the B-ring from the EI-MS fragmentation. Its location was shown to be at C-2′-OH from the evidence that no proton signal due to hydrogen bond was observed near δ 12. The ^{13}C-NMR spectrum (Table III) also supported the above presumption. Therefore, DO-12 was concluded to be 2′-*O*-methylisoliquiritigenin.



New Biisoflavonoids[11] DO-13, colorless needles, mp 168—169 °C, $[\alpha]_D$ −130.8° (MeOH), showed $(M+H)^+$ at *m/z* 559 in the fast atom bombardment mass spectrum (FAB-MS). The ^{13}C-NMR spectrum (Table IV) showed

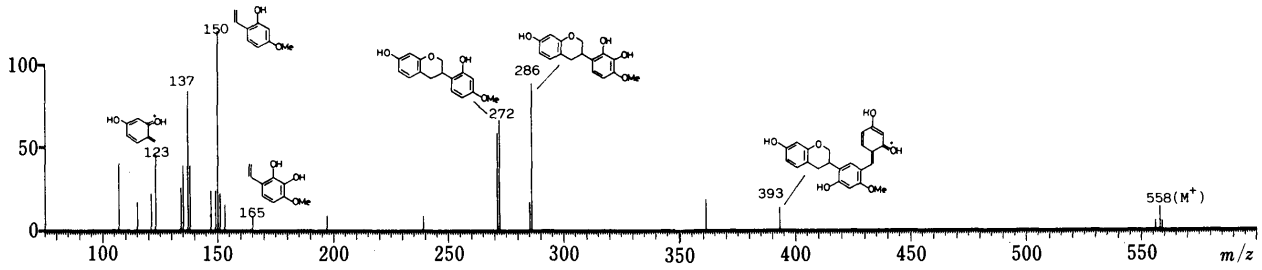


Fig. 1. EI-MS of DO-13

TABLE IV. ^{13}C-NMR Data for DO-13, DO-14, DO-15 and DO-16 (in Acetone-d_6)

	DO-13	DO-14	DO-15	DO-16
Upper unit C-2	69.8	69.4	70.3	70.0
C-3	38.1	37.7	38.0	38.1
C-4	39.0	38.9	39.0	39.0
C-4a	119.8	119.7	118.5	119.4
C-5	130.7[a]	130.6[a]	130.9[a]	130.9[a]
C-6	108.6[b]	108.6[b]	106.7[b]	108.7
C-7	157.2[c]	156.5	157.3	157.2[b]
C-8	103.3[d]	103.4[c]	103.3[c]	103.4[c]
C-8a	154.9[e]	155.7[d]	154.9[d]	154.9[d]
C-1′	118.4	117.8	118.5	118.4
C-2′	144.5	154.5	150.0	152.1
C-3′	132.0	101.9	101.9	136.5
C-4′	147.3	157.5	149.4	149.0
C-5′	103.5[d]	105.3	143.5	103.8[c]
C-6′	118.6	129.1	114.3	123.2
Lower unit C-2	70.4	70.1	70.5	70.5
C-3	32.5	32.2	32.6	32.5
C-4	31.0	30.8	31.0	31.0
C-4a	114.1	114.0	114.4	114.2
C-5	131.0[a]	131.0[a]	131.1[a]	131.0[a]
C-6	108.8[b]	108.4[b]	108.7[b]	108.7
C-7	157.4[c]	156.5	157.3	157.3[b]
C-8	103.4[d]	103.1[c]	103.6[c]	103.5[c]
C-8a	155.8[e]	155.9[d]	155.9[d]	156.2[d]
C-1′	121.1	119.8	120.0	120.9
C-2′	156.2	156.3[d]	156.3[d]	156.3[d]
C-3′	100.0	99.8	100.0	99.0
C-4′	157.9	159.6	158.0	157.4[b]
C-5′	124.2	124.1	124.1	124.1
C-6′	128.7	129.1	128.7	128.6
OMe	55.9	55.0	56.0×2	55.8×2
	56.1	55.8	57.0	60.7

a—*e*) Assignments may be interchanged in each column.

signals due to thirty-two carbons, including six signals at δ 31.0 (t), 32.5 (d), 38.1 (d), 39.0 (d), 69.8 (t), 70.4 (t) assignable to C-2, C-3 and C-4 on the isoflavan derivative, and two methoxyl signals at δ 55.9, and 56.1. Moreover, in the sp^2 carbon region, nine oxygenated carbon signals, five quaternary carbon signals and ten tertiary carbon signals were present. From the above evidence, DO-13 was assumed to be a dimer of an isoflavan derivative. As regards the bonding location, the signal of one of two isoflavan units was shifted by +8.2 ppm at C-4, and the other unit possesses one more quaternary carbon, thus indicating that the molecule has a bond between C-4 and a carbon on the benzene ring. The pentaacetate of DO-13 showed M^+ at 768 in the EI-MS. This ^{1}H-NMR spectrum exhibited signals of five phenolic acetyl groups at δ 2.24, 2.25, 2.28, 2.29 and 2.30, two methoxyl groups, two methylene protons at C-2 of isoflavan, a methine proton at C-3 and one

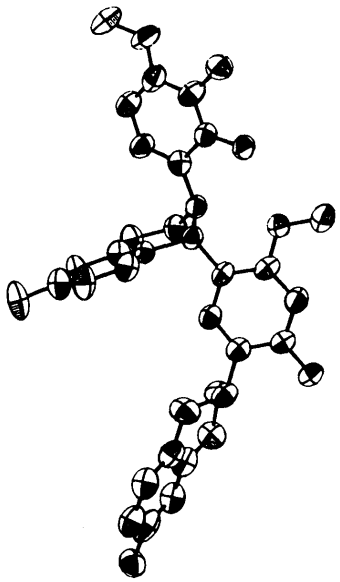


Fig. 2. ORTEP Drawing of DO-13

methylene group at C-4. Moreover, a signal (δ 4.63, d, J= 8 Hz) assignable to H-4 was observed. This fact indicated the steric relationship between H-3 and H-4 to be *trans*. In the aromatic proton region, two ABX-type signals [δ 6.75 (1H, d, J=8 Hz), 6.59 (1H, dd, J=2, 8 Hz), 6.57 (1H, d, J= 2 Hz) and 6.97 (1H, d, J=8 Hz), 6.60 (1H, dd, J=2, 8 Hz), 6.63 (1H, d, J=2 Hz)], two *ortho*-coupling signals [δ 6.75 (1H, d, J=8 Hz), 6.95 (1H, d, J=8 Hz)] and two noncoupling signals [δ 6.54 (2H, s)] were also observed. Furthermore, the EI-MS of DO-13 gave fragment ions at *m/z* 393, 286, 272, 165, 150 and 123 as shown in Fig. 1, produced *via* retro Diels–Alder fission. From the above evidence, the chemical structure of DO-13 was estimated to involve biisoflavan bonding through C-4 of 2′,3′,7-trihydroxy-4′-methoxyisoflavan (=3′-hydroxyvestitol) and C-5′ of vestitol. To verify this structure, an X-ray analysis of DO-13 was performed using a crystal obtained from acetone–benzene; an ORTEP drawing[12] is shown in Fig. 2. Since no information could be obtained about the absolute configuration, we examined a CD spectrum of DO-13. Roux *et al.*[13] isolated (3*S*,4*S*)-*trans*- 2′,7-dihydroxy-4′-methoxy-4-[(3*S*)-2′,7-dihydroxy-4′-methoxyisoflavan-5′-yl]isoflavan (I) and concluded it to have (4*S*) configuration on the basis that the CD spectrum showed a positive curve at 235 nm. Moreover, they elucidated the configurations at C-3 on the upper (*u*) and lower (*l*) isoflavan units by the synthesis of I from (3*S*)-vestitol and medicarpin. The CD spectrum (Fig. 3) of DO-13 showed a positive Cotton effect at 292 nm and a negative strong Cotton effect at 235, which were opposite

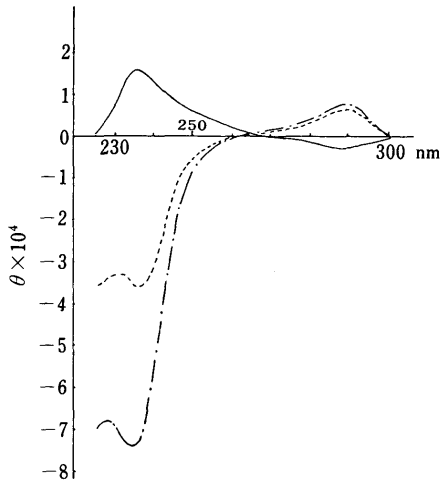
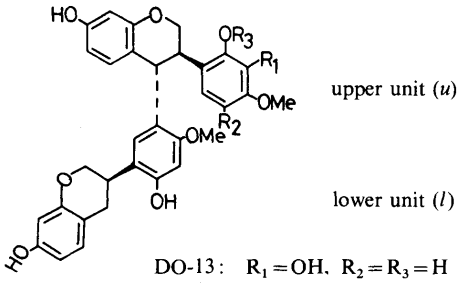


Fig. 3. CD Spectra of I, DO-13 and DO-14
——, I; —·—, DO-13; ------, DO-14.

to those of I, indicating C-4 to have *R* configuration. The configurations of C-3 (*u*) and C-3″ (*l*) were determined from the CD, ^{1}H-NMR spectrum and X-ray analysis. From the above evidence, DO-13 was concluded to be (3*R*,4*R*)-*trans*-2′,3′,7-trihydroxy-4′-methoxy-4-[(3*R*)-2′,7-dihydroxy-4′-methoxyisoflavan-5′-yl]isoflavan.



DO-13: R_1=OH, R_2=R_3=H
DO-14: R_1=R_2=R_3=H
DO-15: R_1=R_3=H, R_2=OMe
DO-16: R_1=OH, R_2=H, R_3=Me

DO-14, pale brown powder, $[\alpha]_D$ −66.7° (MeOH), showed the molecular ion at *m/z* 542 together with other peaks at *m/z* 419, 393, 270, 255, 150, 137 and 123 in the EI-MS, which suggested DO-14 to be a dimeric flavonoid. The ^{1}H-NMR spectrum of DO-14 exhibited eleven aromatic signals between δ 6.19 and 6.90, two methoxyl signals at δ 3.63 and one methylene signal at δ 2.64 (2H, d, *J*=9 Hz), three methine signals at δ 4.58 (1H, d, *J*=9 Hz) and 3.36 (2H, m), and two pairs of signals due to oxygenated methylenes at δ 3.82 (1H, t, *J*=9 Hz) and 4.09 (3H, m) in the sp^3 proton region, which were attributable to the protons attached to C-2, C-3 and C-4. Moreover, the ^{1}H-NMR spectrum of the peracetate of DO-14 showed, along with signals of four acetyl groups and two methoxyl groups, nine proton signals (C-2, C-3 and C-4 of a biisoflavan derivative) and three ABX-type signals [δ 6.73 (1H, d, *J*=8 Hz), 6.54 (1H, dd, *J*=2, 8 Hz), 6.63 (1H, d, *J*=2 Hz), 6.97 (1H, d, *J*=8 Hz), 6.69 (1H, dd, *J*=3, 8 Hz), 6.50 (1H, d, *J*=3 Hz) and 7.05 (1H, d, *J*=8 Hz), 6.59 (1H, dd, *J*=2, 8 Hz), 6.64 (1H, d, *J*=2 Hz)], as well as two isolated two proton signals [δ 6.55 (2H, s)], indicating DO-14 to be a biisoflavan derivative bonding through C-4 and C-5′, like DO-13, and having one less oxygen than DO-13. Furthermore, the ^{13}C-NMR spectrum (Table IV) was almost analogous to that of DO-13, except that signals due to the B-ring part of the upper unit were different from those of DO-13 and signals of 2′-hydroxy-4′-methoxy type, *i.e.* vestitol type, appeared: thus its structure was composed of vestitol units as both upper and lower units, which are linked between C-4 and C-5′. The CD spectrum of DO-14 showed a positive Cotton effect at 291 nm and a negative one at 235 nm, suggesting C-3 (*u*) (*R*), C-4 (*u*) (*R*), C-3 (*l*) (*R*) configurations. This compound corresponds to be the enantiomer of the biisoflavonoid (I) obtained by Roux *et al.*

DO-15, pale brown powder, $[\alpha]_D$ −148.6° (MeOH), showed $(M+Na)^+$ and M^+ at *m/z* 595 and 572, respectively, indicating DO-15 to be a flavonoid dimer, like DO-13 and DO-14. The ^{1}H-NMR spectrum of DO-15 exhibited an analogous pattern in the sp^3 region to that of DO-13, suggesting DO-15 to be a biisoflavan derivative. A signal at δ 4.70 (d, *J*=9 Hz) assignable to 4-H also demonstrated that the bond between C-3 and C-4 should be *trans*. Moreover, it showed the following signals: three methoxyl signals at δ 3.65, 3.67 and 3.73, two ABX type signals [δ 6.49 (1H, d, *J*=8 Hz), 6.26 (1H, dd, *J*=3, 8 Hz), 6.85 (1H, d, *J*=3 Hz) and 6.49 (1H, d, *J*=8 Hz), 6.32 (1H, dd, *J*=2, 8 Hz), 6.24 (1H, d, *J*=2 Hz)], and four non-coupling signals [δ 6.30 (1H, s), 6.45 (1H, s), 6.78 (2H, s)] in the sp^2 proton region. The above evidence suggested that the structure of DO-15 corresponds to that of DO-14 possessing one more methoxyl at either C-6 (*u*), C-5′ (*u*) or C-6 (*l*). The location of the methoxyl group was revealed to be C-5′ in the upper unit of DO-14 since the EI-MS of DO-15 showed fragment ions at *m/z* 393 and 180 produced by retro Diels–Alder fission. The ^{13}C-NMR spectrum (Table IV) of DO-15, when compared with that of DO-13, indicated shifts of +38.2 ppm at C-5′, and −4.5, −8.1 and −14.8 ppm at C-2′, C-4′ and C-6′, respectively, in the B ring of the upper unit, also supporting the above deduced structure. The positive Cotton curve at 291 nm and negative one at 236 nm in the CD spectrum disclosed that the configurations at C-3 (*u*), 4 (*u*) and 3 (*l*) are all *R*. The structure of DO-15 was concluded to be as shown in the formula.

DO-16, pale brown powder, $[\alpha]_D$ −111.3° (MeOH), showed a peak due to $(M+H)^+$ at *m/z* 573, suggesting DO-16 to be a flavonoid dimer, like DO-13. The ^{13}C-NMR (Table IV) spectrum of DO-16 showed signals due to C-2, C-3 and C-4 at δ 31.0, 32.5, 38.1, 39.0, 70.0 and 70.5. It also showed signals of three methoxyl groups (at δ 55.8×2, 60.7), one (δ 60.7) of which is *ortho* to both oxygenated carbon and C-substituted carbon. Aromatic carbon signals except those of the upper unit of B ring were broadly coincident with those of DO-13, DO-14 and DO-15, and substitution with a methoxyl group at C-2′ of DO-13 to form a mucronulatol-type[14] B-ring could account well for the chemical shifts. Moreover, in the EI-MS of DO-16, a fragment ion peak was observed at *m/z* 393,180, derived by retro Diels–Alder fission at the C-ring, also supporting the above structure. The ^{1}H-NMR spectrum of DO-16 acetate showed four signals [δ 2.27 (6H, s), 2.28 (3H, s), 2.30 (3H, s)], three methoxyl signals (each 3H, s, δ 3.69, 3.76 and 3.80), and H-2, H-3 and H-4 of the isoflavan [δ 3.85 (1H, t, *J*=10 Hz), 4.07 (1H, t, *J*=10 Hz), 4.15 (2H, m), 3.17 (1H,

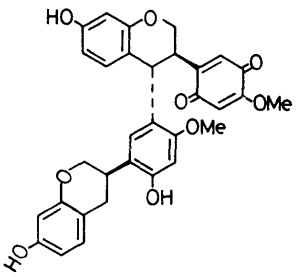
m), 3.43 (1H, m), 2.63 (1H, dd, $J=10$, 16 Hz), 2.74 (1H, dd, $J=6$, 16 Hz), 4.63 (1H, d, $J=7$ Hz), and H-4 (d, $J=7$ Hz)], which indicated *trans* configuration at H-3 and H-4. The sp^2 proton region showed signals [δ 6.74 (1H, d, $J=8$ Hz), 6.56 (1H, dd, $J=3$, 8 Hz), 6.55 (1H, d, $J=3$ Hz) and 6.96 (1H, d, $J=8$ Hz), 6.60 (1H, dd, $J=3$, 8 Hz), 6.64 (1H, d, $J=3$ Hz)] due to two ABXs in the A rings in both the upper and lower units of biisoflavan, two ortho-coupled protons [δ 6.69 (1H, d, $J=9$ Hz) and 6.79 (1H, d, $J=9$ Hz)] in the B ring of the upper unit, and two singlet signals [δ 6.55, 6.56 (each 1H, s)] in the B-ring of the lower unit. The above-mentioned assignment of the ^{1}H-NMR spectrum supported the deduced structure. Configurations at C-3 (*u*), C-4 (*u*), and C-3 (*l*) were determined to be all *R* by measurement of the CD spectrum, which showed a negative Cotton curve at 233 nm. Therefore, the structure of DO-16 was concluded to be as shown in the formula.

DO-17, yellow powder, $[\alpha]_D$ $-123.2°$ (MeOH), showed the molecular ion at *m/z* 556 in the FAB-MS, which suggested it to be a flavonoid dimer. The ^{13}C-NMR spectrum (Table V) of DO-17 showed signals due to C-2, C-3, and C-4 of isoflavan, and two methoxyl signals. Signals due to the sp^2 carbons were good coincident with those of DO-13, except for the B-ring portion, where the signals of δ 109.9 (d), 131.0 (d) 150.2 (s), 159.8 (s), 183.3 (s), 187.9 (s) suggested the occurrence of the benzoquinone form in the B-ring. These signals showed good accordance with those of DO-2, so the structure of DO-17 was assumed to be the combined form through C-4 of claussequinone in the upper unit and C-5′ of vestitol. The ^{1}H-NMR spectrum of DO-17 showed signals due to 4 (*l*)-methylene (δ 2.70, m), 3 (*u*), 3 (*l*), 4 (*u*)-methines [δ 3.42 (1H, m), 3.37 (1H, m), 4.47 (1H, d, $J=8$ Hz)], two oxygenated methylenes at C-2 (*u*), C-2 (*l*) [δ 3.89 (1H, t, $J=10$ Hz), 4.04 (1H, m), 4.13 (2H, m)], and two methoxyl groups (δ 3.72 and 3.81). Moreover, in the sp^2 proton region, we observed two ABX type signals [δ 6.58 (1H, d, $J=8$ Hz), 6.32 (1H, dd, $J=2$, 8 Hz), 6.23 (1H, d, $J=2$ Hz) and 6.79 (1H, d, $J=8$ Hz), 6.35 (1H, dd, $J=2$, 8 Hz), 6.30 (1H, d, $J=2$ Hz)], and four singlet signals [δ 6.01, 6.46, 6.56, 6.66 (each 1H)], supporting the above structure. Furthermore, fragment ion peaks as shown in Chart 2 were consistent with that structure. The stereochemistries at C-3 (*u*), C-4 (*u*) and C-3 (*l*) were also determined to be all *R* from the CD Cotton curves. Consequently, the structure of DO-17 was concluded to be as shown.

TABLE V. ^{13}C-NMR Data for DO-17, Vestitol and Claussequinone (in Acetone-d_6)

	DO-17 Upper unit	Clausse-quinone		DO-17 Lower unit	Vestitol
C-2	67.7	67.8	C-2	70.7	70.3
C-3	39.5	30.6	C-3	32.8	32.4
C-4	39.3	28.7	C-4	31.0	30.8
C-4a	116.6	111.1	C-4a	114.6	114.2
C-5	131.7[a]	130.3	C-5	132.7[a]	130.8
C-6	109.1[b]	108.4	C-6	108.6[b]	108.6
C-7	157.8[c]	156.6	C-7	157.3[c]	156.4
C-8	103.7[d]	102.5	C-8	103.8[d]	103.5
C-8a	155.9[e]	154.1	C-8a	156.2[e]	155.8
C-1′	150.2	148.3	C-1′	120.5	120.7
C-2′	187.9	186.4	C-2′	156.7[e]	155.8
C-3′	109.9	107.5	C-3′	99.8	102.4
C-4′	159.8	158.2	C-4′	157.8	160.1
C-5′	183.3	181.6	C-5′	124.0	105.5
C-6′	131.0[a]	129.9	C-6′	129.8	128.5
OMe		56.3	OMe	55.9	55.2
				56.8	

a—*e*) Assignments may be interchanged in each column.



DO-17

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus (hot-stage type) and are uncorrected. The optical rotations were measured with a JASCO DIP-360 digital polarimeter. The UV spectra were recorded with a Hitachi 556 spectrometer. The EI-MS were measured with a JEOL 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-

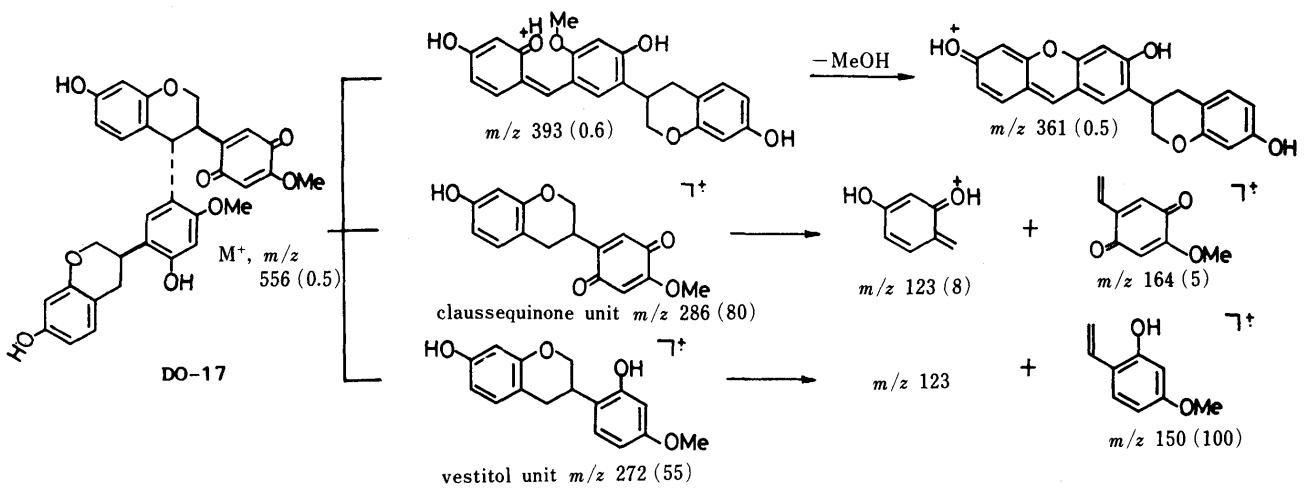


Chart 2. EI-MS Fragment Ion Peaks of DO-17

NMR spectra were recorded with JEOL JNM-60 (60 MHz), JNM-FX-100 (100 MHz) and JNM-GX-400 (400 MHz), and the ^{13}C-NMR spectra with JEOL JNM-FX-100 (25.5 MHz), JNM-FX-200 (50.3 MHz), JNM-GX-270 (67.5 MHz) and JNM-GX400 (100.4 MHz) spectrometers; chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. Column chromatography was carried out with Sephadex LH-20 (25—100 μ, Pharmacia Co., Ltd.), MCI-gel CHP 20P (75—150 μ, Mitsubishi Chemical Industries, Ltd.), silica gel (Merck Co., Ltd.), Bondapak C_{18}/Porasil B (37—75 μ, Waters Associates, Inc.) and Kieselgel 60 (70—230 mesh, Merck). TLC was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) using $CHCl_3$–MeOH = 10 : 1 as the developing solvent for the free compounds, DO-1—DO-17, 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 (Toyo Soda HPLC 803D, UV-8 model II system (280 nm); column, Toyo Soda TSK-80 TM, −120 T (ODS, 4 mm × 250); solvent, 70% MeOH).

Isolation The methanolic extractive (5 kg) of the heartwood (10 kg) of *Dalbergia odorifera* T. CHEN was chromatographed over silica gel (4 kg) using benzene–acetone as the solvent to give frs. 1—7, frs. 2—5 among which were further separated by means of various chromatographies on MCI gel CHP 20P, Sephadex LH-20, silica gel and Bondapak C_{18} to afford DO-1 (4.5 g), DO-2 (60 mg), DO-3 (1.2 g), DO-4 (85 mg), DO-5 (18 mg), DO-6 (338 mg), DO-7 (56 mg), DO-8 (85 mg), DO-9 (598 mg), DO-10 (187 mg), DO-11 (130 mg), DO-12 (127 mg), DO-13 (457 mg), DO-14 (1274 mg), DO-15 (242 mg), DO-16 (1035 mg), DO-17 (77 mg), DO-18 (533 mg), DO-19 (418 mg), DO-20 (241 mg), DO-21 (45 mg), DO-22 (44 mg), DO-23 (64 mg), DO-24 (9 mg), DO-25 (6 mg), DO-26 (8 mg) and DO-27 (6 mg) (Chart 1).

DO-1 [(3*R*)-Vestitol] *Rf* 0.65, colorless needles, mp 135—137 °C. $[\alpha]_D^{22}$ −18.9° (c = 0.50, MeOH). CD ($c = 1.38 \times 10^{-4}$, MeOH) [θ] (nm): 2.22×10^3 (290), 0 (260), -5.79×10^3 (233). EI-MS m/z: 272 (M^+), 150, 137, 123. ^{1}H-NMR (acetone-d_6) δ: 2.87 (2H, m, 4-H), 3.27 (1H, m, 3-H), 3.62 (3H, s, OMe), 3.79 (1H, t, J = 10 Hz, 2-H), 4.27 (1H, dd, J = 4, 10 Hz, 2-H), 6.37, 6.48 (each 1H, d, J = 2 Hz, 8, 3′-H), 6.40, 6.41 (each 1H, dd, J = 2, 8 Hz, 6, 5′-H), 6.90, 6.91 (each 1H, d, J = 8 Hz, 5, 6′-H), 8.40 (2H, br s, ArOH). ^{13}C-NMR: Table VI.

DO-1 Diacetate A mixture of DO-1 (10 mg), acetic anhydride (1 ml) and pyridine (2 ml) was kept standing overnight at room temperature and evaporated under reduced pressure to give a residue, which was subjected to silica gel column chromatography with *n*-hexane : EtOAc = 2 : 1 to afford the acetate (12 mg) of DO-1, *Rf* 0.28 (*n*-hexane : EtOAc = 2 : 1), an amorphous powder. ^{1}H-NMR ($CDCl_3$) δ: 2.29, 2.32 (each 3H, s, OAc), 2.93 (2H, m, 4-H), 3.25 (1H, m, 3-H), 3.79 (3H, s, OMe), 4.00 (1H, t, J = 10 Hz, 2-H), 4.25 (1H, m, 2-H), 6.59 (1H, J = 2 Hz, 8-H), 6.60 (1H, dd, J = 2, 9 Hz, 6-H), 6.66 (1H, J = 2 Hz, 3′-H), 6.81 (1H, dd, J = 2, 8 Hz, 5′-H), 7.07 (1H, d, J = 8 Hz, 5-H), 7.11 (1H, d, J = 8 Hz, 6′-H).

DO-2 [(3*R*)-Claussequinone] *Rf* 0.66, red brown needles, mp 162—165 °C. $[\alpha]_D^{22}$ −65.2° (c = 0.49, MeOH). EI-MS m/z: 286 (M^+), 164, 123. ^{1}H-NMR (acetone-d_6) δ: 2.81 (2H, m, 4-H), 3.32 (1H, m, 3-H), 3.67 (3H, s, OMe), 3.92 (1H, t, J = 10 Hz, 2-H), 4.16 (1H, m, 2-H), 6.18—6.96 (total 5H, m, 5, 6, 8, 3′, 6′-H), 9.16 (1H, br s, ArOH). ^{13}C-NMR: Table VI.

DO-2 Monoacetate DO-2 (10 mg) was acetylated in the same way as DO-1 to give the corresponding monoacetate (9 mg), *Rf* 0.28 (*n*-hexane : EtOAc = 2 : 1), white powder. ^{1}H-NMR ($CDCl_3$) δ: 2.28 (3H, s, OAc), 2.81, 3.06 (each 1H, m, 4-H), 3.49 (1H, m, 3-H), 3.83 (3H, s, OMe), 4.08, 4.29 (each 1H, m, 2-H), 5.98, 6.19 (each 1H, s, 3′, 6′-H), 6.58 (1H, d, J = 2 Hz, 8-H), 6.64 (1H, dd, J = 2, 8 Hz, 6-H), 7.05 (1H, J = 8 Hz, 5-H).

DO-3 (Medicarpin) *Rf* 0.61, colorless needles, mp 164—165 °C. $[\alpha]_D^{18}$ 0° (c = 0.50, MeOH). ^{1}H-NMR (acetone-d_6) δ: 3.36 (1H, m, 6a-H), 3.58 (1H, d, J = 8 Hz, 6-H), 3.68 (3H, s, OMe), 4.30 (1H, dd, J = 10, 10 Hz, 6-H), 5.54 (1H, d, J = 6 Hz, 11a-H), 6.30—7.48 (total 6H, m, 1,2,4,7,8,10-H), 9.52 (1H, br s, ArOH). ^{13}C-NMR: Table VI.

DO-4 (Formononetin) *Rf* 0.68, pale yellow needles, mp 221—223 °C. EI-MS m/z: 268 (M^+). ^{1}H-NMR (acetone-d_6) δ: 3.76 (3H, s, OMe), 6.70—8.15 (total 7H, m, 5,6,8,2′,3′,5′,6′-H), 8.24 (1H, s, 2-H), 10.72 (1H, br s, ArOH). ^{13}C-NMR: Table VI.

DO-5 (Bowdichione) *Rf* 0.60, pale blue needles, mp 264—266 °C. ^{1}H-

TABLE VI. ^{13}C-NMR Data for DO-1, DO-2, DO-4, DO-6 (in Acetone-d_6) and DO-5 (in DMSO-d_6)

	DO-1	DO-2	DO-4	DO-5	DO-6
C-2	70.3	67.8	152.9	156.7	80.4
C-3	32.4	30.6	124.3	116.9	44.5
C-4	30.8	28.7	174.4	173.7	190.8
C-4a	114.2	111.1	116.7	116.2	115.1
C-5	130.8	130.3	129.2	133.0	129.4
C-6	108.6	108.4	115.1	115.8	111.2
C-7	155.8	156.6	158.9	158.6	165.3
C-8	103.5	102.5	102.1	102.5	103.5
C-8a	156.4	154.1	157.5	157.4	164.5
C-1′	120.7	148.3	123.2	139.3	131.1
C-2′	157.1	186.4	130.0	185.5	128.8
C-3′	102.4	107.5	113.5	108.1	116.3
C-4′	160.1	158.2	162.6	163.2	158.5
C-5′	105.5	181.6	113.5	181.8	116.3
C-6′	128.5	129.9	130.0	127.4	128.8
OMe	55.2	56.3	55.0	56.6	—

TABLE VII. ^{1}H-NMR Data for Acetates of DO-13—DO-17

Proton	DO-13 acetate	DO-14 acetate	DO-15 acetate	DO-16 acetate	DO-17 acetate
u-2	3.84 (t, J = 10 Hz)	3.84 (t, J = 10 Hz)	3.84 (t, J = 10 Hz)	3.85 (t, J = 10 Hz)	3.88 (t, J = 10 Hz)
l-2	4.07 (t, J = 10 Hz)	4.11 (t, J = 10 Hz)	4.11 (t, J = 10 Hz)	4.07 (t, J = 10 Hz)	4.00—4.16 (3H, m)
u, *l*-2	4.15 (2H, m)	4.17 (2H, m)	4.19 (2H, m)	4.15 (2H, m)	
u-3	3.41 (m)	3.45 (m)	3.43 (m)	3.43 (m)	3.45 (m)
l-3	3.14 (m)	3.14 (m)	3.13 (m)	3.17 (m)	3.18 (m)
u-4	4.63 (d, J = 8 Hz)	4.62 (d, J = 8 Hz)	4.63 (d, J = 9 Hz)	4.63 (d, J = 7 Hz)	4.49 (d, J = 5 Hz)
l-4	2.61 (dd, J = 10, 16 Hz)	2.61 (dd, J = 10, 16 Hz)	2.60 (dd, J = 10, 15 Hz)	2.63 (dd, J = 10, 16 Hz)	2.66 (dd, J = 10, 16 Hz)
	2.75 (dd, J = 5, 16 Hz)	2.73 (dd, J = 8, 16 Hz)	2.74 (dd, J = 5, 15 Hz)	2.74 (dd, J = 6, 16 Hz)	2.80 (dd, J = 6, 16 Hz)
u-5	6.75 (d, J = 8 Hz)	6.73 (d, J = 8 Hz)	6.73 (d, J = 8 Hz)	6.74 (d, J = 8 Hz)	6.79 (d, J = 9 Hz)
l-5	6.97 (d, J = 8 Hz)	7.05 (d, J = 8 Hz)	6.98 (d, J = 8 Hz)	6.96 (d, J = 8 Hz)	6.95 (d, J = 8 Hz)
u-6	6.59 (dd, J = 2, 8 Hz)[a]	6.54 (dd, J = 2, 8 Hz)[a]	6.55 (dd, J = 2, 8 Hz)[a]	6.56 (dd, J = 3, 8 Hz)[a]	6.60 (dd, J = 2, 9 Hz)
l-6	6.60 (dd, J = 2, 8 Hz)[a]	6.59 (dd, J = 2, 8 Hz)[a]	6.57 (dd, J = 2, 8 Hz)[a]	6.60 (dd, J = 3, 8 Hz)[a]	6.58 (dd, J = 2, 8 Hz)
u-8	6.57 (d, J = 2 Hz)[b]	6.63 (d, J = 2 Hz)[b]	6.55 (d, J = 2 Hz)[b]	6.55 (d, J = 3 Hz)[b]	6.57 (d, J = 2 Hz)[a]
l-8	6.63 (d, J = 2 Hz)[b]	6.64 (d, J = 2 Hz)[b]	6.63 (d, J = 2 Hz)[b]	6.64 (d, J = 3 Hz)[b]	6.62 (d, J = 2 Hz)[a]
u-3′	—	6.50 (d, J = 3 Hz)	6.47 (s)	—	5.91 (s)
u-5′	6.75 (d, J = 8 Hz)	6.69 (dd, J = 3, 8 Hz)	—	6.69 (d, J = 9 Hz)[c]	—
u-6′	6.95 (d, J = 8 Hz)	6.97 (d, J = 8 Hz)	6.67 (s)	6.79 (d, J = 9 Hz)[c]	6.40 (s)
l-3′	6.54 (2H, s)	6.55 (2H, s)	6.57 (s)[c]	6.55 (s)[d]	6.53 (2H, s)
l-6′			6.61 (s)[c]	6.56 (s)[d]	
OMe	3.68, 3.78	3.65, 3.74	3.70 × 2, 3.80	3.69, 3.76, 3.80	3.78, 3.80
OAc	2.24, 2.25, 2.28 2.29, 2.30	2.24, 2.28 × 2, 2.29	2.25, 2.28 × 2, 2.30	2.27 × 2, 2.28, 2.30	2.27, 2.28, 2.32

a—*d*) Assignments may be interchanged in each column.

NMR (DMSO-d_6) δ: 3.83 (3H, s, OMe), 6.23 (1H, s, 2-H), 6.95 (1H, d, J=2 Hz, 8-H), 6.97 (1H, dd, J=2, 8 Hz, 6-H), 7.93 (1H, d, J=8 Hz, 5-H), 7.05, 8.33 (each 1H, s, 3′,6′-H), ^{13}C-NMR: Table VI.

DO-6 (Liquiritigenin) *Rf* 0.64, colorless needles, mp 176—178 °C. $[\alpha]_D^{18}$ −10.5° (c=0.50, MeOH). ^{13}C-NMR: Table VI.

DO-7 (Isoliquiritigenin) *Rf* 0.65, yellow needles, mp 166—168 °C. ^{13}C-NMR (acetone-d_6) δ: 127.3, 131.5, 116.7, 160.8, 116.7, 131.5 (C-1-6), 114.3, 165.5, 103.7, 167.4, 108.6, 133.0 (C-1′—6′), 118.1 (C-α), 145.0 (C-β), 192.6 (C=O).

DO-8 [(3*R*)-5′-Methoxyvestitol] *Rf* 0.60, pale brown crystalline powder. $[\alpha]_D^{18}$ −26.2° (c=0.65, MeOH). CD ($c=1.04\times10^{-4}$, MeOH) [θ] (nm): 0.43×10^4 (290), 0 (260), -3.30×10^4 (237), EI-MS m/z: 302 (M^+), 180, 123. ^{1}H-NMR (acetone-d_6) δ: 2.90 (2H, m, 4-H), 3.50 (1H, m, 3-H), 3.70, 3.73 (each 3H, s, OMe), 3.80—4.40 (2H, m, 2-H), 6.30 (1H, d, J=2 Hz, 8-H), 6.36 (1H, dd, J=2, 8 Hz, 6-H), 6.57, 6.76 (each 1H, s, 3′,6′-H), 6.88 (1H, d, J=8 Hz, 5-H). ^{13}C-NMR: Table I.

DO-9 [(3*R*)-3′,8-Dihydroxyvestitol] *Rf* 0.45, colorless needles, mp 224—226 °C. $[\alpha]_D^{29}$ −5.2° (c=0.48, MeOH). UV λ_{max}^{MeOH} nm (log ε): 269 (3.45), 217 (4.67). CD ($c=6.25\times10^{-5}$, MeOH) [θ] (nm): 0.43×10^4 (242), 0 (236), -1.82×10^4 (232). EI-MS m/z: 304 (M^+), 166, 153, 139, 133, 123. ^{1}H-NMR (acetone-d_6) δ: 2.90 (2H, m, 4-H), 3.31 (1H, m, 3-H), 3.78 (3H, s, OMe), 4.13 (2H, m, 2-H), 6.34, 6.48, 6.53, 6.68 (each 1H, d, J=8 Hz, 5,6,5′,6′-H). ^{13}C-NMR: Table I.

DO-9 Tetraacetate DO-9 (20 mg) was acetylated in the same way as mentioned for DO-1 acetate to give the acetate, 15.7 mg, *Rf* 0.24 (*n*-hexane : acetone = 1 : 1), colorless powder. $[\alpha]_D^{26}$ −79.6° (c=0.50, $CHCl_3$). EI-MS m/z: 472 (M^+), 430, 388, 346, 304, 166, 153, 139, 133. ^{1}H-NMR ($CDCl_3$) δ: 2.30 (total 12H, s, OAc), 2.90 (2H, m, 4-H), 3.35 (1H, m, 3-H), 3.80 (3H, s, OMe), 4.18 (2H, m, 2-H), 6.10—6.60 (4H, m, 5,6,5′,6′-H).

DO-9 Pentamethyl Ether DO-9 (14 mg) in dry acetone (15 ml) was methylated with methyl iodide (1 ml) and anhydrous potassium carbonate (3 g) under reflux for 3 h, then the filtrate was concentrated under reduced pressure to give a residue, which was purified by silica gel column chromatography to afford the permethyl ether of DO-11, 23 mg, *Rf* 0.28 (solv. *n*-hexane : EtOAc = 3 : 1), white powder. $[\alpha]_D^{26}$ −59.9° (c=0.49, $CHCl_3$). ^{13}C-NMR ($CDCl_3$) δ: 70.6 (t), 31.7 (d), 31.6 (t), 123.7 (d), 107.6 (d), 151.8 (s), 142.5 (s), 148.2 (s), 116.5 (s), 127.4 (s), 152.0 (s), 137.3 (s), 152.7 (s), 104.6 (d), 121.4 (d) (C-2—8, C-8a, C-4a, C-1′—6′), 56.1, 56.2, 60.8, 60.9, 61.3 (OMe).

DO-10 [(3*R*)-2′,3′,7-Trihydroxy-4′-methoxyisoflavanone] *Rf* 0.54, pale brown powder. $[\alpha]_D^{18}$ −18.6° (c=0.50, DMSO). CD ($c=2.43\times10^{-4}$, DMSO) [θ] (nm): 0.36×10^4 (288), 0 (240), -2.06×10^4 (234). EI-MS m/z: 302 (M^+), 166, 153, 150, 137, 133, 123. ^{1}H-NMR (DMSO-d_6) δ: 3.75 (3H, s, OMe), 4.08 (1H, dd, J=3, 11 Hz, 3-H), 4.42 (1H, dd, J=3, 11 Hz, 2-H), 4.58 (1H, t, J=11 Hz, 2-H′), 6.36 (1H, d, J=2 Hz, 8-H), 6.42, 6.43 (each 1H, d, J=8 Hz, 5′,6′-H), 6.54 (1H, dd, J=2, 8 Hz, 6-H), 7.69 (1H, d, J=8 Hz, 5-H), 8.62, 10.70 (total 3H, br s, ArOH). ^{13}C-NMR: Table I.

DO-11 (3′-Methoxydaidzein) *Rf* 0.58, pale yellow plates, mp 250—252 °C. EI-MS m/z: 284 (M^+). ^{1}H-NMR (acetone-d_6) δ: 3.81 (3H, s, OMe), 6.80—7.18 (total 5H, m, 6,8,2′,5′,6′-H), 8.00 (1H, d, J=8 Hz, 5-H), 8.26 (1H, s, 2-H). ^{13}C-NMR: Table II.

DO-12 (2′-*O*-Methylisoliquiritigenin) *Rf* 0.60, pale yellow plates, mp 169—171 °C. EI-MS m/z: 270 (M^+), 176, 163. ^{1}H-NMR (DMSO-d_6) δ: 3.85 (3H, s, OMe), 6.43 (1H, dd, J=2, 8 Hz, 5′-H), 6.51 (1H, d, J=2 Hz, 3′-H), 6.80 (2H, d, J=8 Hz, 3,5-H), 7.42 (2H, s, α,β-H), 7.53 (3H, d, J=8 Hz, 2,6,6′-H), 10.10 (2H, br s, ArOH). ^{13}C-NMR: Table III.

DO-13 *Rf* 0.46, colorless needles, mp 168—169 °C, $[\alpha]_D^{18}$ −130.8° (c=0.19, MeOH). CD ($c=3.05\times10^{-4}$, MeOH) [θ] (nm): 0.85×10^4 (292), 0 (270), -7.35×10^4 (235) (Fig. 3). FAB-MS m/z: 559 $(M+H)^+$, 393, 361, 287, 269, 185, 166, 153, 123. EI-MS m/z: Fig. 1. ^{1}H-NMR (acetone-d_6) δ: 2.65—2.90 (2H, m, *l*-4), 3.38 (1H, m, *u*-3), 3.70 (1H, m, *l*-3), 3.70, 3.73 (each 3H, s, OMe), 3.70—3.95, 4.08—4.19 (each 2H, m, *u*-2, *l*-2), 4.70 (1H, d, J=10 Hz, *u*-4), 6.23—6.87 (total 10H, m, *u*-5,6,8,5′,6′,*l*-5,6,8,3′,6′). ^{13}C-NMR: Table IV.

DO-13 Pentaacetate DO-13 (20 mg) was acetylated with acetic anhydride (1 ml) and pyridine (2 ml) to give the corresponding acetate, 23 mg, *Rf* 0.23 (*n*-hexane : EtOAc = 2 : 1), colorless needles. EI-MS m/z: 768 (M^+), 519, 487, 445, 403, 361, 249, 166, 150, 137. ^{1}H-NMR: Table VII.

X-Ray Analysis of DO-13 DO-13 ($C_{32}H_{30}O_9$) was crystallized from acetone-benzene in the monoclinic space group $P2_1$ with a=10.566(1), b=17.612(1), c=9.792(1) Å, β=90.96(1), V=1822.9(2) Å^3, and Z=2. All unique diffraction maxima with $2\theta<120°$ were collected on a Rigaku AFC-5 FOS four-circle diffractometer using a graphite monochromated Cu K_α (λ=1.5418 Å) radiation and the $2\theta-\omega$ scan technique. After correcting for Lorentz and polarization effects, 2577 independent reflections were considered as observed, $F_o>2\sigma(F_o)$. The structure was solved by the direct method with the MULTAN[15] series of programs. A block diagonal least-squares refinement[16] with anisotropic nonhydrogen atoms and isotropic hydrogen atoms lowered the R value to 0.105. The final atomic coordinates are listed in Table VIII.

TABLE VIII. Fractional Atomic Coordinates ($\times10^4$) and Isotropic (Equivalent) Temperature Factors B (iso)

Atom	x	y	z	B (iso)
C(*u*-2)	4248 (11)	2185 (6)	930 (12)	4.70 (32)
C(*u*-3)	3166 (10)	2721 (6)	1232 (10)	4.12 (28)
C(*u*-4)	3543 (10)	3235 (6)	2469 (10)	3.88 (27)
C(*u*-4a)	4859 (9)	3559 (6)	2173 (10)	3.65 (26)
C(*u*-5)	5248 (11)	4233 (7)	2792 (11)	4.86 (33)
C(*u*-6)	6445 (12)	4538 (7)	2588 (13)	6.01 (39)
C(*u*-7)	7293 (12)	4144 (8)	1759 (13)	5.81 (38)
C(*u*-8)	6946 (10)	3479 (7)	1097 (12)	4.56 (31)
C(*u*-8a)	5708 (11)	3192 (6)	1324 (11)	4.33 (29)
C(*u*-1′)	2720 (10)	3201 (6)	40 (11)	4.34 (29)
C(*u*-2′)	1494 (10)	3545 (7)	103 (11)	4.45 (30)
C(*u*-3′)	1042 (13)	3660 (7)	−998 (11)	5.26 (35)
C(*u*-4′)	1731 (13)	4053 (7)	−2166 (12)	5.51 (37)
C(*u*-5′)	2906 (12)	3720 (7)	−2258 (11)	5.35 (36)
C(*u*-6′)	3380 (11)	3310 (7)	−1159 (11)	5.05 (34)
C(*l*-2)	6144 (12)	1124 (7)	5737 (13)	5.41 (36)
C(*l*-3)	5709 (12)	1841 (7)	6450 (11)	5.04 (33)
C(*l*-4)	6732 (12)	2399 (7)	6498 (14)	5.91 (39)
C(*l*-4a)	7934 (12)	1994 (7)	7114 (11)	5.03 (34)
C(*l*-5)	8862 (13)	2426 (7)	7736 (14)	6.01 (39)
C(*l*-6)	9957 (14)	2053 (7)	8247 (13)	6.03 (39)
C(*l*-7)	10047 (15)	1287 (7)	8130 (13)	6.59 (44)
C(*l*-8)	9133 (12)	844 (6)	7532 (12)	5.24 (34)
C(*l*-8a)	8065 (12)	1229 (6)	7052 (12)	4.93 (33)
C(*l*-1′)	4510 (11)	2144 (6)	5696 (11)	4.33 (30)
C(*l*-2′)	3307 (11)	1944 (7)	6245 (11)	4.64 (31)
C(*l*-3′)	2214 (12)	2205 (7)	5549 (12)	5.19 (34)
C(*l*-4′)	2322 (11)	2616 (7)	4385 (10)	4.67 (31)
C(*l*-5′)	3486 (11)	2804 (6)	3784 (10)	4.24 (29)
C(*l*-6′)	4587 (10)	2534 (7)	4507 (10)	4.34 (29)
Me(*u*-4′)	1833 (16)	4666 (9)	−4339 (13)	7.34 (48)
Me(*l*-4′)	50 (13)	2827 (10)	4318 (14)	7.67 (50)
O(*u*-2)	5340 (7)	2547 (4)	619 (8)	4.95 (21)
O(*u*-7)	8497 (8)	4447 (5)	1612 (10)	7.09 (29)
O(*u*-2′)	731 (7)	3480 (5)	1227 (7)	5.38 (23)
O(*u*-3′)	−168 (8)	4267 (6)	−870 (8)	6.37 (27)
O(*u*-4′)	1146 (9)	4449 (6)	−3152 (8)	7.01 (29)
O(*l*-2)	7162 (8)	750 (4)	6501 (9)	5.60 (24)
O(*l*-7)	11165 (8)	949 (5)	8628 (9)	6.11 (26)
O(*l*-2′)	3264 (8)	1516 (5)	7382 (8)	5.49 (24)
O(*l*-4′)	1274 (7)	2878 (5)	3660 (7)	5.47 (23)

DO-14 *Rf* 0.48, pale brown powder. $[\alpha]_D^{22}$ −66.7° (c=0.43, MeOH). UV λ_{max}^{MeOH} nm (log ε): 283 (4.27), 217 (4.66). CD ($c=4.43\times10^{-4}$, MeOH) [θ] (nm): 0.66×10^4 (291), 0 (265), -3.47×10^4 (235) (Fig. 3). FD-MS m/z: 542 (M^+), 271. FAB-MS m/z: 542 (M^+), 432, 392, 360, 270, 255, 161, 150, 137, 123. EI-MS m/z: 542 (M^+), 419, 393, 272, 270, 255, 150, 137, 123. ^{1}H-NMR (acetone-d_6) δ: 2.64 (2H, d, J=9 Hz, *l*-4), 3.36 (2H, m, *u*-3, *l*-3), 3.63 (total 6H, OMe × 2), 3.82 (1H, t, J=9 Hz, *u*-2), 4.09 (3H, m, *u*-2, *l*-2 × 2), 4.58 (1H, d, J=9 Hz, *u*-4), 6.19—6.90 (total 11H, m, *u*-5,6,8,3′,5′,6′,*l*-5,6,8,3′,6′). ^{13}C-NMR: Table IV.

DO-14 Tetraacetate DO-14 (30 mg) was acetylated with acetic anhydride (1 ml) and pyridine (1 ml) in the same way as DO-13 to yield the tetraacetate, 38 mg, *Rf* 0.24 (*n*-hexane : EtOAc = 2 : 1), white powder. EI-MS m/z: 710 (M^+), 519, 192. ^{1}H-NMR: Table VII.

DO-14 Hexamethyl Ether DO-14 (20 mg) was methylated with dry acetone (20 ml), methyl iodide (1 ml) and anhydrous potassium carbonate (3 g) under reflux for 3 h. The reaction mixture was filtered to give the filtrate, which was chromatographed over silica gel using *n*-hexane–AcOEt (2 : 1) as the solvent to give the methyl ether of DO-14, 18 mg, *Rf* 0.22 (*n*-hexane : AcOEt = 2 : 1), white powder. CD ($c=3.08\times10^{-4}$, MeOH) [θ] (nm): 0 (302), 0.78×10^4 (290), 0 (260), -3.89×10^4 (237). ^{1}H-NMR ($CDCl_3$) δ: 2.76 (2H, m, *l*-4), 3.43 (2H, m, *u*-3, *l*-3), 3.70, 3.73, 3.74, 3.75, 3.77, 3.80 (each 3H, s, OMe), 3.84 (1H, t, J=10 Hz, *u*-2), 4.16 (3H, m, *u*-2,

l-2×2), 4.68 (1H, d, J=9 Hz, *u*-4), 6.31—6.97 (total 11H, m, *u*-5,6,8,3′,5′,6′,*l*-5,6,8,3′,6′).

DO-15 *Rf* 0.49, pale brown powder. $[\alpha]_D^{18}$ −148.6° (c=0.16, MeOH). UV λ_{max}^{MeOH} nm (log ε): 288 (4.24), 211 (4.79). CD ($c=4.20\times10^{-4}$, MeOH) [θ] (nm): 0.47×10^4 (291), 0 (260), -6.28×10^4 (236). FAB-MS *m/z*: 595 (M^++Na), 572 (M^+), 393, 301, 243, 180, 167, 123. EI-MS *m/z*: 572 (M^+), 393, 300, 272, 180, 150, 137, 123. ^{1}H-NMR (acetone-d_6) δ: 2.64—2.86 (2H, m, *l*-4), 3.10—3.56 (2H, m, *u*-3, *l*-3), 3.65, 3.67, 3.73 (each 3H, s, OMe), 3.78—3.97, 4.04—4.25 (each 2H, m, *u*-2, *l*-2), 4.70 (1H, d, J=9 Hz, *u*-4), 6.24 (1H, d, J=2 Hz), 6.85 (1H, d, J=3 Hz, *u*-8, *l*-8), 6.26 (1H, dd, J=3, 8 Hz), 6.32 (1H, dd, J=2, 8 Hz, *l*-6, *u*-6), 6.49 (2H, d, J=8 Hz, *u*-5, *l*-5), 6.30, 6.45, 6.78×2 (each 1H, s, *u*-3′,6′,*l*-3′,6′). ^{13}C-NMR: Table IV.

DO-15 Tetraacetate DO-15 (10 mg) was acetylated with acetic anhydride (1 ml) and pyridine (2 ml) to provide the acetate, 14 mg, white powder. EI-MS *m/z*: 740 (M^+), 519, 487, 445, 403, 361, 222. ^{1}H-NMR: Table VII.

DO-16 *Rf* 0.45, pale brown powder, $[\alpha]_D^{28}$ −111.3° (c=0.85, MeOH). UV λ_{max}^{MeOH} nm (log ε): 282 (3.99), 214 (4.60). CD ($c=7.18\times10^{-5}$, MeOH) [θ] (nm): 0.49×10^4 (287), 0 (276), -7.58×10^4 (233). FAB-MS *m/z*: 573 (M^++H), 437, 363, 301, 185, 167, 152, 123. EI-MS: 572 (M^+), 393, 300, 272, 180, 150, 137, 123. ^{13}C-NMR: Table IV.

DO-16 Tetraacetate DO-16 (50 mg) was acetylated to provide the acetate (22 mg), *Rf* 0.21 (*n*-hexane : EtOAc, 3:1), white powder. $[\alpha]_D^{28}$ −69.8° (c=0.50, $CHCl_3$). EI-MS *m/z*: 740 (M^+), 698, 519, 487, 445, 403, 327, 222, 180, 123. ^{1}H-NMR: Table VII.

DO-17 *Rf* 0.51, yellow powder. $[\alpha]_D^{18}$ −123.2° (c=0.50, MeOH). CD ($c=1.26\times10^{-5}$, MeOH) [θ] (nm): 2.38×10^4 (290), 0 (278), -6.04×10^4 (260), -5.50×10^4 (254), -1.40×10^5 (239). FAB-MS *m/z*: 556 (M^+), 278. EI-MS: Chart 2. ^{1}H-NMR (acetone-d_6) δ: 2.70 (2H, m, *l*-4), 3.37 (1H, m, *l*-3), 3.42 (1H, m, *u*-3), 3.72, 3.81 (each 3H, s, OMe), 3.89 (1H, t, J=10 Hz, *u*-2), 4.04 (1H, m, *l*-2), 4.13 (2H, m, *u*-2, *l*-2), 4.47 (1H, d, J=8 Hz, *u*-4), 6.23 (1H, d, J=2 Hz, *u*-8), 6.30 (1H, J=2 Hz, *l*-8), 6.32 (1H, dd, J=2, 8 Hz, *u*-6), 6.35 (1H, dd, J=2, 8 Hz, *l*-6), 6.58 (1H, d, J=8 Hz, *u*-5), 6.01, 6.46, 6.56, 6.66 (each 1H, s, *u*-3′,6′,*l*-3′,6′), 6.79 (1H, d, J=8 Hz, *l*-5), 8.15, 8.33, 8.60 (each 1H, br s, ArOH). ^{13}C-NMR: Table V.

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