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NOVEL BI-ISOFLAVONOIDS FROM *DALBERGIA ODORIFERA*

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Five novel bi-isoflavonoids were isolated from the heartwood of *Dalbergia odorifera* T. Chen (Leguminosae) and their structures were determined.

KEYWORDS —— bi-isoflavonoid; *Dalbergia odorifera*; Leguminosae; X-ray analysis

Five new bi-isoflavonoids (compounds 1-5), along with (3R)-vestitol,[1] (3R)-claussequinone,[2] (3R)-5'-methoxyvestitol, formononetin and 3'-methoxydaidzein, were isolated from a fraction with an antihypercholesteremic activity obtained by separating the methanolic extract of the title plant. This paper deals with the stractural elucidation of these five novel bi-isoflavonoids.

Compound 1, colorless needles, mp 168-169°C, $[\alpha]_D$ -130.8° (MeOH), showed a molecular ion at m/z 558 in the MS giving the molecular formula $C_{32}H_{30}O_9$. The ^{13}C-NMR spectrum (Table I) exhibited signals due to two methoxycarbons, two secondary carbons bearing oxygen functions, three benzyl methine carbons, a benzyl methylene carbon, nine aromatic carbons substituted by oxygen groups, and ten aromatic carbons having a proton. The ^{1}H-NMR spectrum (Table II) of the acetate showed signals due to five phenolic acetoxyl, two methoxyl groups, two sets of aromatic ABX system (δ 6.75, 6.59, 6.57; 6.97, 6.60, 6.63), and aromatic protons two ortho coupled (δ 6.75, 6.95) and two noncoupled (δ 6.54). In the aliphatic proton range, nine proton signals were observed at δ 2.61-4.63. These ^{1}H- and ^{13}C-NMR spectra led us to assume the structure of the bi-isoflavonoid as shown in the formula for 1 by comparing with those of vestitol. To verify this structure unambiguously, the X-ray analysis of a single crystal of 1 (recrystallized from acetone-benzene) was undertaken. The crystal data were as follows: size ca. 0.15 x 0.20 x 0.30 mm; monoclinic; space group $P2_1$ (Z=2); cell dimensions a=10.566(1), b=17.612(1), c=9.792(1) Å, β=90.06(1), V=1822.9(2) Å^3. The 2577 unique intensities were collected by the 2θ-ω scan method within $2\theta<120°$ on a Rigaku AFC-5 FOS four-circle diffractometer using graphite monochromated Cu-Kα (λ=1.5418 Å) radiation. Twentyfour plausible positions were revealed by the direct method (MULTAN)[3] and several cycles of isotropic least-squares and subsequent Fourier synthesis gave the positions of the

Table I. ^{13}C-NMR Data for Compounds 1-5

	1	2	3	4	5
Upper unit					
C-2	69.8	69.4	70.3	70.0	67.7
3	38.1	37.7	38.0	38.1	39.5
4	39.0	38.9	39.0	39.0	39.3
5	130.7[a]	130.6[a]	130.9[a]	130.9[a]	131.7[a]
6	108.6[b]	108.6[b]	106.7[b]	108.7	109.1[b]
7	157.2[c]	156.5	157.3	157.2[b]	157.8[c]
8	103.3[d]	103.4[c]	103.3[c]	103.4[c]	103.7[d]
8a	154.9[e]	155.7[d]	154.9[d]	154.9[d]	155.9[e]
4a	119.8	119.7	118.5	119.4	116.6
1'	118.4	117.8	118.5	118.4	150.2
2'	144.5	154.5[d]	150.0	149.0	187.9
3'	132.0	101.9	101.9	136.5	109.9
4'	147.3	157.5	149.4	152.1	159.8
5'	103.5[d]	105.3	143.5	103.8[c]	183.3
6'	118.6	129.1	114.3	123.2	131.0[a]
Lower unit					
C-2	70.4	70.1	70.5	70.5	70.7
3	32.5	32.2	32.6	32.5	32.8
4	31.0	30.8	31.0	31.0	31.0
5	131.0[a]	131.0[a]	131.1[a]	131.0[a]	132.7[a]
6	108.8[b]	108.4[b]	108.7[b]	108.7	108.6[b]
7	157.4[c]	156.5	157.3	157.3[b]	157.3[c]
8	103.4[d]	103.1[c]	103.6[c]	103.5[c]	103.8[d]
8a	155.8[e]	155.9[d]	155.9[d]	156.2[d]	156.2[e]
4a	114.1	114.0	114.4	114.2	114.6
1'	121.1	119.8	120.0	120.9	120.5
2'	156.2	156.3[d]	156.3[d]	156.3[d]	156.7[e]
3'	100.0	99.8	100.0	99.0	99.8
4'	157.9	159.6	158.0	157.4[b]	157.8
5'	124.2	124.1	124.1	124.1	124.0
6'	128.7	129.1	128.7	128.6	129.8
OMe	55.9	55.0	56.0x2	55.8x2	55.9
	56.1	55.8	57.0	60.7	56.8

in $(CD_3)_2CO$ (* in CD_3OD)
a-e : Assignments may be interchanged in each vertical column.

Table II. ^{1}H-NMR Data for the Acetates of Compounds 1-5 (in $CDCl_3$)

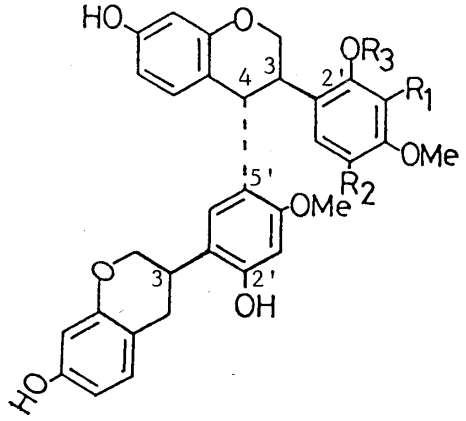
Proton	1-Acetate	2-Acetate	3-Acetate	4-Acetate	5-Acetate
u-2	3.84 (t, J=10 Hz)	3.84 (t, J=10 Hz)	3.84 (t, J=10 Hz)	3.85 (t, J=10 Hz)	3.88 (t, J=10 Hz)
1-2	4.07 (t, J=10 Hz)	4.11 (t, J=10 Hz)	4.11 (t, J=10 Hz)	4.07 (t, J=10 Hz)	4.00- 4.16 (3H, m)
u,1-2	4.15 (2H, m)	4.17 (2H, m)	4.19 (2H, m)	4.15 (2H, m)	
u-3	3.41 (m)	3.45 (m)	3.43 (m)	3.43 (m)	3.45 (m)
1-3	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)
1-4	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)
1-5	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=3,8 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)
1-6	6.60 (dd, J=2,8 Hz)[a]	5.59 (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]
1-8	6.63 (d, J=2 Hz)[b]	6.64 (d, J=3 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)
1-3'	6.54 (2H, s)	6.55 (2H, s)	6.57 (s)[c]	6.55 (s)[d]	6.53 (2H, s)
1-6'			6.61 (s)[c]	6.56 (s)[d]	
OMe	3.68, 3.78	3.65, 3.74	3.70x2, 3.80	3.69, 3.76, 3.80	3.78, 3.80
OAc	2.24, 2.25, 2.28	2.24, 2.28x2, 2.29	2.25, 2.28x2, 2.30	2.27x2, 2.28, 2.30	2.27, 2.28, 2.32

a-d: Assignments may be interchanged in each vertical column.

remaining non-hydrogen atoms and eight disordered solvent atoms. The structure was refined by the block diagonal least-squares (UNICS III)[4] to an R-value of 0.105 for all reflections. An ORTEP[5] drawing of 1 (without solvent atoms) is shown in Fig. 1 (the relative stereostructure).

As regards the naturally occurring bi-isoflavonoid derivative, Roux et al.[6] had obtained a substance as the first example from the same genus, Dalbergia nitidula Welw. ex Bak. and synthetically substantiated its structure as (3S,4S)-3,4-trans-2', 7-dihydroxy-4'-methoxy-4-[(3S)-2',7-dihydroxy-4'-methoxyisoflavan-5'-yl)] isoflavan (6: corresponding to the enantiomer of compound 2).

The proton signal (1H, d, J=8-10 Hz) attributable to H-4 in the ^{1}H-NMR spectra of 1 (in acetone-d_6) and its acetate suggested the conformation of the C-ring [in the upper unit (u)] to be a half chair one having the di-equatorial substitutions



Upper unit (u)

Lower unit (l)

Compounds 1: R_1=OH, R_2=R_3=H
2: R_1=R_2=R_3=H
3: R_1=R_3=H, R_2=OMe
4: R_1=OH, R_2=H, R_3=Me

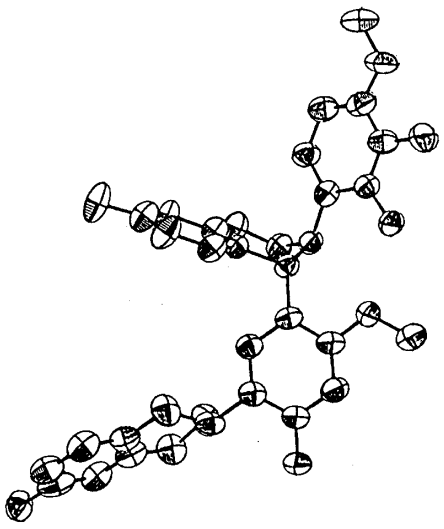


Fig. 1. Structure of 1

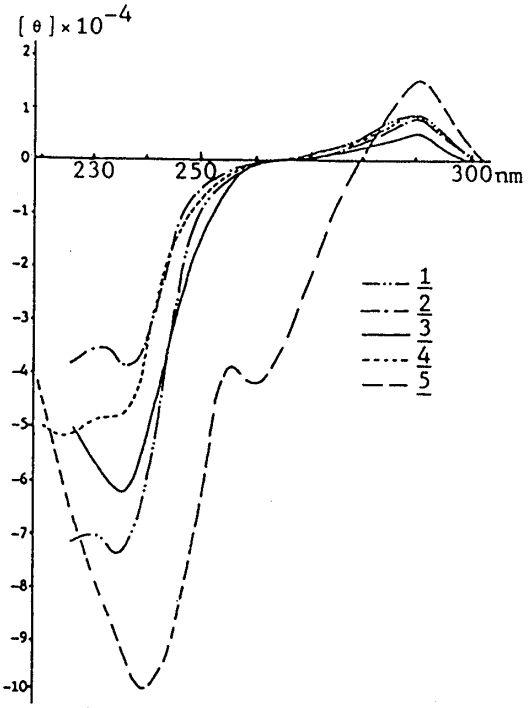


Fig. 2. CD Spectra of Compounds 1-5 (MeOH)

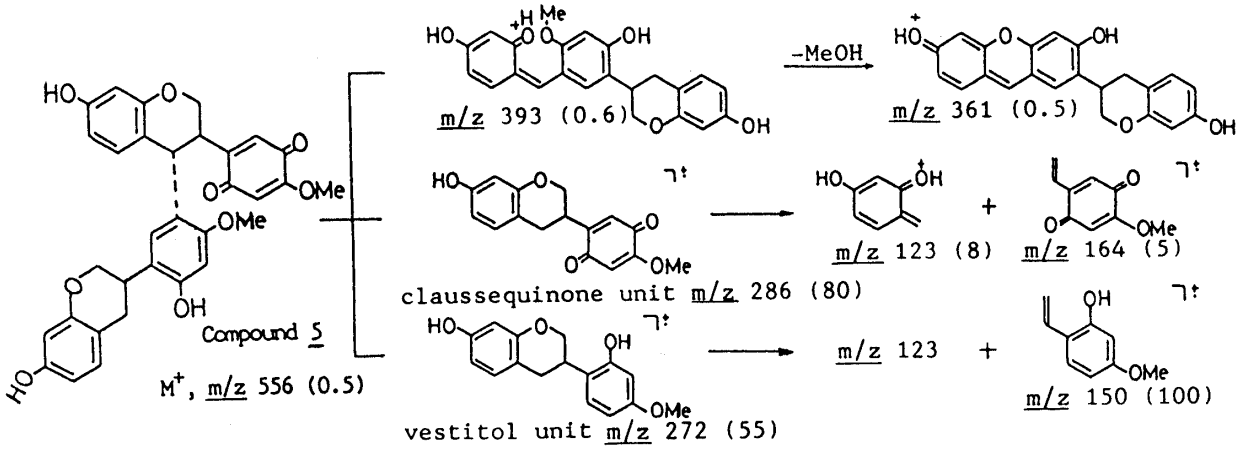


Chart 1. Mass Fragmentation Pattern of Compound 5

at C-3 and -4 as well as 6, while the CD spectrum (Fig. 2) of 1 exhibited a positive Cotton effect at 292 nm ([θ] +8.53 x 10^3) and a negative one at 235 nm ([θ] -7.35 x 10^4), indicating it to be an enantiomer type of 6. Thus, it was revealed that 1 took the 3R,4R (u) and 3R (lower unit) configurations. The conformation in the crystalline state, indicated by X-ray analysis, was a half-chair form (u) having the di-axial substituents at C-3 and -4. This conformation apparently was different from that in the solution of 1 and its acetate. Consequentyl, 1 is represented as (3R,4R)-3,4-trans-7,2',3'-trihydroxy-4'-methoxy-4-[(3R)-2',7-dihydroxy-4'-methoxy-isoflavan-5'-yl] isoflavan.

Analogous compounds, 2, a pale yellow powder, $C_{32}H_{30}O_8$, $[\alpha]_D$ -66.7° (MeOH), 3, a pale yellow powder, $C_{33}H_{32}O_9$, $[\alpha]_D$ -148.6° (MeOH), and 4, a pale yellow powder, $C_{33}H_{32}O_9$, $[\alpha]_D$ -111.3° (MeOH), were also deduced as shown in the formulae by comparison of their ^{13}C-NMR (Table I), ^{1}H-NMR (acetates, Table II) and CD (Fig. 2) spectra with those of 1.

Compound 5, a yellow powder, $[\alpha]_D$ -123.2° (MeOH), $C_{32}H_{28}O_9$, appeared to be composed of a vestitol and a claussequinone unit. These two residues were in the same binding mode as 1-4 according to its ^{1}H-NMR (Table II), ^{13}C-NMR (Table I) and CD (Fig. 2) spectra. Its mass fragmentation pattern was assumed to be as shown in Chart 1.

It is noteworthy to report these five novel compounds as the second examples among the naturally occurring bi-isoflavonoids.

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