Phytochemistry, Vol. 21, No. 3, pp. 767–772, 1982.
Printed in Great Britain.

0031-9422/82/030767-06$03.00/0
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NEOFLAVANOIDS OF *DALBERGIA PARVIFLORA**

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(*Received* 21 *October* 1980)

Key Word Index—*Dalbergia parviflora*; Leguminosae; heartwood; neoflavanoids; *R*(−)-latifolin; *R*(−)-5-*O*-methyllatifolin; *R*(+)-methoxydalbergione; *R*(+)-dalbergiphenol; cearoin; arylbenzofurans; parvifuran; isoparvifuran; ^{13}C NMR.

Abstract—Besides two arylbenzofurans, parvifuran and isoparvifuran, the heartwood extract of *Dalbergia parviflora* yielded four neoflavanoids: *R*(−)-latifolin, *R*(−)-5-*O*-methyllatifolin, *R*(+)-4-methoxydalbergione, 2,5-dihydroxy-4-methoxybenzophenone (cearoin) and the new *R*(+)-dalbergiphenol. The structures of these compounds have been elucidated by physical methods.

INTRODUCTION

In our first report [1] the heartwood of *Dalbergia parviflora*, a shrub found in the Malay Peninsula and the southern part of Thailand, known there as khri, yielded two arylbenzofurans, parvifuran and isoparvifuran as minor constituents. We now report the neoflavanoid constituents and the substituted benzophenone, cearoin, isolated from the petrol extract of the heartwood which was collected in Thailand. Some neoflavanoids of the dalbergione type have been claimed to have antimicrobial activity and adverse dermatological action [2, 3].

RESULTS AND DISCUSSION

Extraction of *D. parviflora* heartwood with petrol provided two principal constituents of the neoflavanoid group *R*-latifolin [4–8] (**1**) (0.7%) and *R*-5-*O*-methyllatifolin [8] (**2**) (0.3%). *R*-Latifolin was previously found in *D. latifolia* and *D. cochinchinensis* [8, 9] and *R*-5-*O*-methyllatifolin in *D. cochinchinenis* [8].

Column chromatography of the extract also yielded two minor constituents, *R*-4-methoxydalbergione [10–12] (**5**), a dalbergione type reported to be found in *D. latifolia* and in a few other *Dalbergia* species [9–12], and the 2,5-dihydroxy-4-methoxy-benzophenone, cearoin [13] (**6**), which was found in *D. melanoxylon* [13], *D. volubilis* [14], *D. cearensis* and *D. miscolobium* [15]. The identification of these compounds was confirmed by their mps and the optical rotations for **1**, **2**, **5** and spectroscopic data (IR, MS and ^1H NMR) in comparison with reported values.

Additionally ^{13}C NMR spectral data of these constituents have been obtained and render support for their structure elucidations (see Table 1). For *R*-latifolin (**1**), *R*-5-*O*-methyllatifolin (**2**) and *R*-4-methoxydalbergione (**5**) the ^{13}C chemical shifts of the $\diagdown CH_A–CH_X=CH_2$-element are in agreement with their structures in all cases. Substitution patterns of **1** and **2** could also be derived. The chemical shifts of C-1′–C-6′ in ring B are of comparative size for the corresponding carbon atoms in **1** and **2** due to the hydroxyl substitution at C-2′, which appears as a one bond singlet and is shifted downfield to *ca* 153 ppm. Upfield shifts are observed for C-3′ and C-5′, with hydroxyls in the *ortho* and *para* positions, respectively.

In the highly substituted ring A, C-3 and C-6 resonate as one bond doublets. The rather high upfield shift of C-3 (δ 97.13 and 98.18 ppm in **1** and **2** respectively) is due to its location between two methoxyl groups. C-6 with only one oxygen function (hydroxyl in **1** and methoxyl in **2**) in the neighbourhood is found at a lower field, δ 115.10 ppm in **1** and δ 113.45 ppm in **2**. The difference is based on the distinct substituents *ortho*-hydroxyl and *ortho*-methoxyl at C-5. The C-3 signal shows no further splitting due to the substitutions in positions 1, 2, 4 and 5. On the contrary for C-6, long-range splitting caused by H_A and 5-OH is observed in **1**. The latter coupling disappears on D_2O exchange. The same effect is also visualized for C-3′ coupling with 2′-hydroxyl in ring B.

The one bond singlet for C-5 is located at δ 139.99 ppm in **1**, with a fine splitting (five lines) due to *ipso*-hydroxyl, H-3, and H-6 couplings. In **2**, the methoxylation in position five affects a downfield shift to δ 143.74 ppm. The one bond singlet signals of the methoxygenated C-2 and C-4 in **1** shift downfield to δ 149.41 and 145.43 ppm, respectively, with the hydroxyl either in the *para* or *ortho* positions. Both carbon signals show long-range splittings. The assignment of the signal at δ 145.43 ppm for C-4 is confirmed by D_2O exchange, which causes the loss of the 5-hydroxyl splitting. No such effect is observed for C-2. In the case of compound **2**, the 5-OMe

*Part 2 in the series "Constituents of *Dalbergia parviflora*". For Part 1 see ref. [1].

Table 1. ^{13}C NMR spectral data of compounds **1–6***

	1	**2**†	**3**	**4**‡	**5**	**6**§
C-1	122.61	121.46	124.74	123.72	150.79	111.43
	sdd	*sd*	*sd*	*s*	*sdd*	*sdd*
C-2	149.41	150.26	150.52	155.18	186.01	155.64
	sbr dd	*sbr dd*	*s(dd)*‖	*sdd*	*sdd*	*sbr dd*
C-3	97.13	98.18	97.54	97.21	107.66	100.62
	d	*d*	*d*	*d*	*d*	*dd*
C-4	145.43	148.53	145.10	149.92	158.32	157.93
	s quintet	*sdd*	*sdd*	*sdd*	*sdd*	*s quintet*
C-5	139.99	143.74	139.39	132.80	182.06	138.15
	sdd	*sbr dd*	*s quintet*	*m*¶	*sd*	*sbr d*
C-6	115.10	113.45	115.27	122.99	126.94	116.78
	dd	*dd*	*ddd*	*dd*	*ddd*	*dd*
C-1′	129.24	129.14	143.25	142.65	139.23	139.00
	s(dd)‖	*s(dd)*‖	*sbr*‖	*sbr m*	*sbr m*	*sdd*
C-2′	153.58	153.75	127.98	127.94	128.32	128.38
	sbr dd	*sbr*‖	*dd*	*dd*	*dd*	*dd*
C-3′	116.16	116.25	128.42	128.41	128.54	128.38
	ddd	*ddd*	*dd*	*ddd*	*dd*	*dd*
C-4′	128.35	128.31	125.84	125.86	131.34	131.44
	ddd	*dbr d*	*ddd*	*ddd*	*dd*	*ddd*
C-5′	120.46	120.44	128.42	128.41	128.54	128.38
	dd	*dd*	*dd*	*ddd*	*dd*	*dd*
C-6′	127.51	127.60	127.98	127.94	128.32	128.38
	dd	*dd*	*dd*	*dd*	*dd*	*dd*
$\underline{C}\text{-}H_A$	40.01	40.35	46.97	46.73	46.84	C=O 198.76
	dbr m	*dbr m*	*dbr m*	*dbr m*	*dbr m*	*s*
$\underline{C}\text{-}H_X$	138.91	139.00	140.39	140.03	137.08	—
	dd	*dd*	*dd*	*dd*	*ddd*	
$=\underline{C}H_2$	116.47	116.54	115.73	115.96	117.92	—
	t(dd)‖	*t(dd)*‖	*t(dd)*‖	*tbr m*	*tm*	
2-O$\underline{C}H_3$	55.98	56.08	56.06	55.91	—	—
	q	*q*	*q*	*q*		
4-O$\underline{C}H_3$	57.01	56.87	56.91	55.91	56.01	55.96
	q	*q*	*q*	*q*	*q*	*q*

*Solvent: $CDCl_3$ if not stated otherwise, δ ppm downfield from TMS, δ TMS = 0 measured always from int. $CDCl_3$ and corr. by using the equation δ TMS = δ $CDCl_3$ − 76.89.

†5-OMe: 56.55, *q*.

‡$\underline{C}H_3CO_2$: 20.39, *q*; CO_2: 169.02, *s*, *d*.

§Solvent DMSO-d_6, δ TMS = δ DMSO-d_6 − 39.7.

‖Unresolved splitting.

¶Hidden signal in coupled spectrum.

substitution caused the downfield shift of C-4 to δ 148.53 ppm as compared with **1**. The singlets at δ 122.61 ppm in **1** and δ 121.46 ppm in **2** are assigned to the carbon-substituted C-1.

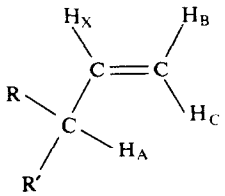
The mass spectrum of **1** shows a loss of a methyl group from the M^+ (*m/z* 286) to *m/z* 271 of relatively small intensity, typical for two aromatic methoxyls in a *meta* position to each other [16]. In the case of **2** the loss of two methyl groups from the M^+ (*m/z* 300) to give the fragment ion *m/z* 270 is observed due to the *meta*- and *ortho*-dimethoxylation [16] in positions 2, 4 and 5. Cleavage of the arylpropene part from the M^+ [17–18] gives the base peak for the ring A element *m/z* 154 in **1** and *m/z* 168 in **2**.

Structure elucidation of *R*-4-methoxydalbergione (**5**) and cearoin (**6**) was also confirmed by ^{13}C NMR. C-3 in **5** resonates at δ 107.66 and C-6 at δ 126.94 ppm. Both show an upfield shift in comparison with the values of unsubstituted benzoquinone [19] due to the substitution in positions 1 and 4. The downfield shift effect of *ipso*-methoxyl on C-4 is considered to be higher than the *ipso*-arylpropene on C-1. Ring B carbon chemical shifts and splittings are typical for monosubstituted aromatic carbon atoms.

For the benzophenone structure of cearoin (**6**), ring B carbon shifts and $\diagdown$C=O$\diagup$ are similar to those of unsubstituted benzophenone [20]. A doublet signal of double intensity was observed for C-2′ and C-6′ and similarly a second doublet signal for C-3′ and C-5′. In ring A doublet signals of C-3 and C-6 shifted upfield to δ 100.62 and 116.78 ppm due to oxygenation in positions 2, 4 and 5. Both showed further fine splittings as doublets (J = 6.5 and 3.1 Hz, respectively)

due to the *ortho*-hydroxyl in positions 2 and 5, which disappeared on D_2O exchange. The hydroxyl group in the *ipso* positions 2 and 5 caused the singlet signals of C-2 and C-5 to shift downfield to δ 155.64 and 138.15 ppm. C-2 shows a doublet of doublets (H-6, H-3; $J_{C^2H^6} = 7.9$ Hz, $J_{C^2H^3} = 3.1$ Hz) with further line broadening through 2-OH, which disappears after D_2O exchange. C-5 shows a doublet (H-3; $J_{C^5H^3} = 5.1$ Hz) with additional broadening by H-6 and 5-hydroxyl. The latter interaction is missing after addition of D_2O. C-4 with a methoxyl group in the *ipso* position also shifted downfield to δ 157.93 ppm, and showed a splitting as a quintet signal. C-1 shifted upfield owing to the *ortho*- and *para*-substituted oxygenated pattern. 2-Hydroxyl and $\rangle$N=O tend to form a hydrogen bond which affects the chemical shifts of $\rangle$C=O, C-1, C-2 and C-6.

Besides *R*-latifolin, *R*-5-*O*-methyllatifolin and *R*-4-methoxydalbergione, a new neoflavanoid **3** was isolated from the heartwood extract by CC as an easily oxidized light-brown oil. This compound has the molecular formula $C_{17}H_{18}O_3$. IR bands show absorptions for phenolic hydroxyl, aromatic methoxyl, –CH=CH– and phenyl groups with a mono- and 1,2,4,5-substitution pattern similar to **1** and **2**. The ^{1}H NMR shows two sets of multiplets in the olefinic range, one at δ 4.81–5.32 ppm for 3 H with the proton coupling constants of J_{CX} 17.0, J_{BX} 10.0, J_{AX} 6.0 and $J_{AB} = J_{AC} = J_{BC} = 1.6$ Hz, and another set at δ 6.07–6.53 ppm for one proton with the coupling constants of $J_{CX} = 17.0$, $J_{BX} = 10.0$ and $J_{AX} = 6.0$ Hz. This splitting pattern is similar to the allyl system of dalbergiones and *R*-latifolin [4, 21].



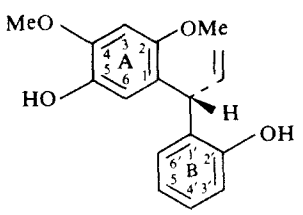
Therefore **3** should have the same allylic pattern as **1**. In contrast only one proton equivalent signal for the hydroxyl, and two signals for the methoxyl appear in **3**. Ring A protons in **3** show similar chemical shifts to those in **1**. Two singlets for one proton each appear at δ 6.59 and 6.83 ppm for *para*-positioned aromatic protons, each buttressed by two substituents. The B-ring protons show resonance as a broad singlet at δ 7.33 ppm with 5H-equivalents. This is due to the lack of one hydroxyl group in ring B which is found in **1**.

Comparing the ^{13}C NMR spectral data of $\rangle CH_A$–CH_X=CH_2 in **3** with **1** a downfield shift occurs for CH_A in **3** (δ 46.97) from δ 40.01 ppm in **1** owing to the lack of a hydroxyl in the 2′ position. Smaller effects are found on CH_X and CH_2 (the downfield shifts are *ca* 1 ppm). Methoxy carbons in **3** have similar chemical shifts as in **1**. Two one-bond doublet signals of double intensity for four carbon atoms and another doublet for one carbon atom were observed in the normal aromatic range, which can be assigned to C-2′–C-6′ for the mono-substituted benzene ring B. A signal at δ 143.25 ppm corresponds to C-1′ with allylic substitution. Another two one-bond doublets are shifted upfield to δ 97.54 and 115.27 ppm with further doublet of doublets splitting for the latter, belonging to the *para*-position carbon atoms C-3 and C-6 in the aromatic ring A with substitution in 1, 2, 4 and 5. By comparison of ring A proton chemical shifts of **1** and **3** a similar substitution pattern in ring A is suggested. Thus the most upfield-shifted carbon at δ 97.54 ppm is located between two oxygen functions (methoxyl), and the carbon at δ 115.27 ppm has only one oxygen function (hydroxyl) in the neighbourhood. A one-bond singlet at δ 139.39 ppm with fine splitting to a multiplet can be assigned to C-5 which couples to the *ipso*-hydroxyl, H-3 and H-6. Two downfield singlets at δ 150.52 and 145.10 ppm were assigned to C-2 and C-4 both with the *ipso*-methoxyl, and the hydroxyl group in *para* and *ortho* positions, respectively. The substituent at C-1 is therefore the allyl system bearing a 3-phenyl group which should constitute the arylpropene fragment identified already in **1** and **2**. The singlet signal of C-1 in **3** shifts 2 ppm downfield, all other signals of ring A carbons retain similar shift values in comparison with those of **1**.

The mass spectrum of **3** shows a base peak for the M^+ at *m/z* 270. The fragmentation pattern of **3** is partly comparable to **1**. The loss of a methyl group from M^+ [16] yielded the fragment ion *m/z* 255 which is more stable than the corresponding fragment ion at *m/z* 271 of **1**. Further fragmentation of *m/z* 255 gives the phenylcyclopropene fragment ion and tropylium ion at *m/z* 115 and 91, respectively. Cleavage of ring B and C_2H_4 from M^+ in **3** provided the fragment ion *m/z* 165.

The proposed structure **3** was confirmed by its monoacetate derivative **4** which is stable and can be crystallized as colorless crystals (mp 98.5–99°), $[\alpha]_D^{20}$ −5.3° (MeOH; *c* 0.97) with the molecular formula $C_{19}H_{20}O_4$. In the IR spectrum an additional absorption for the acetate group appears with the loss of the hydroxyl absorption. In the ^{1}H NMR spectrum an acetoxyl peak was observed at δ 2.25 ppm. In the ^{13}C NMR spectrum C-2, C-4 and C-6 shift to a lower field (δ 155.18, 149.92 and 122.99 ppm) in comparison with those of **3** due to the effect of the acetoxyl group on the *para* and *ortho* positions. For C-5 with an acetoxyl in the *ipso* position an upfield shift was observed. The chemical shift of the acetate-methyl is found in the normal range. The change at C-5 to the acetate derivative shifted the 4-methoxyl to coincide with the 2-methoxyl at δ 55.91 ppm. This result confirms the assignment of 2- and 4-methoxyl in **3** at δ 56.06 and 56.91 ppm respectively.

The combined spectroscopic data led to the structure 3 - (5 - hydroxy - 2,4 - dimethoxyphenyl) - 3 - phenyl - prop - 1 - ene for **3** which is identical with that of *S*-dalbergiphenol previously isolated from *D. sissoo* [22]. Compound **3** is optically active having a specific rotation of $[\alpha]_D^{22} = +31.9°$ in $CHCl_3$ with opposite sign to that of *S*-dalbergiphenol [22] ($[\alpha]_D^{25} = -33°$ in $CHCl_3$). It indicates that **3** has the *R*-configuration. The CD spectrum of **3** shows positive Cotton effects at 297 nm due to the α-band absorption of the substituted benzene chromophore, and at



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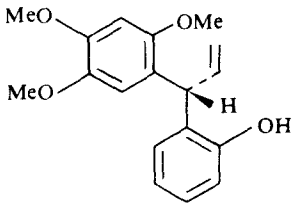

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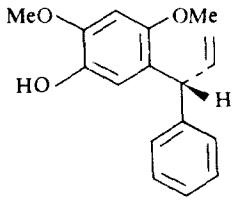

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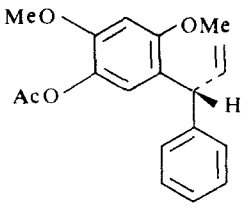

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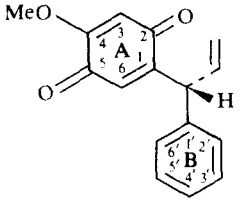

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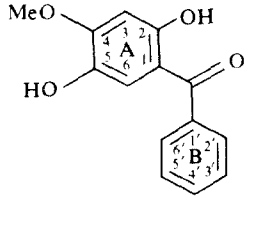

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238 nm for the *p*-band absorption [23]. A negative Cotton effect appears at 217 nm. The absolute configuration of **3** has been confirmed by oxidation either with chromic acid or with $NaIO_4$ which yielded *R*-4-methoxydalbergione ($[\alpha]_D^{22} + 15.2°$ in $CHCl_3$) identical with *R*-4-methoxydalbergione **5** isolated from the same plant source ($[\alpha]_D^{22} + 16.0°$ in $CHCl_3$, IR, mmp). Its absolute configuration is well defined [12]. Since these oxidation reactions do not affect the stereochemistry of the asymmetric center of the substrate [24, 25], it can be concluded that **3** also has the *R*-configuration.

It is interesting to note that *R*-dalbergiphenol(**3**)co-occurs with *R*-4-methoxydalbergione (**5**), *R*-latifolin (**1**) and *R*-5-*O*-methyllatifolin (**2**) in *D. parviflora*, while *S*-dalbergiphenol was found together with the so-called *S*-dalbergenone (*S*-4-methoxydalbergione [11, 12]) in *D. sissoo* [22]. Oxidation of *S*-dalbergiphenol has been shown to yield *S*-dalbergenone [22]. The common feature in *Dalbergia* species to produce only one configuration line [26, 27] is again observed for *D. parviflora*. Co-occurrence of dalbergiquinols, dalbergione and a benzophenone derivative of related structures in this heartwood lends support to the proposed biosynthesis in *Dalbergia* species [26]. A study on the pharmacological activity of these neoflavanoids is under study and will be published elsewhere.

EXPERIMENTAL

General. D. parviflora (Roxb.) heartwood, specimen no. 68143 at The Forest Herbarium (BKF), Bangkok, was collected in Thailand and identified by the Forest Product Research Division, Forest Department, Bangkok, Thailand. The air-dried heartwood was extracted with petrol. The separation of the constituents was performed on a Si gel column (0.053–0.2 mm) Macherey-Nagel with different solvents and solvent mixtures. The fractionation was controlled by TLC using Polygram Sil G/UV_{254}, (Macherey-Nagel) with $CHCl_3$–EtOAc (9:1) as developing solvent. Spots were detected under UV light. Mps are uncorr. MS were recorded at high resolution using a data system. ^1H NMR spectra were recorded at 60 MHz and ^{13}C NMR spectra were obtained at 20 MHz. CD spectra were recorded with a dichrograph connected to a computer.

Isolation of constituents. Air-dried powdered heartwood (2.4 kg) was extracted exhaustively with 20 l. petrol (bp 40–60°) in a Soxhlet apparatus. The extract was evapd to 1/2 of the initial vol. and kept cool, the resultant crystals known as solid fraction I, (16.6 g) consisted mainly of *R*(−)-latifolin. Successive evapn of the mother liquor I to 1/4 of the original vol. yielded a brownish oil which was separated. From the mother liquor II a mixture of *R*(−)-latifolin **1** and *R*(−)-5-*O*-methyllatifolin **2** was crystallized. This procedure was repeated to 1/8 and 1/16. The crystals were combined as solid fraction II (5.47 g). Thereafter the mother liquor was evapd to dryness and the residue combined with the oily parts as oily fraction I (37.37 g).

Separation of solid fraction I/II. *R*(−)-latifolin and *R*(−)-5-*O*-methyllatifolin were separated on a Si gel column (60 g:2 g solid fraction) eluting with $CHCl_3$–EtOAc (9:1).

Separation of oily fraction I. Parts of the oily fraction (12.5 g) were chromatographed on a Si gel column (250 g) eluting with petrol–C_6H_6 (1:1) (2.5 l.), (1:1) (1.2 l.), (1:3) (4 l.), (1:5) (1 l.), (1:5) (2.5 l.) and $CHCl_3$ (3.8 l.) to give fractions 1a, 1b, 2, 3a, 3b and 4 respectively. Fraction 1a consisted of lipids which were not studied further. Fraction 1b yielded a small amount of residue as brown oily crystals (56.5 mg) which were chromatographed again on a Si gel column (20 g) eluting with petrol–Et_2O (19:1). This procedure was repeated ×6 until parvifuran (8.0 mg) and isoparvifuran (7.0 mg) were obtained [1]. Fraction 2 yielded an easily oxidized brown viscous oil (1.31 g). Separation on a Si gel column (25 g) and eluting with $CHCl_3$–EtOAc (9:1) yielded a light-brown oil **3** (0.694 g). The refined oil was still sensitive to O_2 due to its phenolic character. It was converted into its acetate derivative **4**, using Ac_2O–pyridine [4]. Fraction 3a yielded a dark-brown oil with some yellow

crystals (0.19 g) which were further separated on a Si gel column (8 g) eluting with $CHCl_3$–EtOAc (9:1); this procedure was repeated twice. The orange colored fractions from each separation were combined and recrystallized from Me_2CO to give a yellow amorphous solid of cearoin (**6**) (74.4 mg). The residue of fraction 3b is a brown oil (1.13 g) which contained *R*(+)-4-methoxydalbergione (**5**). It solidified from di-*iso*-propyl ether as a greenish yellow solid which crystallized from petrol (40–60°) as yellow crystals (327 mg). The residue of fraction 4 consists of brown oily crystals (3.48 g) which were found to contain *R*(−)-latifolin (**1**) and *R*(−)-5-*O*-methyllatifolin (**2**). Further separation (see solid fraction I) yielded **1** (1.84 g) and **2** (1.47 g).

R(−)-*Latifolin* **1**. Crystallized from C_6H_6 as colorless crystals (total 16.697 g or 0.7% on a dry wt basis). Mp 122.5–123.0° (lit. [4] mp 122–123°). $[\alpha]_D^{20}$ −26.7° (MeOH; *c* 1.0) (lit. [8] $[\alpha]_D^{22}$ −26.7°, MeOH). CD (*c* = 0.0011 mol/l., EtOH, room temp.) $[\theta]_{330}$ 0, $[\theta]_{282}$ −5940, $[\theta]_{276}$ −5775, $[\theta]_{240}$ +8180, $[\theta]_{227}$ +4710, $[\theta]_{220}$ +490, $[\theta]_{205}$ +32890, $[\theta]_{195}$ −68970. MS (probe 70 eV) *m/z* (rel. int.): 287 (15), M^+ 286 (74), 271 (2), 255 (26), 167 (15), 154 (100), 133 (12), 131 (12), 107 (12). (Found: M, 286.1216. $C_{17}H_{18}O_4$ requires 286.1205.) IR [4]. ^1H NMR (60 MHz, $CDCl_3$, δ ppm, TMS): 3.9 and 3.93 (6H, 2*s*, 2 × OMe), 4.8–5.4 (3H, *m*, $=CH_2$, $-CH-CH=CH_2$, *J* = 17.0, 10.0, 6.0 and 1.6 Hz), 5.19 (1H, *s*, OH), 5.96 (1H, *s*, OH), 6.2–6.57 (1H, *m*, $-CH=CH_2$, *J* = 17.0, 10.0 and 6.0 Hz), 6.52 (1H, *s*, H-3), 6.78 (1H, *s*, H-6), 6.85–7.19 (4H, *m*, H-3′, 4′, 5′, 6′, *J* = 7.0 and 2 Hz).

R(−)-5-O-*Methyllatifolin* **2**. Crystallized from C_6H_6–di-*iso*-propylether (1:1) as colorless crystals (total 7.58 g or 0.3% dry wt basis). Mp 109.5–110.0° (lit. [8] mp 106–107°). $[\alpha]_D^{20}$ −40.1° (MeOH; *c* 0.78) (lit. [8] $[\alpha]_D^{20}$ −40.2°, MeOH). CD (*c* = 0.0016 mol/l., EtOH, room temp.) $[\theta]_{330}$ 0, $[\theta]_{282}$ −5190, $[\theta]_{277}$ −5310, $[\theta]_{239}$ +11090, $[\theta]_{228}$ +9405, $[\theta]_{215}$ −2640, $[\theta]_{205}$ +27390, $[\theta]_{195}$ −64130. MS (probe, 70 eV) *m/z* (rel. int.): 301 (36), M^+ 300 (72), 270 (10), 269 (16), 194 (6), 181 (12), 169 (40), 168 (100), 167 (8), 154 (8), 153 (16), 131 (9), 115 (3), 107 (8), 91 (3), 77 (6), 69 (4), 32 (11) and 28 (55). (Found: M, 300.1369. $C_{18}H_{20}O_4$ requires 300.1362.) IR [8]. ^1H NMR [8].

R(+)-*Dalbergiphenol* **3**. Easily oxidized light-brown oil (total 1.835 g or 0.08% dry wt basis), $[\alpha]_D^{22}$ +31.9° ($CHCl_3$); *c* 0.64). CD (*c* = 0.0022 mol/l., EtOH, room temp.) $[\theta]_{330}$ 0, $[\theta]_{297}$ +3696, $[\theta]_{291}$ +3475, $[\theta]_{276}$ +169, $[\theta]_{269}$ +224, $[\theta]_{238}$ +15910, $[\theta]_{217}$ −39710. MS (probe 70 eV) *m/z* (rel. int.): 271 (18), M^+ 270 (100), 269 (11), 256 (32), 255 (10), 253 (16), 165 (15), 115 (30), 91 (55), 77 (12) and 69 (20). UV λ_{max}^{EtOH} (log ε): 208 (4.69), 231 (4.17) and 296 (3.97) nm. IR ν_{max}^{KBr} neat cm^{-1}: 3500, 3440 (OH), 2830 (OMe), 1630, 1445, 990 and 905 (−CH=CH_2). (Found: M, 270.1248. $C_{17}H_{18}O_3$ requires 270.3312.) ^1H NMR (60 MHz, $CDCl_3$, δ ppm, TMS): 3.74 (3H, *s*, OMe), 3.91 (3H, *s*, OMe), 5.25 (1H, *s*, OH), 4.81–5.32 (3H, *m*, $CH-CH=CH_2$ and $=CH_2$, *J* = 17.0, 10.0, 6.0 and 1.6 Hz), 6.07–6.53 (1H, *m*, $-CH=CH_2$, *J* = 17.0, 10.0 and 6.0 Hz), 6.59 and 6.83 (2H, 2*s*, H-3, H-6), 7.33 (5H, *s*, H-2′-6′). Oxidation of **3**: 73 mg **3** in HOAc (0.2 ml) with $Na_2Cr_2O_7$ (150 mg) in HOAc (0.2 ml) at 35°, 7 min. [24, 28] afforded **5** (21 mg).

R(+)-*Dalbergiphenol monoacetate derivative* **4**. Acetylation of **3** yielded **4** which crystallized from C_6H_6–petrol (40–60°) (1:4) as colorless crystals. Mp 98.5–99°. $[\alpha]_D^{20}$ −5.3° (MeOH; *c* 0.97). IR ν_{max}^{KBr} cm^{-1}: 2840 (OMe), 1760 (>C=O), 1635, 1450, 990 and 915 (−CH=CH_2), 1410 and 1370 (OAc). (Found: C, 73.44; H, 6.60. Calc. for $C_{19}H_{20}O_4$ C, 73.06; H, 6.45%.) ^1H NMR (60 MHz, $CDCl_3$, δ ppm, TMS): 2.25 (3H, *s*, OAc), 3.73 (3H, *s*, 2-OMe), 3.80 (3H, *s*, 4-OMe), 4.65–5.27 (3H, *m*, $CH-CH=CH_2$, $=CH_2$, *J* = 17.0, 10.0, 6.0 and 1.7 Hz), 5.9–6.45 (1H, *m*, $-CH=CH_2$, *J* = 17.0, 10.0 and 6.0 Hz), 6.47 (1H, *s*, H-3), 6.75 (1H, *s*, H-6), 7.17 (5H, *s*, H-2′–H-6′).

R(+)-4-*Methoxydalbergione* **5**. Crystallized from petrol (40–60°) as yellow crystals (total 0.986 g or 0.04% dry wt basis). Mp 111–112° (lit. [12] mp 114–116°). $[\alpha]_D^{22}$ +16.0° ($CHCl_3$; *c* 1.2) (lit. [12] $[\alpha]_D^{22}$ +13°, $CHCl_3$). IR [12].

Cearoin (2,5-*dihydroxy*-4-*methoxybenzophenone*) **6**. Crystallized from Me_2CO as a yellow amorphous solid (total 0.22 g or 0.01% dry wt basis). Mp 184.5–185.5° (lit. [13] mp 182–184° from C_6H_6-petrol (60–80°). MS [14]. IR [14]. ^1H NMR (60 MHz, DMSO-d_6, δ ppm, TMS): 3.83 (3H, *s*, OMe), 6.58 (1H, *s*, H-3), 6.90 (1H, *s*, H-6), 7.55 (5H, *s*, H-2′-H-6′), 8.81 (1H, *s*, OH), 12.15 (1H, *s*, OH).

Acknowledgements—We are indebted to Dr. Narong Tonanonta and Mr. Chamlong Pengklai, Forest Department, Thailand for the identification and depositing the specimen and Professor Snatzke, Lehrstuhl für Strukturchemie, Ruhr-Universität Bochum, for recording CD spectra; one of us (N.M.) to the German Academic Exchange Service for the scholarship granted and the Department of Medical Sciences, Bangkok, Thailand for the allowance of leave.

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