Dihydroflavonols from *Lannea coromandelica*

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Abstract

The dihydroflavonols, \((2R,3S)\)-(+)\-3\',5\-dihydroxy-4',7\-dimethoxydihydroflavonol and \((2R,3R)\)-(+)\-4',5,7\-trimethoxydihydroflavonol were isolated from the stem bark of *Lannea coromandelica*, along with the known \((2R,3R)\)-(+)\-4',7\-di-O\-methylthihydroqueretin, \((2R,3R)\)-(+)\-4',7-di-O\-methylthihydrokaempferol and \((2R,3R)\)-(+)\-4'-O\-methylthihydroquercetin. All five compounds were isolated for the first time from the genus *Lannea*; furthermore, \((2R,3S)\)-(+)\-3\',5\-dihydroxy-4',7\-dimethoxydihydroflavonol, was a rare \textit{cis}\-type isomer. The structures of all compounds were elucidated by spectroscopic methods including 2D NMR and CD analysis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *Lannea coromandelica* L. (Anacardiaceae); \textit{cis}\-type Dihydroflavonol, \((2R,3S)\)-(+)\-3\',5\-dihydroxy-4',7\-dimethoxydihydroflavonol; \((2R,3R)\)-(+)\-4',5,7\-trimethoxydihydroflavonol; Isolation; Structure elucidation

1. Introduction

*Lannea coromandelica* L. (Anacardiaceae) is a deciduous tropical tree widely distributed in Bangladesh, India and some other tropical countries. Plants belonging to this genus are used in folk medicine for treatment of elephantiasis, impotence, ulcers, vaginal troubles, halitosis, heart disease, dysentery, gout and rheumatism (Yusuf et al., 1994; Oliver, 1968). Various phytochemicals have been isolated from *Lannea* spp., including quercetin-3\-O\-arabinoside and ellagic acid (Subramanian and Nair, 1971), 6,6\-dimethyl\-\(\{2,3;7,6\}\)-pyrano\-8\-(\(\gamma\gamma\)-dimethylallyl)flavanone (Sultana and Ilyas, 1986a), rutin and quercetin (Sulochana and Sastry, 1968), and lanceolatin-B and \(7,2\'\)-dimethoxy-4',5\'-methylenedioxyflavone (Sultana and Ilyas, 1986b) from the leaves and flowers; phlobatannin and leucocyanidin (Nair et al., 1963), \(\beta\)-sitosterol, phiscion and phiscion anthranol B from the bark (Subramanian and Nair, 1971); and a ferulic acid ester (Govindachari et al., 1971) from the roots. Two cytotoxic hydroquinones, lanneaquinol and \(2'\-(R)\)-hydroxylanneaquinol, were recently reported from *L. welwichii* (Groweiss et al., 1997). We investigated the chemical constituents of *L. coromandelica* bark and isolated five dihydroflavonols (compound 1–5), two of which (1 and 2) are novel plant compounds. All the compounds are reported here for the first time from the genus *Lannea*; furthermore, compounds 1 is a rare \textit{cis}\-type isomer. Stereostructure determination of naturally occurring \textit{cis}\-type dihydroflavonols is described briefly from a historical perspective.

2. Results and discussion

Compound 1 immediately gave an intense purple–pink colour when treated in MeOH solution with granular magnesium and conc. HCl (Shinoda test), indicative of a flavonoid ring system (Dean, 1963). Ultraviolet absorption maxima at 291 and 317 (\textit{sh}) nm suggested that it was a flavanone analogue (Bohm, 1975). An intense molecular ion peak was observed at
Thus, the structure of the first isolate is confirmed as the cis-isomer of 3',5-dihydroxy-4',7-dimethoxydihydroflavonol (1), a new natural product.

In the FD MS spectrum, compound 2 showed an intense molecular ion peak at m/z 330 (M^+ 100%). The HR-EI MS spectrum of the compound exhibited the exact molecular mass (found, 330.1073 and calcld., 330.1103) corresponding to the formula C_{18}H_{18}O_6. The ^1H-NMR data were also consistent with the deduced formula. Compound 2 also immediately responded to Shinoda test to afford an intense purple–pink colour indicative of a flavonoid ring system. The UV \( \lambda _{max} \) at 283 and 310 (sh) nm were closely related to dihydroflavonol (Bohm, 1975). Compound 2 showed a white-blue florescence under UV light characteristic of 5-methoxy flavonoids. The EI MS spectrum showed a fragment indicating the loss of HCO, m/z 301 (88%) and the base peak was obtained by RDA fragmentation, giving rise to ions at m/z 181 (100%) from dimethoxyated A-ring and 150 (24%) from monomethoxylated B-ring. The ^1H-NMR spectrum exhibited the typical AX system of H-2 and H-3 at \( \delta \ 5.01 \) (H-2) and 4.43 (H-3, \( J_{2, 3} = 11.9 \) Hz). The magnitude of the coupling constant (\( J_{2, 3} = 11.9 \) Hz) indicated a trans-type dihydroflavonol (Clark-Lewis, 1968). Among the three substituents (3 \( \times \) OCH_3), one methoxy group was allocated to C-7 position because of the signal features H-3' and H-5' at \( \delta \ 7.00 \) (2H, d-like, \( J = 8.8 \)), and H-2' and H-6' at \( \delta \ 7.52 \) (2H, d-like, \( J = 8.8 \)). The remaining two aromatic protons, H-6 and H-8, were resonating at \( \delta \ 6.15 \) and 6.25, (each 1H, d). Since the UV spectrum in methanol was unaltered on addition of NaOAc and AlCl_3, two of the three methoxy groups were allocated to C-7 and C-5 positions (Mabry et al., 1970). The B-ring mass fragment from 2 and the ^1H-NMR spin patterns for B-ring protons were in agreement with those of known compound 4, where only a methoxy group was located on C-4'. Compound 2 was therefore deduced to be 4',5,7-trimethoxydihydroflavonol. The absolute configuration of 2 was determined to be (2R,3R) by comparison of its CD curve with those of reported cis-type dihydroflavonols (Nonaka et al., 1987) (Table 2).

Thus, the structure of the first isolate is confirmed as

\[
\text{(2R,3S)-(+)\text{-}3',5\text{-dihydroxy-4',7\text{-dimethoxydihydroflavonol}} (1) , \text{a new natural product.}}
\]

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\]
these reported for (2R,3R)-dihydroquercetin-4′,7-di-O-methyl ether (Ruangrungsi et al., 1981). The structure of 3 was confirmed by analysis of its 1D and 2D NMR spectra (1H-1H COSY, HMBC, HMQC and NOESY), and the absolute configuration was confirmed by analysis of its CD spectra (Table 2). Thus, the structure of 3 was elucidated as (2R,3R)-(+)-4′,7-di-O-methylidihydroquercetin, which was previously isolated from the leaves of Blumea balsamifera (Compositae) (Ruangrungsi et al., 1981).

The molecular formula of compound 4 was deduced from the HR-EI MS spectrum to be C₁₆H₁₄O₇ as deduced from the HR-EI MS spectrum, exhibited the typical AX system of H-2 and H-3 in its 1H-NMR spectrum, with signals at δ 5.07 (H-2, J₂,₃ = 11.5 Hz) and 4.64 (H-3, dd, J₂,₃ = 11.5 Hz and J₃,OH = 4.3 Hz), where H-3 signal was split further by coupling with the C-3-OH proton resonating at δ 4.70 (J₃,OH = 4.3 Hz). The large coupling constant (J₂,₃ = 11.5 Hz) showed a trans-diaxial relationship and indicated a dihydroflavonol structure for 5. Its B-ring proton and carbon signals were similar to the respective signals of compound 3. The substitution of two remaining OH-groups at C-5 and C-7 was confirmed by UV spectrum (bathochromic shifts with NaOAc and AlCl₃). The absolute configuration of 5 was confirmed as (2R,3R) by CD measurement (Table 2). Thus, the structure of compound 5 is represented by (2R,3R)-(+)-4′-O-methylidihydroquercetin. This compound was previously found in the leaves of Blumea balsamifera along with compound 3 (Ruangrungsi et al., 1981).

Table 2
CD data and absolute configurations of Lannea coromandelica dihydroflavonols

<table>
<thead>
<tr>
<th>Compound</th>
<th>g/100 ml MeOH</th>
<th>Reading</th>
<th>Absolute configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (0.0190)</td>
<td>[0]₂₈₀ 90.0, [0]₂₉₀ – 10100, [0]₃₁₀ 0, [0]₃₃₄ + 12400, [0]₃₈₆ 0</td>
<td>2R,3S</td>
<td></td>
</tr>
<tr>
<td>II (0.0015)</td>
<td>[0]₂₈₂ 90.0, [0]₂₈₈ – 18000, [0]₃₁₆ 0, [0]₃₃₂ + 9000, [0]₃₈₁ 0</td>
<td>2R,3R</td>
<td></td>
</tr>
<tr>
<td>III (0.0397)</td>
<td>[0]₂₇₀ 90.0, [0]₂₉₅ – 38100, [0]₃₁₇ 0, [0]₃₃₃ + 10500, [0]₃₈₆ 0</td>
<td>2R,3R</td>
<td></td>
</tr>
<tr>
<td>IV (0.0371)</td>
<td>[0]₂₇₄ 90.0, [0]₃₀₀ – 17400, [0]₃₁₅ 0, [0]₃₃₂ + 8460, [0]₃₈₀ 0</td>
<td>2R,3S</td>
<td></td>
</tr>
<tr>
<td>V (0.0250)</td>
<td>[0]₂₇₇ 90.0, [0]₂₉₄ – 31600, [0]₃₁₃ 0, [0]₃₃₀ + 9090, [0]₃₇₉ 0</td>
<td>2R,3R</td>
<td></td>
</tr>
<tr>
<td>(+)-Taxifolin (0.0397)</td>
<td>[0]₂₇₄ 90.0, [0]₂₉₇ – 4280, [0]₃₂₈ 0, [0]₃₃₇ + 901, [0]₃₇₅ 0</td>
<td>2R,3R</td>
<td></td>
</tr>
<tr>
<td>(-)-Taxifolin (0.0920)</td>
<td>[0]₂₇₄ 90.0, [0]₂₉₇ – 4020, [0]₃₁₃ 0, [0]₃₃₂ – 977, [0]₃₇₅ 0</td>
<td>2S,3S</td>
<td></td>
</tr>
<tr>
<td>(+)-Epitaxifolin (0.0658)</td>
<td>[0]₂₸₆ 90.0, [0]₂₉₅ – 3190, [0]₃₂₂ 0, [0]₃₄₁ – 1520, [0]₃₇₅ 0</td>
<td>2S,3R</td>
<td></td>
</tr>
<tr>
<td>(-)-Epitaxifolin (0.0789)</td>
<td>[0]₂₸₆ 90.0, [0]₂₉₅ – 4180, [0]₃₂₂ 0, [0]₃₄₁ + 2030, [0]₃₇₅ 0</td>
<td>2R,3S</td>
<td></td>
</tr>
</tbody>
</table>

*Nonaka et al. (1987).*

**Table 1**
1H- and 13C-NMR assignments and HMBC correlations of compound 1

<table>
<thead>
<tr>
<th>Carbon number</th>
<th>Chemical shift of carbon δ (ppm) (CD₃OD)</th>
<th>Chemical shift of proton, δ (ppm) &amp; J (Hz) (DMSO)</th>
<th>HMBC correlation H → C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>82.2</td>
<td>6.03, d (2.2), C-4, C-1′, C-9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>77.8</td>
<td>4.80, d (2.2), C-4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>191.6</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>163.3</td>
<td>11.47, s (OH), C-8</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>95.8</td>
<td>6.16, d (2.3), C-8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>170.3</td>
<td>3.80, s (OCH₃), C-7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>95.0</td>
<td>6.29, d (2.3), C-6, C-9</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>165.4</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>103.6</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>1′</td>
<td>129.3</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>2′</td>
<td>119.4</td>
<td>6.77, d (2.0), C-4′</td>
<td></td>
</tr>
<tr>
<td>3′</td>
<td>147.8</td>
<td>9.28, s (OH), C-4</td>
<td></td>
</tr>
<tr>
<td>4′</td>
<td>149.3</td>
<td>3.91, s (OCH₃), C-4′</td>
<td></td>
</tr>
<tr>
<td>5′</td>
<td>112.7</td>
<td>6.95, d (8.3), C-1′, C-3′</td>
<td></td>
</tr>
<tr>
<td>6′</td>
<td>114.8</td>
<td>6.67, dd (8.3 &amp; 2.0), C-4′</td>
<td></td>
</tr>
<tr>
<td>2 × OCH₃</td>
<td>57.0, 56.9</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
The \(^{1}\text{H}\)- and \(^{13}\text{C}\)-NMR data of known compounds 3, 4 and 5 were previously measured using low resolution instruments. Moreover, \(^{13}\text{C}\)-NMR data of 3 and 5 were not reported earlier. Hence, we have presented the spectroscopic data for compounds 3, 4 and 5.

The substitution pattern of 4'-\text{OCH}_3 and 3'-\text{OH} in B-ring in \textit{L. coromandelica} dihydroflavonols (1, 3 and 5) is an isoflavanoid acid-type. Owing to the asymmetric carbons C-2 and C-3, dihydroflavonols can occur in four stereoisomeric forms. However, in nature, they occur predominantly as the cis-trans isomers with the C-2 phenyl and C-3 hydroxy group in equatorial positions (Bohm, 1975); 2,3-cis-type isomers are rare in nature. Clark-Lewis et al. (1968) first synthesized 2,3-cis-analogues (cis-3-methoxylflavanone) by the oxidation of a flavan-3,4-diol. They discussed the relative thermodynamic stability of cis- and trans-dihydroflavonols and suggested that, owing to hydrogen bonding between the carbonyl group and the equatorial 3-hydroxyl group, the 2,3-trans isomer should be favored. The \text{CD}, optical rotatory dispersion and absolute configuration of some cis- and trans-dihydroflavonols were studied by Gaffield (1970). The isolation of a racemic 2,3-cis-dihydroflavonol (3-O-methyl-2,3-cis-fustin) from the heartwood of \textit{Trachylobium verrucosum} (Gaertn.) Oliv. was claimed as early as 1972 (Merwe et al., 1972). A 7-O-glycoside of (--)cis-5,7-dihydroxy-3'-methoxy-2,3-cis-dihydroflavonol was first isolated in pure form from the peels of \textit{Citrus junos} (Kumamoto et al., 1985). The racemic cis-dihydroflavonol was also reported (Moriarty and Prakash, 1985) as a synthetic product from the oxidation of flavanone by hypervalent iodine. In 1986, Ingham and co-workers isolated a 2,3-cis-dihydroflavonol, shuterone B, from the fungus-inoculated leaflets of \textit{Shuteria vestita} (Ingham et al., 1986), and Foo (1986) isolated 3',4',7,8-tetrahydroxydihydroflavonol from \textit{Acacia melanoxylon}.

The latter compound was suggested to be the precursor of proanthocyanidins with 2,3-cis flavanol units previously found in the same plant (Foo, 1987). The absolute configuration of shuterone B was established as 2\(S\),3\(R\); a year later, the absolute stereochemistry of 3',4',7,8-tetrahydroxydihydroflavonol was confirmed as 2\(R\),3\(S\) (Foo, 1987). In 1987, Nonaka et al. reported a group of dihydroquercetin 3-O-\(\beta\)-xylopyranosides, namely (2\(R\),3\(R\))-(+)- and (2\(S\),3\(S\))-(--)taxifolin 3-O-xylosides, and (2\(S\),3\(R\))-(+)- and (2\(R\),3\(S\))-(--)epitaxifolin 3-O-xylosides, from \textit{Thujaopsis dolabrata} (Cupressaceae). They rigorously determined the absolute configurations of all isolates together with those of the corresponding aglycones, and their CD patterns were correlated with the stereostructures. One year later, Kasai et al. (1988) isolated four diastereomers of dihydroquercetin 3-O-\(\alpha\)-rhamnosides from the leaves of \textit{Engelharditia chrysolepis} (Juglandaceae) and deduced their absolute configurations. The co-occurrence of cis and trans isomers of a dihydroflavonol in \textit{Pinus sylvestris} has been reported by Lundgren and Theander (1988). Clearly, few cis-type dihydroflavonols of natural origin are yet known.

The biosynthetic significance of the occurrence of 2,3-cis-dihydroflavonol 1 in \textit{Lannea coromandelica} is not clear at present due to lack of phytochemical data on this plant. Therefore, detailed phytochemical investigations on plants of the \textit{Lannea} genus are necessary in order to formulate the possible biosynthetic pathway of a cis-type isomer.

\section*{3. Experimental}

\subsection*{3.1. General procedures}

Mp.s were uncorrected. Instrumental analyses were conducted using a JEOL JMS-AX 500 (EI) and JEOL JMS-SX102A (FD) for mass spectrometry, a HITA-CHI U-3210 spectrophotometer for UV spectrometry, a JEOL JNM-EX 270 for 1D (\(^{1}\text{H}\)- and \(^{13}\text{C}\)-) NMR spectrometry, a JASCO Model J-20 spectrometer for CD, a digital polarimeter JAS CO DIP-370 for specific rotation and a Bruker AMX500 for 2D (\(^{1}\text{H}-\text{H COSY}, \text{NOESY, HMQC and HMBC}\) NMR spectrometry. TMS was used as the internal standard in NMR spectrometry. Gibbs and vanillin reagents were used to detect dihydroflavonols on TLC plates. The
Shinoda test was used to confirm the dihydroflavonol skeleton. Analytical and prep. TLC separations were carried out on thin layer plates (Merck Kieselgel 60 F254, 0.25 mm thickness) using CHCl3:MeOH (25:1, solvent A; 25:2, solvent B & 25:4, solvent C). Silica gel 60 (spherical, 100–210 μm) (SiO2, Kanto Chemical), Sephadex LH-20 (Pharmacia) and RP-18 (Cosmosil 75C18-OPN, Nacalai, Tesque) were used for open column chromatography.

3.2. Plant material

The bark stem of *L. coromandelica* was collected in March 1998 in Comilla, Bangladesh and identified by M. Iqbal Hossain, BADC, Bangladesh. Voucher specimens are on deposit at the National Herbarium, Dhaka, Bangladesh. The material was then air dried and coarsely powdered.

3.3. Extraction and isolation

The dried powdered bark stem (1.9 kg) of *L. coromandelica* was extracted with acetone (280 g) and successively fractionated according to the solubility in n-hexane (1.5 g), diethyl ether (3.5 g), ethyl acetate (19.0 g) and methanol (255.0 g). The methanol solubles (70 g) were subjected to column chromatography (CC) on silica gel (1.45 kg) eluting with n-hexane–CHCl3–MeOH with increasing amounts of CHCl3 and MeOH dark (UV365, long wave); Sephadex LH-20 (Pharmacia) and RP-18 (Cosmosil 75C18-OPN, Nacalai, Tesque) were used for open column chromatography.

### 3.3.1. Colorless powder from MeOH

 Colourless powder from MeOH; mp 183.5–184°C; under UV light, quenched (UV254, short wave) and dark (UV565, long wave); RI 0.02 (Solvent B) and 0.13 (Solvent C); \( \text{Rf}^\text{ID} = 0.24 \); \( \text{Rf}^\text{ID} = 156 \); (MeOH: c 0.2); CD data (Table 2), UV \( \lambda_{\text{max}} \) MeOH: 231 (sh), 291, 317 (sh); + NaOMe: 238 (sh), 292, 364; + AlCl3: 224, 293 (sh), 316, 381; + AlCl3/HCl: 225, 292 (sh), 317, 388; + NaOAc: 291, 328 (sh), FDMS: \( m/z 332 ([M]^+ 100), 314 ([M-H2O]^+, 67) \); HR-FD MS: [M+H]^+: 332.0924, calc. for C13H15O6 332.0895. EIMS (m/z): 332 ([M]^+, 2), 330 ([M-2H]^+, 34), 314 ([M-HO]^+, 100), 285 (19), 271 (22), 243 (16), 167 (16), 166 (4), 151 (4), 143 (6), 138 (5), 137 (3), 133 (7), 105 (5), 48 (8), 40 (8), \( 1^\text{H}-\text{NMR spectral data (270 MHz, CD2OD): } \delta \) 6.87 (1H, \( d, J = 8.3 \) Hz, H-5'), 6.83 (1H, \( d, J = 2.3 \) Hz, H-2'), 6.79 (1H, \( dd, J = 8.3 \) & 2.3 Hz, H-6'), 6.13 (1H, \( d, J = 8.3 \) Hz, H-8), 6.03 (1H, \( d, J = 2.3 \) Hz, H-6), 5.75 (1H, \( d, J = 5.0 \) Hz, H-2'), 5.03 (1H, \( d, J = 5.0 \) Hz, H-3), 3.82 and 3.84 (each 3H, \( s \), 2 × OCH3), \( 1^\text{H}-\text{NMR spectral data (270 MHz, acetone-D6): } \delta \) 11.65 (1H, \( s \), 5-OH), 7.71 (1H, 3'-OH), 6.89 (1H, \( d, J = 8.3 \) Hz, H-5'), 6.84 (1H, \( d, J = 2.1 \) Hz, H-2'), 6.77 (1H, \( dd, J = 8.3 \) and 2.1 Hz, H-6'), 6.14 (1H, \( d, J = 2.1 \) Hz, H-8), 6.10 (1H, \( d, J = 3.2 \) Hz, H-2), 6.00 (1H, \( d, J = 2.1 \) Hz, H-6), 5.02 (1H, \( d, J = 3.2 \) Hz, H-3), 3.80 and 3.88 (each 3H, \( s \), 2 × OCH3); \( 1^\text{H}-\text{NMR (DMSO) and } 13^\text{C}-\text{NMR spectral data: see Table 1.} \)

### 3.3.2. Colourless powder from EtOAc

Colourless powder from EtOAc; under UV light, quenched (short wave) and yellow blue fluorescence (long wave); RI 0.66 (Solvent A); \( [\alpha]_D^{29} = +30' \) (MeOH: c 0.2) (Takahashi et al., 1988, \( [\alpha]_D^{29} = -12.9' \), CHCl3, c 1.25); CD data (Table 2), UV \( \lambda_{\text{max}} \) MeOH: 228, 283, 310 (sh); + NaOMe: 227 (sh), 282, 310 (sh); + AlCl3: 221, 283, 315, 348 (sh); + NaOAc: 237 (sh), 285, 310 (sh), FD MS: \( m/z 330 ([M]^+, 100) \), HR-EIMS: [M]^+: 330.1073, calc. for C18H18O6 330.1103, EIMS (m/z): 330 ([M]^+, 15), 301 (88), 193 (20), 181 (100), 167 (10), 150 (24), 148 (8), 121 (28), 77 (5), 40 (5). \( 1^\text{H}-\text{NMR spectral data (acetone-}d_6, 270 MHz): } \delta \) 7.52 (2H, d-like, \( J = 8.8 \) Hz, H-2', H-6'), 7.00 (2H, d-like, \( J = 8.8 \) Hz, H-3', H-5'), 6.25 (1H, \( d, J = 2.3 \) Hz, H-8), 6.15 (1H, \( d, J = 2.3 \) Hz, H-6), 5.01 (1H, \( d, J = 11.9 \) Hz, H-2), 4.43 (1H, \( dd, J = 11.9 \) & 3.6 Hz, H-3), 4.29 (1H, \( d, J = 3.6 \) Hz, 3-OH), 3.87, 3.84 and 3.82 (each 3H, \( s \), 3 × OCH3).

### 3.3.3. Colourless needles from EtOAc

Colourless needles from EtOAc; mp 184–186°C (MeOH) (Ruangrungsi et al., 1981, 164–167°); under UV light, quenched (short wave) and yellow (long wave); RI 0.56 (Solvent B); \( [\alpha]_D^{29} = +32.8' \) (MeOH: c 0.0148) (Ruangrungsi et al., 1981, \( [\alpha]_D = +14.8' \)); CD data (Table 2), UV \( \lambda_{\text{max}} \) MeOH: 228 (sh), 289, 324 (sh); + NaOMe: 240 (sh), 290, 359; + AlCl3: 224, 293 (sh), 315, 373; + AlCl3/HCl: 223, 290 (sh), 314, 382;
3.7. (2R,3R)-(-)+4',7-di-O-methylhydrokaempferol (4)

Colourless needles from EtOAc; mp 185–186°C (Nuñez-Alarcon et al., 1993, 84–186°C); under UV light, quenched (short wave) and yellow (long wave); Rf, 0.89 (Solvent B), [α]D24 +34.4º (MeOH, c 0.4575) (Lima and Polonsky, 1973, [α]D +89º, pyridine, c 1); CD data (Table 2), UV λmax MeOH: 217, 290, 324 (sh); +NaOMe: 244 (sh), 288, 359; +AlCl3: 225, 316, 384; +AlCl3/HCl: 225, 314, 386; +NaOAc: 290, 326 (sh), FDMS m/z (%): 316 ([M]+, 100); HR-EIMS: [M]+ 361.0916, calcd. for C17H16O7 361.0947, 1H-NMR spectral data (270 MHz, acetone-6): δ 11.67 (1H, s, 5-OH), 7.52 (2H, d-like, J = 8.7 Hz, H-2', H-6'), 7.00 (2H, d-like, J = 8.7 Hz, H-3', H-5'), 6.09 (1H, d, J = 2.3 Hz, H-8), 6.06 (1H, d, J = 2.3 Hz, H-6), 5.16 (1H, d, J = 11.6 Hz, H-2), 4.75 (1H, d, J = 3.6 Hz, 3-OH), 4.70 (1H, dd, J = 11.6 Hz and 3.6 Hz, H-3), 3.86 (3H, s, 4'-O-Me), 3.84 (3H, s, 7-O-Me), EI MS and 13C-NMR data were identical with literature values (Rosti et al., 1997).

3.8. (2R,3R)-(-)+4'-O-methylhydroquercetin (5)

Colourless amorphous powder from EtOAc; mp 181.5–182.5°C (Ruangrungsi et al., 1981, 173–174°C); under UV light, quenched (short wave) and dark (long wave); Rf, 0.32 (Solvent A), [α]D0 +20.4º (MeOH, c 0.75) (Ruangrungsi et al., 1981, [α]D +14.9º); CD data (Table 2), UV λmax MeOH: 289, 332 (sh); +NaOMe: 246, 326; +AlCl3: 271 (sh), 315, 385; +AlCl3/HCl: 292 (sh), 314, 375; +NaOAc: 286 (sh), 327; +NaOAc/H2BO3: 290, 325 (sh), FDMS m/z (%): 318 ([M]+, 100); HR-EIMS calcd. for C16H14O7 [M]+ 318.0739, found, 318.0704, EI MS data were identical with literature values (Ruangrungsi et al., 1981), 1H-NMR spectral data (270 MHz, acetone-d6): δ 11.71 (1H, s, 5-OH), 7.70 (1H, s, 3'-OH), 7.09 (1H, d, J = 2.0 Hz, H-2'), 7.03 (1H, dd, J = 8.3 and 2.0 Hz, H-6'), 6.98 (1H, d, J = 8.3 Hz, H-5'), 6.00 (1H, d, J = 2.3 Hz, H-8), 5.96 (1H, d, J = 2.3 Hz, H-6), 5.07 (1H, d, J = 11.5 Hz, H-2), 4.70 (1H, br s, 3-OH), 4.64 (1H, br d, J = 11.5 Hz, H-3), 3.88 (3H, s, 4'-OCH3).

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