Research Article **www.ijcps.com**

International Journal of Chemical and Pharmaceutical Sciences
2015, June., Vol. 6 (2)

ISSN: 0976-9390
IJCPS

Bioactive neo and isoflavonoids from the roots of *Dalbergia coromandeliana*

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Received: 13 July 2015, Revised and Accepted: 15 July 2015

ABSTRACT

Two new compounds 3-*tert*-butyl-4'-methoxydalbergione 1 and 6-phenyl-5a,6,7,7a-tetrahydrochromeno[3,2-a]xanthene-13,14-dione 3 in addition with three known compounds 2, 4, 5 were isolated from the roots of *Dalbergia coromandeliana.* The structure of the compounds 1-5 were elucidated on the basis of spectral and chemical studies. All the compounds 1-5 were assessed for antioxidant activity using the DPPH assay. Compound 4 possessed highest antioxidant activity.

Keywords: *Dalbergia coromandeliana;* 3-tert-butyl-4'-methoxydalbergione; 6-phenyl-5a,6,7,7a-tetrahydrochromeno[3,2-a]xanthene-13,14-dione; Antioxidant.

1. INTRODUCTION

The genus *Dalbergia* such as *Dalbergia odorifera*, a Chinese medicinal herb, has been widely used to treat blood disorders, ischemia, swelling, necrosis and cardiovascular disease [1]. *Dalbergia coromandeliana* Prain (Fabaceae) is a stiff shrub with white flowers arranged in a disticous manner.

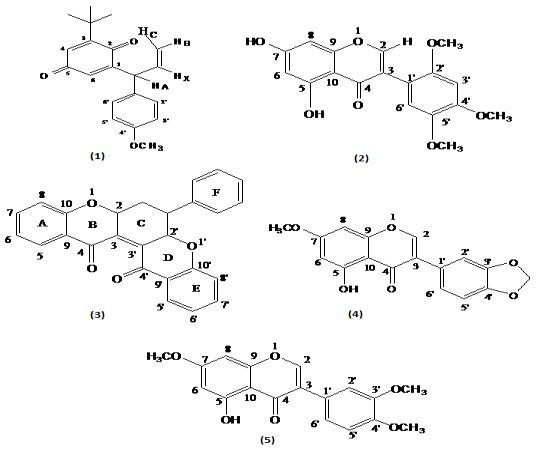

Figure – 1: Structures of compounds 1-5 isolated from *Dalbergia coromandeliana* Roots

In previous investigation of this plant, many neoflavonoids, isoflavonoids and isoflavonoid glycosides have been isolated [2]. In the present work we report the isolation and structural elucidation of two new compounds 1, 3 along with three known isoflavonoids 2, 4, 5 (Figure 1). All the compounds were evaluated for antioxidant activity by DPPH radical assay.

2. MATERIALS AND METHODS

The IR spectra were recorded on an 8400S SHIMADZU spectrometer and the UV spectra on a SHIMADZU UV-1700 UV – Vis spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker 300 MHz spectrometer in $CDCl_3$ (Chemical shifts in δ, ppm relative to TMS as an internal standard). Melting points were determined in open capillaries and are uncorrected. Thin layer chromatography (TLC) was carried out on Merck silica gel 60. Column chromatography was done with silica gel 60-120 mesh (E. Merck).

2.1. Plant material

The roots of *D. Coromandeliana* were collected from the forests of Alagar Hills near Madurai in Tamil Nadu, India and identified at the St. Joseph College herbarium, Trichy, India.

2.2. Extraction and isolation

The air-dried roots (1.0 kg) were cut into small pieces and extracted with $CHCl_3$ (3×5 l) and MeOH (3×5 l). The $CHCl_3$ extract on purification over a silica gel column using pet.ether (60-80 °C), pet-ether-benzene step gradient yielded compounds 1 (15 mg), 4 (30 mg), benzene-chloroform as eluent gave compound 2 (30 mg). The MeOH extract on purification over a silica gel

column, employing chloroform as eluent gave compounds **3** (20 mg) and **5** (15 mg).

2.3. 3-tert-Butyl-4'methoxydalbergione (1)

Yellow crystals (MeOH), m.p. 96-98 °C; UV, (λ_{max}^{MeOH}) (nm): (υ_{max}^{KBr}) 235, 261; IR, (cm^{-1}): 2917 (-OMe), 1670, 1653(>C=O),1608, 1491, 1356, 1234; ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (9H, s, 3 × CH_3), 3.80 (3H, s, OCH_3), 4.92 (1H, d, J = 6.8 Hz, H_A), 5.00 (1H, d, J = 17.2 Hz, H_C), 5.29 (1H, d, J = 7.8 Hz, H_B), 5.91 (1H, s, H-4), 6.05-6.15 (1H, m, H_X), 6.48 (1H, s, H-6), 7.19 (2H, d, H-3',5'), 7.31 (2H, d, H-2', 6'); ^{13}C NMR (75 MHz, $CDCl_3$): 182.12 (C-5- carbonyl), 186.17 (C -2-carbonyl), 157.46 (C-3), 149.47 (C-1), 137.22 (C-1'), 131.60 (C-6), 128.79 (C-H_X), 128.58 (C-4), 127.23 (C-2',6'), 118.25 (=CH_2), 107.91 (C-3', 5'), 56.32 (OCH_3), 47.02 (C-H_A), 35.52 ( ), 29.73 (CH_3).

2.4. 6-Phenyl-5a,6,7,7a-tetrahydrochromeno[3,2-a]xanthene-13,14-dione (3)

Yellow crystals (MeOH), m.p. 170-172 °C; UV, (λ_{max}^{MeOH}) (nm): 276, 365; IR, (υ_{max}^{KBr}) (cm^{-1}): 1650, 1626 (>C=O), 1544, 1490, 1379, 1239, 1061; ^1H NMR (300 MHz, $CDCl_3$): δ3.40 – 3.49 (2H, m, H- α); 4.15 – 4.25(1H, m, H-β); 4.64 - 4.85(2H, m, H – 2, H -2'); 7.20 – 7.61 (11H, m, A, E, F – ring protons); 7.90 (1H, s, H – 5); 7.93 (1H, s, H – 5'); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.86 (C=O); 127.47 – 139.13 (aromatic carbons); 79.58 (C-13); 76.60 (C – 2); 41.54 (C - α); 39.31 (C-β).

2.5. Free Radical Scavenging Activity

The free radical scavenging activity of five compounds was measured using DPPH according to the method described by Shimada *et al*, 1992 [3]. About 2 ml of 0.1 mmol/L solution of DPPH in ethanol was added to 2 ml of the test solution at different concentrations (5-25 μM). After 30 minutes, the absorbance was measured at 517 nm using SHIMADZU UV-1700 UV – Vis spectrophotometer. The Low value of the absorbance of the reaction mixture indicated higher free radical scavenging activity. The results were expressed as percentage of inhibition,

$$\% \text{ inhibition} = [(A_{control} - A_{sample})/A_{control} \times 100]$$

All tests were performed in triplicate. Ascorbic acid was used as the reference compound.

2.6. Statistical analysis

Data were analyzed using the software Sigmaplot for Windows (Version 11.0). Values were expressed as mean values of three independent experiments followed by student *t*-test. Statistical significance was acceptable to a level of $p < 0.05$.

3. RESULTS AND DISCUSSION

3.1. Chemistry

The methanolic extract of *Dalbergia coromandeliana* roots was subjected to silica gel column chromatography afforded two new compounds 1 and 3 in addition with three known compounds 2, 4, 5 [4,5].

Compound 1 was appeared as fine yellow crystals, m.p. 96-98 °C. The UV absorption band at 235, 261 nm which was reminiscent of the ultraviolet spectrum of *p*-benzoquinone substituted at C-2 and C-3 [6]. The *p*-benzoquinone nature of the compound was further evident from the FTIR bands at 1670 and 1653 cm^{-1}. The ^1H NMR spectrum of compound 1 showed the characteristics of a >CH_A-CH_X=CH_2- element at δ 4.92 (1H, d, J = 6.8 Hz, H_A); δ 5.00 (1H, d, J = 17.2 Hz =CH_2 *trans*), δ 5.29 (1H, d, J = 7.8 Hz =CH_2 *cis*), and δ 6.05-6.15 (1H, m, J= Hz, CH_X); the singlets at δ 3.80 (3H, s) were assigned to methoxyl protons at C-4' and a *tert*-butyl signal at δ 1.25 (9H, s, 3 × CH_3). Two sharp one-proton singlet at δ 5.91 and δ 6.48 were ascribed to the quinonoid ring protons at C-4 and C-6 protons respectively. Since the other signals showed an A_2B_2 aromatic proton system at δ 7.19 (2H, d, H-3', 5') and δ 7.31 (2H, d, H- 2', 6'). We could confirm the position of the methoxyl group at C-4' and the *tert*- butyl group at C-3 position. From the above data, we suggest compound 1 to be 3-*tert*-butyl-4'-methoxydalbergione.

Compound 3, isolated as yellow colored crystals, showed an M^+ peak at 394 corresponding to the molecular formula $C_{26}H_{18}O_4$. This was corroborated by the ^{13}C NMR spectrum, which showed 26 carbon resonances. The UV absorption maxima of compound 3 in methanol at 276 nm and 365 nm suggested that compound 3 was a xanthone. The IR spectrum of compound 3 showed strong absorption bands at 1666 cm^{-1} and 1626 cm^{-1} indicates the presence of two carbonyl group. The ^1H NMR spectrum showed four multiplet and two singlets. On the basis of the ^1H NMR data, the compound was regarded as 6-phenyl-5a,6,7,7a-tetrahydrochromeno[3,2-a]xanthene-13,14-dione 3 and the following salient features were useful in arriving at this conclusion. Examination of the spectrum in the aromatic region showed the presence of two singlets observed in 7.93 δ (1H) and 7.90 δ (1H) were ascribed to H – 5' and H – 5 respectively. In the aromatic region, the signals appeared between 7.26 δ - 7.61 δ accounted for eleven protons in the molecule were assigned to A, E, F – ring protons. A two - proton multiplet at 4.64 δ - 4.85 δ was

assigned to H – 2 and H – 2'. The other multiplet observed at 4.15 δ - 4.25 δ integrating to one proton was ascribed at H – β. The remaining two – proton multiplet at 3.40 δ - 3.49 δ was assigned to H – α proton. In ^{13}C NMR spectrum a signal observed in 196.86 δ was due to carbonyl carbon.

3.2. Biological activity

DPPH is a stable free radical at room temperature and accepts an electron or hydrogen radical to become a stable diamagnetic molecule. The reaction in DPPH radical is a measure of antioxidant activity. The reduction capability of DPPH radicals was determined by the decrease in its absorbance at 517 nm, which is induced by antioxidants. It is usually noticeable as a change in color from purple to yellow. The scavenging activity of the isoflavones on DPPH radical was evaluated according to Blois method. All the compounds showed significant antioxidant activity (Table 1 and Figure 2). Among the five compounds, 5-hydroxy-7-methoxy-3',4'-methylenedioxyisoflavone 4 showed higher antioxidant activity (97.96% at 25µg) than standard ascorbic acid (95.02% at 25µg). The potential antioxidant activity of the compound 4 was due to the presence of conjugated double bonds, methyl group, chelated hydroxyl group and methylenedioxy group.

Table – 1: Antioxidant activity of isoflavones and neoflavone

Compound No	% of Inhibition				
	5µg	10µg	15µg	20µg	25µg
1	93.42	93.88	94.35	94.81	95.37
2	95.64	95.83	96.11	96.20	96.38
3	92.96	93.51	94.16	94.62	95.09
4	96.57	97.12	97.40	97.68	97.96
5	92.68	93.33	93.76	94.25	94.72
Ascorbic acid	92.38	93.40	94.11	94.51	95.02

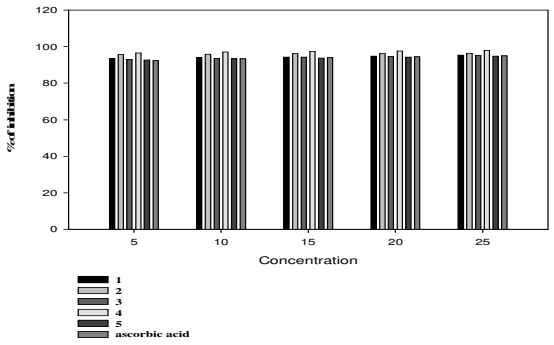

Figure - 2: Antioxidant properties of isoflavones and neoflavone compared to the standard (ascorbic acid) at different concentrations.

4. CONCLUSION

The present study reported two novel compounds named 3-*tert*-butyl-4'-methoxydalbergione **1** and 6-phenyl-5a,6,7,7a-tetrahydrochromeno[3,2-a]xanthene-13,14-dione **3** in addition with three known compounds **2, 4, 5** from *Dalbergia coromandeliana* roots for the first time. Among these five compounds, compound **4** possesses highest antioxidant activity.

Acknowledgements

The authors are thankful to the Management, Principal of the Ayya Nadar Janaki Ammal College, Sivakasi, Tamil Nadu, India for providing the necessary facilities to carry out this work.

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