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RESEARCH ARTICLE

ISOLATION OF TWO NEW FLAVONOIDS FROM THE CHLOROFORM EXTRACT OF *PONGAMIA PINNATA* ROOTS

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ABSTRACT

The chemical examination of chloroform extract of *Pongamia pinnata* roots has been carried out. Two new compounds, 3-(4-acetylphenyl)-7-methyl-4H-chromen-4-one 1 and 2-(benzo[d][1,3]dioxol-6-yl)-7-hydroxy-4H-chromen-4-one 4, in addition to two known compounds 2 (pongachromene) and 3 (demethoxykanugin) were isolated from the roots of *Pongamia pinnata.* The structures of the compounds 1-4 have been elucidated on the basis of spectral studies.

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INTRODUCTION

Flavones and their derivatives are the most common compounds isolated from *Pongamia pinnata*. *Pongamia pinnata* is one of the commonest and most useful medicinal plant of India. The Flavone class of compounds is distributed in all parts of this plant (Muqarrabun *et al.,* 2013). The root is effective for treating gonorrhea, cleaning gums, teeth, and ulcers and is used in vaginal and skin diseases (Muthu *et al.,* 2006). *Pongamia pinnata* is an important medicinal plant found in tidal forests of India and has been largely used in the traditional Indian system of medicine for bronchitis, whooping cough, rheumatic arthritis and diabetes (Kumar *et al.,* 2013). The present study has been undertaken with an objective of isolating flavonoids derivatives from the roots of *Pongamia pinnata*. In the previous investigations of this plant, many flavonoids, isoflavonoids and flavonoid glycosides have been reported (Muqarrabun *et al.,* 2013).

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In the present investigation, two new compounds. 1 and 4. have been identified along with two known compounds, 2 and 3.

MATERIALS AND METHODS

The IR spectra were recorded on an 8400S SHIMADZU spectrometer. 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 100-200 mesh (E. Merck).

Plant Material

The roots of *Pongamia pinnata* (L.) Pierre (Family - Leguminosae) were collected from ANJA College, Sivakasi is located in Virudhunagr district, Tamil Nadu, India. Morphology characters of plant was studied critically and the plant was identified with the help of the further illustrations on the flora of Tamil Nadu Carnatic, Rapinet Herbarium,

Tiruchirapalli (Matthew *et al.,* 1988). The plant was identified by Scientist 'D' & Head of Office Dr. C. Murugan, Botanical survey of India, Tamil Nadu Agricultural University, Coimbatore. A voucher specimen (No. TPH 1551) has been deposited in the Department of Botany, Ayya Nadar Janaki Ammal College, Sivakasi.

Extraction and isolation

The air-dried roots (1.0 kg) were cut into small pieces and extracted with Chloroform (3×5 l). The Chloroform extract on purification over a silica gel column using pet. ether (60-80 °C), pet-ether-benzene step gradient yielded 1 (15 mg), 2 (100 mg) and 3 (500 mg), benzene as eluent gave 4 (15 mg).

3-(4-Acetylphenyl)-7-methyl-4H-chromen-4-one (1): Yellow crystals (EtOH), m.p. 142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (3H, s, $COCH_3$), 2.53 (3H, s, CH_3), 7.25 (1H, s, H-8), 7.58 (1H, d, J = 9 Hz, H-6), 7.77-7.80 (2H, AA'BB' pattern, H-2', H-6'), 8.10 (1H, s, H-2), 8.19 (1H, d, J = 9 Hz, H-5), 8.28-8.31 (2H, AA'BB' pattern, H-3',H-5'); ^{13}C NMR (75 MHz, $CDCl_3$): 22.31 (CH_3), 30.10 ($CO\underline{C}H_3$), 127.52 (C-8), 127.54 (C-10), 127.83 (C-3), 127.88 (C-6), 131.67 (C-2',C-6'), 133.77 (C-3',C-5'), 133.95 (C-5), 133.98 (C-4'), 134.31 (C-1'), 134.43 (C-7), 135.33 (C-2), 145.68 (C-9), 183.37 (C=O), 183.81 ($\underline{C}OCH_3$).

2-(Benzo[d][1,3]dioxol-6-yl)-3,7-dimethoxy-4H-chromen-4-one (or) Demethoxykanugin (3): Yellow crystals (EtOH), m.p. 159 °C; IR, υ_{max}^{KBr} (cm^{-1}): 857 (OCH_2O), 1030 (OCH_3), 1447 (C=C), 1642 (C=O), 3097 (C-H); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (3H, s, OCH_3); 3.85 (3H, s, OCH_3); 6.00 (2H, s, O-CH_2-O); 6.81 (1H, s, H-8); 6.86-6.89 (2H, m, H-6, H-5'); 7.54 (1H, s, H-2'); 7.61 (1H, d, J = 9 Hz, H-6'); 8.04 (1H, d, J = 9 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.14, 60.24 (2 OCH_3); 100.27 (O-CH_2-O); 101.98 (C-8); 108.67 (C-6); 108.87 (C-2'); 114.55 (C-5'); 118.40 (C-10); 123.67 (C-6'); 125.12 (C-1'); 127.36 (C-5); 141.12 (C-3); 148.22 (C-4'); 149.81 (C-3'); 154.89 (C-2); 157.14 (C-9); 164.34 (C-7); 174.63 (C=O).

2-(Benzo[d][1,3]dioxol-6-yl)-7-hydroxy-4H-chromen-4-one (4): Yellow crystals (EtOH), m.p. 220 °C; IR, υ_{max}^{KBr} (cm^{-1}): 932 (O-CH_2-O), 1447 (C=C), 1641 (C=O), 3115 (C-H), 3447 (O-H); ^{1}H NMR (300 MHz, $CDCl_3$): δ6.12 (2H, s, O-CH_2-O); 6.78 ((1H, s, H-8); 6.97 (1H, d, J = 9 Hz, H-6); 7.22 (1H, s, OH); 7.42 (1H, s, H-2'); 7.54-7.59 (2H, m, H-5', H-6'); 7.79 (1H, s, H-3); 8.16 (1H, d, J = 9 Hz, H-5); ^{13}C NMR (75 MHz,

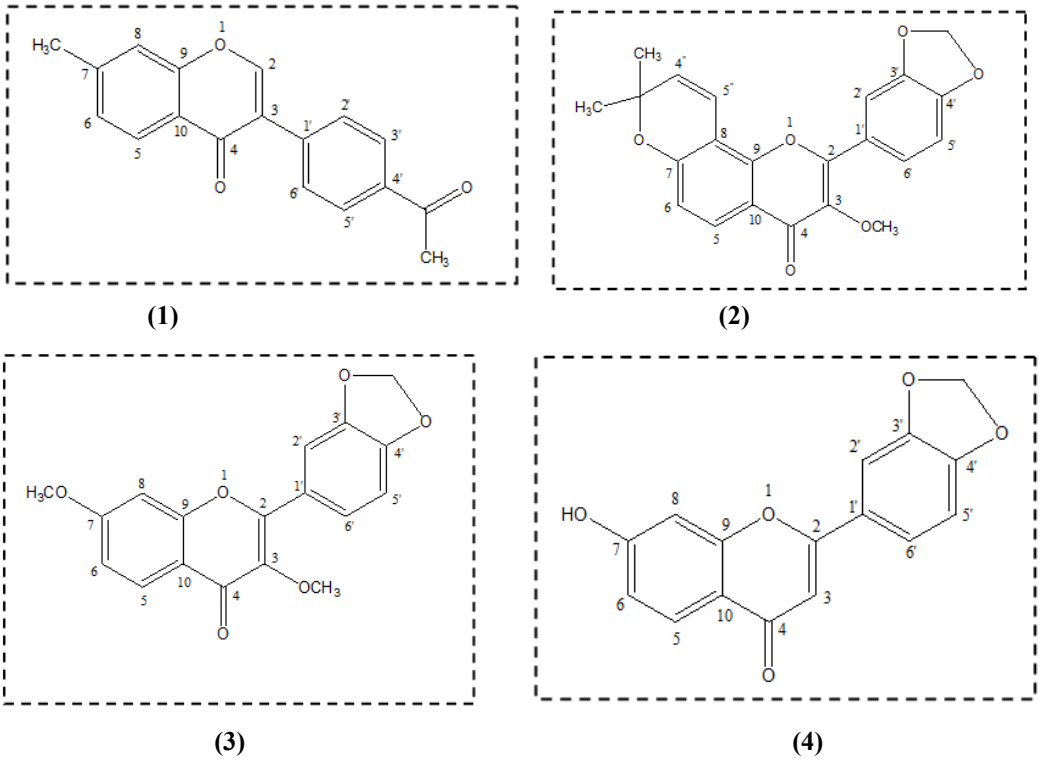

Fig.1. Structures of compounds 1-4 isolated from *Pongamia pinnata* Roots

Pongachromene (2): Yellow crystals (EtOH), m.p. 226 °C; IR, υ_{max}^{KBr} (cm^{-1}): 767 (cis C=C), 874 (2,2-dimethylchromene), 938 (OCH_2O), 1040 (OCH_3), 1365 (gem-diMe), 1632 (C=O), 3052 (C-H); ^{1}H NMR (300 MHz, $CDCl_3$): δ1.48 (6H, s, 2CH_3); 3.86 (3H, s, OCH_3); 5.69 (1H, d, J = 12 Hz, H-5"); 6.05 (2H, s, O-CH_2-O); 6.80-6.85 (2H, m, H-6, H-5'); 6.91 (1H, d, J = 12 Hz, H-4"); 7.57 (1H, s, H-2'); 7.64 (1H, d, J = 9 Hz, H-6'); 7.96 (1H, d, J = 9 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.48, 30.05 (2CH_3); 60.32 (OCH_3); 78.08 (C-O); 102.00 (O-CH_2-O); 104.53 (C-6); 108.81 (C-2'); 108.83 (C-8); 109.49 (C-5'); 115.27 (C-10); 115.49 (C-5"); 118.44 (C-6'); 123.63 (C-1'); 126.42 (C-4"); 130.67 (C-5); 141.07 (C-3); 148.28 (C-4'); 149.83 (C-3'); 151.58 (C-9); 154.56 (C-2); 157.65 (C-7); 174.76 (C=O).

RESULTS AND DISCUSSION

The chloroform extract of *Pongamia pinnata* roots was subjected to silica gel column chromatography affording two new compounds 1 and 4 in addition with two known compounds 2 (pongachromene) and 3 (demethoxykanugin)

(Figure 1) (Mukerjee *et al.,* 1969; Saha *et al.,* 1991; Koysomboon *et al.,* 2006; Pathak *et al.,* 1983; Mittal & Seshsdri., 1956; Talapatra *et al.,* 1982; Tanaka *et al.,* 1992; Yin *et al.,* 2004).

Compound 1: The solid obtained from petroleum ether – benzene mixture (85 ml : 15 ml) eluate of the column, on crystallization from ethanol yielded compound 1 as yellow coloured solid, melting at 142 °C. It was found to be homogeneous on TLC. The ^{1}H NMR spectrum of the compound confirms the presence of various functional groups present in the compound 1. The high field singlet (δ 1.61) equivalent to three protons is highly characteristic of an acetyl methyl group and the three protons singlet (δ 2.53) is due to methyl group attached to the phenyl ring. The H-5 and H-6 protons of phenyl ring-A appear as two doublets at 8.19 (J = 9 Hz) and δ 7.58 (J = 9 Hz) respectively. The B-ring aromatic protons appear as an A_2B_2 pattern at δ 8.28 and δ 7.77 ppm. The remaining two one proton singlets appear at δ 8.10 and δ 7.25 which are due to H-2 and H-8 respectively. The ^{13}C NMR spectrum of the isolated compound exhibits sixteen signals against eighteen carbons. The carbonyl carbons of acetyl group and flavone nucleus appear at δ 183.81 and 183.37 ppm respectively. On the basis of foregoing discussion, the structure of compound 1 has been established as 3-(4-acetylphenyl)-7-methyl-4H-chromen-4-one[3-(4-acetylphenyl) -7-methyl isoflavone].

Compound 4: The solid obtained from benzene (100 ml) eluate of the column, on crystallization from ethanol yielded compound 4 as yellow solid, melting at 220 °C. It was found to be homogeneous on TLC. The IR spectrum shows absorption bands for OH and C=O stretching at 3447 and 1641 cm^{-1} respectively. The ^{1}H NMR spectrum of the compound confirms the presence of various functional groups present in the compound 4. The downfield singlet (δ 6.12) equivalent to two protons is highly characteristic of a methylenedioxy group and the one proton singlet (δ 7.22) is due to OH group attached to the phenyl ring. The H-5 and H-6 protons of phenyl ring-A appear as two doublets at 8.16 (J = 9 Hz) and δ 6.97 (J = 9 Hz) respectively. The B-ring aromatic protons appear as AB pattern at δ 7.54 and 7.59 ppm. The remaining three one proton singlets appear at δ 6.78, 7.42 and 7.79 ppm due to H-8, H-2$^{'}$ and H-3 respectively. The ^{13}C NMR spectrum of the isolated compound exhibits sixteen signals for sixteen carbons. The carbonyl carbon of flavone nucleus appeared at δ 177.97. Based on the data, the structure of compound 4 has been established as 2-(benzo[d][1,3]dioxol-6-yl)-7-hydroxy-4H-chromen-4-one [7-hydroxy-3',4'-metylenedioxyflavone]. The chemical shift values of 3 and 4 are comparable subject to the changes in the substituent pattern. The presence of hydroxyl group in 4 is evidenced by the IR data as well. The compound 4 has been synthesized by two different routs (Dong *et al.,* 2009; Liu *et al.,* 2004) and the ^{1}H NMR data has been reported by one group (Dong *et al.,* 2009). As the reported data is recorded in acetone d-6 and the present characterization has been effected in $CDCl_3$, there are slight changes in the chemical shift values. However the reported mp varies slightly with ours.

Conclusion

The present study reported two novel compounds named 3-(4-acetylphenyl)-7-methyl-4H-chromen-4-one 1 and 2-(benzo[d] [1,3]dioxol-6-yl)-7-hydroxy-4H-chromen-4-one 4 for the first time in addition to two known compounds, 2 and 3, from *Pongamia pinnata* roots.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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