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Short Communication

A NEW NAPHTHOQUINONE ISOLATED FROM *POLYGONUM MULTIFLORUM* (POLYGONACEAE)

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ABSTRACT

Objective: This research is mainly focused towards isolation and structural elucidation of pure compounds from the extract and fractions of *Polygonum multiflorum* through silica gel column chromatography.

Methods: The air dried rhizomes were extracted with Me_2CO (acetone), MeOH (methanol) and H_2O (water). The Me_2CO extract was fractionated into $CHCl_3$ (chloroform) and residue. The chloroform-soluble portion and MeOH extract were subjected to silica gel column chromatography for the isolation of pure compounds. The isolated compounds were then determined by the use of spectroscopic analysis of HRFABMS, ^1H, ^{13}C NMR, UV and IR spectra.

Results: $CHCl_3$ soluble portion of Me_2CO and MeOH extract of *P. multiflorum* led to the isolation of one new naphthoquinone and eight known compounds including four anthraquinones, one naphthoquinone and two stilbenes.

Conclusion: The obtained results will be very useful for the further evaluation various biological studies.

Keywords: Naphthoquinones, Anthraquinones, Stilbenes, Isolation, *Polygonum multiflorum*, Spectroscopic analysis

Polygonum is a member of Polygonaceae family that contains 300 species distributed worldwide in temperate climate [1]. They vary widely from prostrate herbaceous annual plants under 5 cm high, erect, herbaceous perennial plants growing 3-4 m and some others woody perennial vines growing up to 20-30 m high in trees. *Polygonum* species are used as traditional folklore medicines such as cardiovascular protection [2], anti-inflammation [3], neuro-protection [4], mitigation of biochemical processes involved in age-related neurodegenerative disorders such as Alzheimer's [5] and Parkinson's disease [6]. Previous phytochemical constituents were recognized from the *Polygonum* species are flavonoids [7], triterpenoids [8], anthraquinones [9], coumarins [10], phenyl propanoids [11, 12], lignans [13], sesquiterpenoids [14, 15], stilbenoids [16] and tannins [1]. Among them, flavonoids are most common components and have been used as chemotaxonomic markers and playing an important role in the systematics of Polygonaceae species [17]. *Polygonum multiflorum* possesses many biological effects, such as lipid lowering, antioxidation, toxin detoxification, antitumor, lubricating intestine, cardiovascular disorders, neurological disorders and other diseases commonly associated with aging [18, 19]. Modern chromatographic separation studies have demonstrated that many bioactive compounds were isolated from *P. multiflorum* like stilbene glycosides [20-22] and 2,3,5,4'-Tetrahydroxystilbene-2-O-*β*–D-glucopyranoside have been reported as anti-oxidative, anti-inflammatory, endothelial protective and oncogenic enzyme inhibitory activities [23]. In view of the medicinal importance of *P. mutiflorum* and in our continuation investigations found new chemical constituents from this species, a new naphthoquinone namely as 7-acetyl-6-methyl-2, 3, 8-trihydroxy-1,4-naphthoquinone (1) together with eight known compounds (2-9) including four anthraquinones, stilbenes, and two naphthoquinones.

IR spectra were recorded in KBr disks on a Perkin-Elmer 983 G spectrophotometer. UV spectra were obtained on a Shimadzu UV-160 spectrometer. ^1H and ^{13}CMR spectra were determined on a Bruker AM-300 spectrometer using DMSO-d_6 and MeOH-d_4 with TMS as an internal standard, and 2D NMR spectra were recorded by using the Bruker standard pulse programs. FABMS were measured on a JEOL JX-HX110 mass spectrometer in glycerol matrix. Column chromatography (CC) separations were carried out by using Acme silica gel 100-200 mesh. The purity of the samples was checked by Thin layer chromatography (TLC) on pre-coated aluminum sheets silica gel 60 F254 (20 X 20 cm, 0.2 mm thickness, Merck) and compounds were detected under UV light (254 and 366 nm).

The rhizomes of *Polygonum multiflorum* (2.0 kg) were supplied in August 2012 and authenticated by Dr. P. Santhan, Toxanamist, Durva Herbal Centre, Chennai, Tamil Nadu, India. A voucher specimen (MVBR 89) has been deposited in Holy Mary Institute of Technology and Science, Hyderabad, India. The air dried and powdered rhizomes (2.0 kg) of *Polygonum multiflorum* was extracted with acetone (Me_2CO), methanol (MeOH) and water (H_2O) (3.5 L x 4) successively at room temperature. The Me_2CO extract was concentrated under reduced pressure to yield a brown syrup (60 g), which was further dissolved in water and partitioned (1: 1) with $CHCl_3$. The $CHCl_3$-soluble fraction (60 g) was purified over a silica gel column (100-200 mesh) using *n*-hexane/EtOAc step-gradient mixtures as eluents yielded 4 sub-fractions. The first sub-fraction was re-chromatographed over a silica gel column using *n*-hexane-EtOAc 8:2 and 7:3 eluates yielded 1 (20 mg) and 2 (15 mg), respectively. The second sub-fraction was purified by column chromatography using CH_2Cl_2/MeOH 9:1 yielded 3 (15 gm). Based on the TLC pattern subfractions 3 and 4 were combined it and then purified by over a silica gel column using CH_2Cl_2/MeOH solvent mixtures (8:2, 7:3) as eluents yielded 5 (35 mg), 7 (42 mg), and 9 (18 mg), respectively. The methanol extract (20 g) was purified by over a silica gel column using EtOAc/MeOH step gradient mixtures as elutes yielded 3 (2 g), 4 (1.2 g), 6 (125 mg), and 8 (1.5 g), respectively.

Compound (1), was isolated as an amorphous red powder (20 mg), showed a [M+H]+ peak at *m/z* 263.1050 in its HRFABMS, which is consistent with the molecular formula $C_{13}H_{10}O_6$. The ^{13}C NMR spectrum of 1 showed resonances for all 13 carbons present in the molecule. A positive response to sodium dithionite and the UV absorption maxima at 215, 254, 275, and 336 nm suggested that 1 could be a 1,4-naphthoquinone [24]. It exhibited IR absorption bands at 3420, 1705 and 1645 cm^{-1} due to hydroxyl, ester carbonyl and carbonyl functions, respectively. The presence of three downfield carbon resonances at δ 181.9, 192.7 and 205.0 in its ^{13}C NMR spectrum indicated an additional carbonyl function apart from the two quinonoid carbonyls. The additional acetyl carbonyl was further confirmed by acetyl methyl proton at δ 2.54 was ^2J correlation with the carbon resonance at δ 205.0 in its HMBC spectrum (fig. 1).

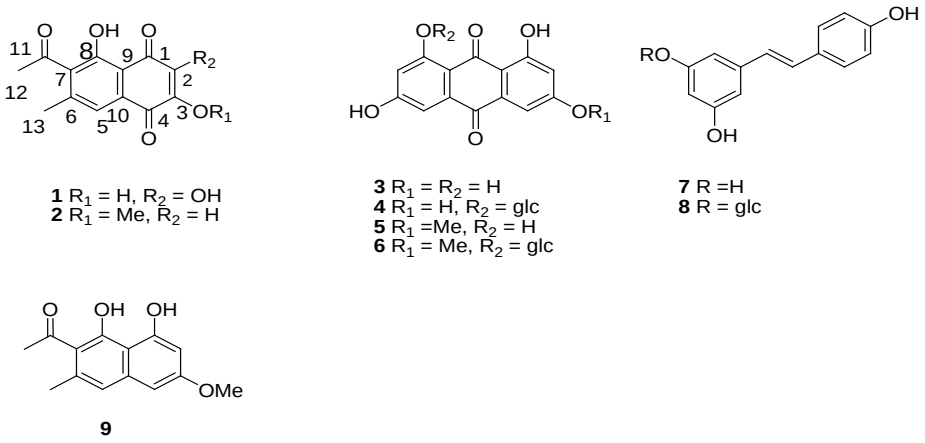

Fig. 1: The chemical structures of compounds 1-9

The 1 H NMR spectrum of 1 showed the presence of an aromatic proton signal at δ 7.44 (1H, s), an acetyl methyl group at δ 2.54 (3H, s), and an aromatic methyl signal at δ 2.29 (3H, s), which were correlated to the carbon resonances at δ 161.6, 31.9 and 19.8, respectively in its HMQC spectrum. Compound 1 did not respond to craven's test [25], which suggested that the 1, 4-naphthoquinone ring in 1 is fully substituted. In the HMBC spectrum of 1, the correlations of the aromatic proton at δ 7.44 with C-4 (δ 192.7), C-6 (δ 137.7), C-7 (δ 143.8) C-9 (δ 131.8) and C-10 (δ 113.8), and aromatic methyl signal at δ 2.29 with C-5 (δ 161.6), C-6 (δ 137.7), C-7 (δ 143.8) and acetyl methyl signal at δ 2.54 with C-7 (δ 143.8) and C-11 (δ 205.0), respectively indicated that these three groups are located at 5, 6 and 7 positions, respectively. These assignments were further supported by NOE correlations observed between methyl signal δ 2.29 and acetyl methyl group (δ 2.54) and aromatic proton signal (δ 7.44). Thus, the structure of compound 1 was established as, 7-acetyl-6-methyl-2, 3, 8-trihydroxy-1,4-naphthoquinone.

7-acetyl-6-methyl-2,3,8-trihydroxy-1,4-naphthoquinone (1)

Red amorphous powder; UV (MeOH) λ_{max} (log ε) 215 (4.4) 254 (4.2) 275 (4.1) 336 (3.8) nm; IR (KBr) ν_{max} 3420 (OH) 1705 (acetyl C=O), 1645 (quinone C=O) 1540, 1218, 772 cm^{-1}; ^{1}H NMR (MeOH-d_4, 300 MHz) δ 7.44 (1H,s,H-8), 2.54 (3H,s,Me-12), 2.29 (3H,s Me-13); ^{13}C NMR (MeOH-d_4, 75 MHz) δ 205.0 (C-11), 192.7(C-4), 181.9 (C-1), 161.6 (C-5), 158.7 (C-2), 157.2 (C-8), 143.8(C-3 and C-7), 137.7 (C-6), 131.8 (C-9), 113.8 (C-10), 31.9 (C-12), 19.8 (C-13); FABMS (positive mode) *m/z* 263.1050 $[M+H]^+$(10), 262.1 (18), [M+H-Me] (100); HRFABMS *m/z* 263.1050 $[M+H]^+$(calcd for $C_{13}H_{10}O_6$+H 263.0555).

The structures of the known compounds were identified as 3-methoxy-7-acetyl-6-methyljuglone (2) [26-29], emodin (3), emoidin-8-0-β–D-glucopyranoside (4) physicion (5) physcion-8-0-β–D-glucopyranoside (6) [30], resveratrol (7), piceid (8) [31] and torachrysone (9) [32], by comparison of their spectroscopic data with those reported data in the literature. Torachrysone (4) was isolated for the first time from this plant. In the present paper, we report the isolation and structural elucidation of new compound 1 from *P. multiflorum.*

CONFLICT OF INTERESTS

The authors that there is no conflict of interests

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