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Flavonoid and megastigmane glycosides from *Artabotrys hexapetalus* leaves

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ABSTRACT

From the leaves of *Artabotrys hexapetalus* (Annonaceae), a megastigmane glucoside (**1**), along with four flavonoid glycosides (**2–5**), were isolated and identified by various spectroscopic techniques and by comparison of the data with those in the literature. The occurrence of megastigmane glucoside and quercetin triglycoside is being reported for the first time from this plant. The chemotaxonomic significance of these compounds was summarized.

1. Subject and source

A whole plant of the species *Artabotrys hexapetalus* (L.f.) Bhandari (synonym; *Artabotrys uncinatus* (Lam.) Merr, *Artabotrys odoratissimus* R. Br.) was collected from Warinchamrap, Ubon Ratchathani Province, Thailand, in November 2008. A voucher specimen (RW004) was deposited at the Faculty of Pharmaceutical Sciences, Ubon Ratchathani University, and was identified by comparison with authentic herbarium specimens (BKF 095932) at the Forest Herbarium, Department of National Parks, Wildlife and Plant Conservation, Bangkok, Thailand.

2. Previous work

Previous phytochemical studies of *A. hexapetalus* have resulted in the isolation of alkaloids (Wu et al., 1989; Connolly et al., 1994; Hsieh et al., 1999, 2001; Lan et al., 2007), anthraquinones (Singh et al., 2005), butyrolactones (Wong and Brown, 2002; Bordoloi et al., 2009), flavonoids (Singh and Sahai, 1996; Li et al., 1997a, b; Li and Yu, 1998; Singh et al., 2008), neolignans (Yu et al., 2002), phenolic compounds (Singh et al., 2008), terpenoids (Liang et al., 1979; Hasan et al., 1987, 1991; Zhang et al., 1988, 1989; Yu et al., 2001, 2002; Singh et al., 2006; Phan et al., 2007; Gupta et al., 2010), and volatile compounds (Jirovetz et al., 1998; Mahidol et al., 2005; Srivastava et al., 2009; Bhattacharyya et al., 2010). In addition, aliphatic compounds (Jain et al., 1998; Mehta et al., 1999) and fatty acids (Sharma et al., 2002; Singh et al., 2009) have been investigated.

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3. Present study

Dried powdered leaves (300 g) were defatted with hexane. The sample was then extracted with ethyl acetate and methanol (3 × 1 L). The extracts were concentrated under reduced pressure. The ethyl acetate extract (8 g) was fractionated by vacuum liquid chromatography using a glass column of silica gel 60 (50.0 g). Elution was performed using a polarity gradient of dichloromethane and methanol (200 ml each, from 0% methanol to 100% methanol) to obtain ten fractions. Fraction AE 6 was further separated using an RP-18 column; elution with a mixture of methanol and water (70:30) yielded compound **1** (6 mg). The methanol extract (30.0 g) was separated by vacuum liquid chromatography with silica gel 60 (300.0 g) as the stationary phase, and the mobile phase was a mixture of methanol and ethyl acetate (500 ml each, from 100% to 0% ethyl acetate). Fractions AM 1-AM 7 were obtained. Fraction AM 5 was further subjected to Sephadex LH 20 column chromatography with methanol as the eluent to obtain five fractions. Fraction AM 5–3 was purified by RP-18 column chromatography with 40% methanol-water as the mobile phase, yielding compound **2** (4 mg). Fraction AM 5–4 was isolated using RP-18 column chromatography, using 30% methanol-water as the eluent to yield compound **3** (4 mg). Fraction AM 6 was isolated using Sephadex LH 20 with methanol as the eluent and then purified by RP-18 column chromatography. A mixture of methanol and water (60:40) was used as the mobile phase to yield compound **4** (10 mg). Fraction AM 7 was isolated by RP-18 column chromatography, using a mixture of acetonitrile and water (75:25) as the eluent, yielding compound **5** (3 mg).

The structures of the isolated compounds were determined by UV spectrophotometry (Shimadzu 2101 PC spectrophotometer), 1D and 2D NMR experiments (^{1}H 500 MHz, ^{13}C 125 MHz, HSQC, HMBC, NOESY; Bruker 500 spectrometer), mass spectrometry (MAT 95 XL mass spectrometer; Thermo Finnigan), HR-ESI^{+}-MS (liquid chromatograph-mass spectrometer; Waters) and comparison with literature data. The isolated compounds were identified as 7*E*-9-hydroxy-4,7-megastigmane-3-one-10-*O*-β-D-glucopyranoside (**1**) (Khan et al., 2005), quercetin 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinofuranoside (**2**) (Li et al., 1997a, b), apigenin 7-*O*-β-D-glucopyranoside (**3**) (Moussaoui et al., 2010), and quercetin 3-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (**4**) (Abdullah et al., 2008). Compound **5** was determined to be quercetin 3-rhamnosyl rutinoside, but only partial data for this compound have been reported (Fuentes-Alventosa et al., 2008). We report herein the essential spectroscopy data for quercetin 3-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside] (**5**): UV max (CH_3OH): 210.2, 256.6, 268.2, 355.6; HRESI^{+}-MS: *m/z* (%) 779.1976 $[M + Na]^{+}$ (calcd for $C_{33}H_{40}O_{20}$ 779.2011); ^{1}H NMR (500 MHz, methanol-d_4): δ 6.17 (1H, d, J = 2.1 Hz, H-6), 6.36 (1H, d, J = 2.1 Hz, H-8), 7.59 (1H, d, J = 2.1 Hz, H-2′), 6.87 (1H, d, J = 8.3 Hz, H-5′), 7.61 (1H, dd, J = 2.1, 8.3 Hz, H-6′), 5.58 (1H, d, J = 7.6 Hz, H-1″), 3.53 (1H, t, J = 7.6, 9.0 Hz, H-2″), 3.64 (1H, dd, J = 8.0, 9.0 Hz, H-3″), 3.29 (1H, m, H-4″), 3.32 (1H, m, H-5″), 3.82 (1H, d, J = 1.5, 11.0 Hz, H-6″), 3.38 (1H, d, J = 5.8, 11.0 Hz, H-6″), 4.49 (1H, d, J = 1.5 Hz, H-1‴), 3.58 (1H, q, J = 1.5 Hz, H-2‴), 3.48 (1H, dd, J = 3.2, 9.6 Hz, H-3‴), 3.25 (1H, t, J = 1.4, 9.6 Hz, H-4‴), 3.40 (1H, dd, J = 3.2, 6.3, H-5‴), 1.07 (3H, d, J = 6.3 Hz, CH_3-6‴), 5.21 (1H, d, J = 1.4 Hz, H-1⁗), 4.00 (1H, q, J = 1.4 Hz, H-2⁗), 3.79 (1H, m, H-3⁗), 3.34 (1H, m, H-4⁗), 4.07 (1H, dd, J = 2.8, 6.3, H-5⁗), 1.00 (3H, d, J = 6.3 Hz, CH_3-6⁗); ^{13}C NMR (125 MHz, methanol-d_4): δ 149.6 (C-2), 134.4 (C-3), 179.3 (C-4), 163.1 (C-5), 99.9 (C-6), 165.9 (C-7), 94.8 (C-8), 158.5 (C-9), 105.8 (C-10), 123.5 (C-1′), 117.4 (C-2′), 145.9 (C-3′), 158.9 (C-4′), 116.1 (C-5′), 123.4 (C-6′), 100.5 (C-1″), 78.9 (C-2″), 80.1 (C-3″), 71.9 (C-4″), 77.1 (C-5″), 68.3 (C-6″), 102.2 (C-1‴), 72.1 (C-2‴), 72.3 (C-3‴), 73.9 (C-4‴), 69.7 (C-5‴), 17.8 (CH_3-6‴), 102.6 (C-1⁗), 72.4 (C-2⁗), 72.3 (C-3⁗), 74.1 (C-4⁗), 69.9 (C-5⁗), 17.5 (CH_3-6⁗).

4. Chemotaxonomic significance

Artabotrys, the liana genus of Annonaceae, consists of 100 species. Members are abundant throughout tropical Africa and Asia (Kubitzki et al., 1998). In the present study, a megastigmane glycoside (**1**) and four flavonoid glycosides (**2**–**5**) were purified from the leaves of *A. hexapetalus* (Fig. 1). 7*E*-9-hydroxy-4,7-megastigmane-3-one-10-*O*-β-D-glucopyranoside

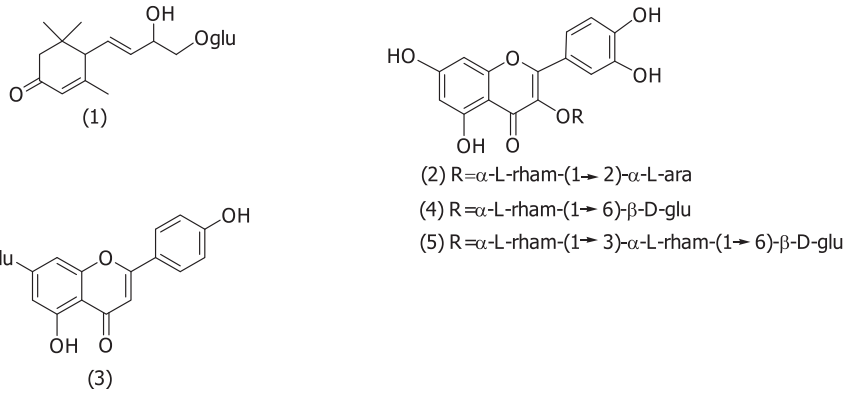

Fig. 1. Chemical structures of compound **1**–**5** of *A. hexapetalus* leaves.