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Acylated flavonol diglucosides from *Ammania auriculata*

Abstract: Chemical investigation of the extract of the whole *Ammania auriculata* plant resulted in the identification of 13 polyphenols, including the hitherto unknown flavonoids, kaempferol 3-*O*-β-(6″-galloylglucopyranoside)-7-*O*-β-glucopyranoside, and its quercetin analogue. The structures of all isolates were elucidated by conventional methods, spectroscopic analysis, including 1D and 2D NMR, and by HRESI-MS as well.

Keywords: *Ammania auricultata* (Lythraceae); flavonols; 3-*O*-β-(6″-*O*-galloylglucoside)-7-*O*-β-glucoside.

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1 Introduction

In Egypt, several plants rich in phenolics have been intensively investigated for their biological activities and their constitutive phenolics (e.g., [1–4]). Among those plants, little is known about the phytochemistry of *Ammania auriculata* Willd. (Lythraceae) (syn. *Ammannia arenaria* Kunth.) [5], apart from two reports describing the presence of kaempferol, quercetin, kaempferol-3-*O*-α-L-arabinofuranoside, kaempferol-3-*O*-β-D-xylopyranoside and ellagic acid in the whole plant [6], and 2,3-hexahydroxydiphenoyl-(α/β)-glucopyranose, 2,3-di-*O*-galloyl-(α/β)-glucopyranose, 1,6-di-*O*-galloyl-(α/β)-glucopyranose, kaempferol-3-*O*-β-(6″-*p*-coumaroylglucopyranoside), 1-monogalloyl-2,3-hexahydroxy-(α)-glucopyranose, quercetin 3-*O*-β-(6″-galloylglucopyranoside), gallic acid 3-*O*-β-glucoside, 2,3,6-tri-*O*-galloyl-(α/β)-glucose [7]. The plant is used as a counter irritant for rheumatic pains [8]. This species occurs throughout tropical and subtropical regions of the world, from Southeastern North America through Central America and the Caribbean to Argentina, from Egypt to South Africa and east through Pakistan and India east to China, as well as in Northern Australia. During the current study, we isolated and identified an additional 13 phenolic compounds (**1**–**13**) from the aqueous ethanol extract of whole *A. auriculata* plant. All compounds have been characterized for the first time from this plant. The isolates include two galloylated flavonol glucosides (**12** and **13**), both of which have not been reported previously to occur in nature.

2 Results and discussion

Dried specimens of whole flowering *A. auriculata* plants were exhaustively extracted with aqueous ethanol (3:1, v/v). The obtained extract was subjected to a series of column and preparative paper chromatographic separations to yield compounds **1**–**13**.

Compound **12,** a yellow amorphous powder, had chromatographic properties (dark purple spot on paper chromatogram under UV light, turning lemon yellow when fumed with ammonia vapor, moderate migration in aqueous and organic solvents) and color reactions (a lemon yellow color with Naturstoff reagent), which suggested a kaempferol derivative bearing a free 4′ hydroxyl group and an *O*-glycosylated one at the 3-position. The UV spectra of **12** in MeOH (268 nm, 316 nm, 360 nm) and upon addition of the diagnostic shift reagents, together with the R_f values were typical of those of 3-*O*,7-*O* diglycosylated

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kaempferol [9, 10] and confirmed the presence of a free hydroxyl at the C-4′-position (stable MeONa) and a glycosylated hydroxyl at the C-7 position (no shift with NaOAc). Normal acid hydrolysis of **12** (2 N aqueous HCl, 3 h, 100 °C) yielded glucose (comparative paper chromatography, Co-PC), kaempferol and gallic acid (Co-PC, UV spectra and ^{1}H NMR). Compound **12** was hydrolyzed after incubation with β-glucosidase to yield kaempferol 3-*O*-β-(6″-galloylglucoside) [11]. Consequently, **12** is kaempferol 3-*O*-(galloylglucoside)-7-*O*-glucoside. The result of negative ESI-MS analysis of **12** indicated a molecular ion peak at $[M–H]^-$ 761, corresponding to a molecular mass (*Mr*) of 762. The accurate MSMS analysis of that ion revealed a fragmentation pattern (*m/z*: 447 [M–galloyl glucose]$^-$, 285 [kaempferol]$^-$, 152 [galloyl]$^-$), consistent with the proposed structure. The molecular formula was concluded to be $C_{34}H_{34}O_{20}$ from its negative HRESI-MS, which showed an $[M–1]^-$ ion at *m/z*=762.6249 (calculated for $C_{34}H_{34}O_{20}$: 762.6253). To determine the site of attachment of all moieties in the molecule of **12** and to allow the full assignment of all carbon and proton resonances, NMR spectroscopic analysis of **12**, including 1D ^{1}H and ^{13}C, and 2D TOCSY, HMQC and HMBC, was then carried out. The ^{1}H NMR spectrum (DMSO-d_6, room temperature) revealed two distinct β-anomeric hexose proton resonances at ppm 5.02 and 5.31 (each d, *J*=8.5 Hz) attributed to the anomeric glucoside moieties at the kaempferol 7- and 3-positions, respectively. The spectrum also showed a pair of glucose proton resonances at 4.26 (dd, *J*=12 Hz and 5.5 Hz) and 4.12 ppm (m), assignable to the two methylenic glucose protons whose hydroxyl group is acylated by the galloyl moiety. The spectrum proved, in addition, the presence of a 7-*O*-substituted kaempferol moiety by the two distinct low field proton resonances at δ 6.32 (d, *J*=2.5 Hz) and 6.72 (d, *J*=2.5 Hz), assignable to the H-6 and H-8 of this moiety. In this spectrum, the singlet at δ ppm 6.99 was obviously due to the galloyl moiety. The ^{13}C NMR analysis confirmed the suggested structure of **12**. As expected, the spectrum (DMSO-d_6, room temperature) exhibited 12 distinct glucose carbon resonances (see Experimental). The two β-glucose anomers at positions C-7 and C-3 of the flavonol moiety were recognized from the downfield resonances at δ ppm 99.8 and 102.91, respectively, while the most upfield resonances at δ ppm 60.10 and 63.17 were assigned to the methylenic C-6 glucose carbon bearing a free hydroxyl (located at the 7-position of the kaempferol moiety) and to the methylenic C-6 of the galloylated glucose (attached at the 3-position), respectively. The deshielding of the latter resonance (δ 63.17) is obviously due to the acylation by gallic acid. Assignment of the remaining glucose carbons was aided by comparison with the reported ^{13}C chemical shifts of kaempferol 3,7-di-*O*-glucoside [12]. The presence of only a single galloyl moiety in **12** followed from the single carboxyl carbon resonance at δ 166.4 and from the recognized characteristic pattern of the remaining galloyl carbon resonances [13], (see Experimental). The recorded chemical shifts of the kaempferol carbon resonances in the ^{13}C NMR spectrum confirmed substitution at the 3- and 7-positions. This followed from the relative upfield shifts of the kaempferol C-3 and C-7 resonances to 134.3 and 161.5, respectively [14]. Furthermore, the measured chemical shift values of the carbon resonances of the two glucose moieties confirmed that the sugar cores exist in the pyranose form [15]. The TOCSY spectrum confirmed that the methylinic proton resonances at δ 4.26 (dd, *J*=12 and 4.5 Hz) and 4.12 (m) of the C-6 galloylated glucose moiety belong to the glucoside moiety whose anomeric proton resonates at δ 5.31 ppm. That the galloylated glucose linked to the hydroxyl group at C-3 of the aglycone was unambiguously confirmed by a ^3J long-range correlation between its anomeric proton (δ ppm 5.31) and C-3 (δ ppm 134.3) of the kaempferol moiety in the hetronuclear multi bond connectivity (HMBC) spectrum. This spectrum also showed a cross peak correlating to the second anomeric proton resonance at δ 5.02 to the kaempferol carbon C-7 at δ ppm 161.5. Consequently, **12** is identified as kaempferol 3-*O*-β-(6″-galloylglucopyranoside)-7-*O*-β-glucopyranoside, which has not been reported previously in nature (Figure 1).

Compound **13** was isolated as a faint yellow amorphous powder which appeared dull purple on chromatograms under UV light, turning orange when fumed with ammonia vapor. It gave glucose, quercetin and gallic acid (Co-PC), on normal acid hydrolysis. Compound **13** exhibited an M*r* of 778 in negative ESI-MS ($[M–H]^-$ at m/z=777). These data together with R_f values and UV spectral analysis (see Experimental) indicated that **13** is the quercetin analogue of **12**. ^{1}H and ^{13}C NMR spectroscopic analysis of **13** confirmed its structure to be quercetin 3-*O*-β-(6″-galloylglucopyranoside)-7-*O*-β-glucopyranoside, which has not been reported before as a natural product (Figure 1).

2.1 Known isolates

Gallic acid **1** [13], 1-*O*-galloyl 3,6-hexahydroxydiphenoyl glucose corilagin **2** [16], myricetin 3-*O*-β-glucopyranose **3** [17], quercetin 3-*O*-β-glucopyranose **4** [18], kaempferol 3-*O*-glucopyranoside **5** [19], 2,3-hexahydroxydiphenoyl-6-galloyl-(α/β)-glucopyranose **6** [20], 2,3-di-*O*-galloyl-4,6-hexahydroxydiphenoyl-(α/β)-glucopyranose, tellimagrandin II **7** [21], 1,2,3-tri-*O*-galloyl-(α)-

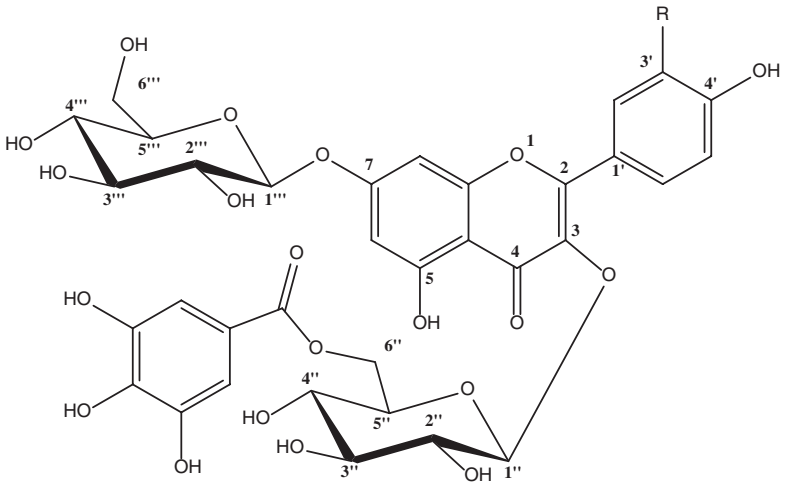

Figure 1: Compound **12**: R=H, compound **13:** R=OH.

glucopyranose **8** [22], 1,2,3-tri-*O*-galloyl-(β)-glucopyranose **9** [13], 1,4,6-tri-*O*-galloyl-(β)-glucopyranose **10** [13] and 2,3,6-tri-*O*-galloyl-(α/β)-glucopyranose **11** [7].

3 Experimental

3.1 General

NMR spectra were acquired in DMSO-d_6 on a Jeol ECA 500 MHz NMR spectrometer (JEOL USA, Inc., MA, USA), at 500 MHz (El-Menya, Egypt). Standard pulse sequence and parameters were used to obtain 1D ^{1}H and ^{13}C, and 2D COSY, HSQC and HMBC spectra, respectively. ^{1}H chemical shifts (δ) were measured in ppm, relative to tetramethyl silane (TMS) and 13C NMR chemical shifts to acetone-d_6, and were converted to TMS scale by adding 29.8 ppm. HRESI mass spectra were measured using a Finnigan LTQ FT Ultra mass spectrometer (Thermo FisherScientific, Bremen, Germany) equipped with a Nanomate ESI interface (Advion). An average electrospray voltage of 1.7 kV and a transfer capillary temperature of 200 °C were applied. Collision induced dissociation was performed in the ion trap using a normalized collision energy of 35%, activation time of 30 ms, 0.25 activation Q and a precursor ion isolation width of 2 amu. High resolution product ions were detected in the Fourier transform ion cyclotron resonance cell of the mass spectrometer. UV spectra were recorded on a Shimadzu UV-Visible-1601 spectrophotometer (Kyoto, Japan). Flame atomic absorption analysis was performed on a Varian Spectra-AA220 instrument (Cairo, Egypt), lamp current: 5 mA, fuel: acetylene, oxidant: air. Chromatographic analysis (PC) was carried out on Whatman No. 1 paper, using solvent systems: H_2O; 15% HOAc; 6% HOAc; *n*-butanol-acetic acid-water (BAW; *n*-BuOH–HOAc–H_2O, 4:1:5, v/v/v/, upper layer).

3.2 Plant material

Flowering whole plants of *A. auriculata* Willd. were collected with their roots from the rice fields near Banha City, 40 km north of Cairo, Egypt, in April 2012. A flowering voucher specimen (A 362) was deposited in the herbarium of the National Research Center (NRC), the identity of which was verified by Dr. S. Kawashty, Professor of Botany at NRC.

3.3 Extraction

Flowering whole plants were air-dried, and a 3 kg sample of the powder was extracted (3 times) with 5 L EtOH/H_2O (3:1, v/v) under reflux for 8 h each. The extract was filtered and dried in vacuo to yield a dark brown amorphous powder (250 g).

3.4 Isolation and identification of phenolic compounds

The dried aqueous EtOH extract (115 g) was loaded onto a Sephadex LH-20 (900 g) column (120 cm×7.5 cm). Elution then started with H_2O followed by isocratic elution in 10% steps from 10% MeOH-H_2O (v/v) to 100% MeOH. Following removal of the solvents, 10 fractions (I–X) were obtained. Fraction I eluted with H_2O, II with 10%, III with 20%, IV with 30%, V with 40%, VI with 50%, VII with 60%, VIII with 70%, IX with 80% and X with 90% MeOH, respectively. The fractions were individually collected and subjected to 2D PC. Compound **1** (108 mg) was isolated in pure form from 2.05 g of fraction II (eluted with 10% MeOH), by repeated precipitation (three times) from acetone by ether. Compounds **2** (104 mg) and **3** (75 mg) were individually separated in pure form by fractionation of 2.3 g of fraction IV (eluted with 30% MeOH) over a small Sephadex LH-20 (15 g) column using an MeOH/H_2O mixture of decreasing polarity for elution. Compound **3** (92 mg) was individually isolated in pure form from 679 mg of V (eluted with 40% MeOH), by fractionation on a Sephadex LH-20 (13 g) column and 40% MeOH for elution, followed by preparative PC using BAW for final purification. Compound **4** (83 mg), was separated in pure form from 701 mg of fraction VI (eluted with 50% MeOH) by preparative PC, using water-saturated *n*-BuOH as solvent. Compound **5** (74 mg) was isolated in pure form from 807 mg of fraction VII (eluted with 60% MeOH) by polyamide column (35 g) fractionation and gradient elution with H_2O/MeOH mixtures of decreasing polarities, whereby

three successive subfractions were individually eluted, i.e., subfraction i by 20%, subfraction ii by 30% and subfraction iii by 50% MeOH. Purification by preparative PC using BAW as solvent yielded pure samples of compound **6** from iii.

Compound **7** (91 mg) was individually obtained in pure form from 812 mg of fraction VII through repeated preparative PC (three times). Sephadex LH-20 column chromatography of 835 mg of fraction VIII (eluted with 70%), using water-saturated *n*-BuOH for elution, yielded four subfractions (i–iv). A pure sample of compound **8** (72 mg) was separated from subfraction i through polyamide S_6 column fractionation, using 50% MeOH for elution.

Compound **9** was obtained from 67 mg of subfraction ii through an MCI gel (CHP-20P) column fractionation, using gradient elution with H_2O/MeOH mixtures of decreasing polarities. On successive preparative PC (twice) of 735 mg of fraction IX, using 6% AcOH, four individual bands were detected on the chromatograms under UV light. Sephadex LH-20 column purification, using H_2O as solvent, of each of the materials eluted from the four bands afforded pure samples of **10** (44 mg), **11** (32 mg), **12** (54 mg) and **13** (66 mg).

3.5 Kaempferol 3-*O*- β-(6″-galloylglucopyranose)-7-*O*-β-glucopyranoside (12)

Mr: 762, ESI-MS: negative ion: m/z (rel. int.): 762 (52), [M-H]-, 447 (30), [M-galloylglucose]-, 285 (39), [kaempferol]-. R_f values: 54 (H_2O), 59 (15% HOAc), 44 (BAW). UV in MeOH λ_{max} nm: 268, 316, 360; NaOAc: 268, 317, 366; NaOAc+H_3BO_3: 268, 318; $AlCl_3$: 275, 312, 392; NaOMe: 277, 362. Normal acid hydrolysis gave glucose (Co-PC), kaempferol and gallic acid (Co-PC, ^{1}H NMR). β-Glucosidase [lyophilized, chromatographically pure, salt-free enzyme from almond, BDH Merck, Poole Dorset, UK (E.C. 3.2.1.21)] for 24 h, at 37 °C in acetate buffer, pH 5.1, enzymatic hydrolysis yielded kaempferol 3-O-β-(6″-galloylglucoside), ^{1}H NMR of **12**: galloyl moiety: δ ppm 6.99 (s); kaempferol moiety: δ ppm 6.32 (d, *J*=2.5 Hz, H-6), 6.72 (d, *J*=2.5 Hz, H-8), 6.86 (d, *J*=7.5 Hz, H-3′ and H-5′), 8.0 (d, *J*=7.5 Hz, H-2′ and H-6′), 11.8 (s,OH-5); β-glucoside moieties: δ ppm 5.02 (d, *J*=8.5 Hz, anomeric glucose proton at flavone C-7), 5.31 (d, *J*=8.5 Hz, anomeric at flavone C-3), 4.26 (dd, *J*=12 and 5.5 Hz, one methylenic H2-6 proton), 4.12 (m, one methylenic H-6 proton), 3.3–3.9 (m, glucose protons). ^{13}C NMR of **12**: kaempferol moiety: δ ppm 156.9 (C-2), 134.3 (C-3), 177.6 (C-4), 160.8 (C-5), 99.2 (C-6), 161.5 (C-7), 94.6 (C-8), 156.0 (C-9), 104.5 (C-10), 121.2 (C-1′), 129.8 (C-2′ and C-6′), 115.7 (C-3′ and C-5′), 159.9 (C-4′); galloyl moiety: 121.9 (C-l), 109.6 (C-2 and C-6), 145.5 (C-3 and C-5), 138.9 (C-4), 166.4 (C=O); C-7-glucose moiety: 99.8 (C-1), 73.1 (C-2), 76.4 (C-3), 69.7 (C-4), 76.5 (C-5), 60.1 (C-6); C-3-glucose moiety: 102.91 (C-1), 74.3 (C-2), 77.1 (C-3), 69.5 (C-4), 76.8 (C-5), 63.17 (C-6).

3.6 Quercetin 3-*O*- β-(6″-galloylglucopyranose)-7-*O*-β-glucopyranoside (13):

Mr: 778, ESI-MS: negative ion: m/z (rel. int.): 777 (60), [M-H]-, 463 (28), [M-galloyl glucose]-, 301 (36) , [quercetin]-, 151 (33), [galloyl]-. R_f values: 50 (H_2O), 55 (15% AcOH), 40 (BAW). UV λ_{max} nm in MeOH: 254, 266, 294 (shoulder), 313, 354; +NaOAc: 256 (shoulder), 266, 300, 374; +NaOAc/H_3BO_3: 272, 299, 438 (shoulder); +$AlCl_3$: 243, 274, 367. Normal acid hydrolysis gave glucose (Co-PC), quercetin and gallic acid [Co-PC, UV spectral data; ^{1}H NMR of **13**: galloyl moiety: δ ppm 6.97; quercetin moiety: ppm 6.36 (d, *J*=2.5 Hz, H-6), 6.75 (d, *J*=2.5 Hz, H-8), 6.8 (d, *J*=7.5 Hz, H-5′), 7.52 (m, H-2′ and H-6′), 12.6 (s, OH-5); β-glucoside moieties: ppm 5.16 (d, *J*=8.5 Hz, anomeric proton of C-7 glucoside), 5.50 (d, *J*=8.5 Hz, anomeric proton of C-3 glucoside), 4.4 (dd, *J*=12 and 5.5 Hz, one methylenic H2-6 proton), 4.24 (m, one methylenic H-6 proton), 3.3–3.9 (m, glucose protons). ^{13}C NMR of **13**: quercetin moiety: δ ppm 156.5 (C-2), 133.9 (C-3), 177.5 (C-4), 161.8 (C-5), 99.7 (C-6), 160.5 (C-7), 94.3 (C-8), 156.4 (C-9), 104.4 (C-10), 122.2 (C-1′), 115.4 (C-2′), 144.7 (C-3′), 148.9 (C-4′), 115.9 (C-5′), 121.3 (C-6′); galloyl moiety: 121.7 (C-l), 109.5 (C-2 and C-6), 145.5 (C-3 and C-5), 138.9 (C-4), 166.4 (C=O); glucose moiety at flavonol C-7: 99.8 (C-1), 73.1 (C-2), 76.4 (C-3), 69.7 (C-4), 76.5 (C-5), 60.1 (C-6); glucose moiety at flavonol C-3: 102.91 (C-1), 74.3 (C-2), 77.1 (C-3), 69.5 (C-4), 76.8 (C-5), 63.17 (C-6).

4 Conclusion

The present study has revealed that *A. auriculata* is capable of synthesizing and accumulating several ellagitannins, gallotannins and acylated flavonol glycosides [7], together with normal flavonol glycosides [6].

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