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Six new anthraquinone glycosides from *Lasianthus acuminatissimus* Merr.

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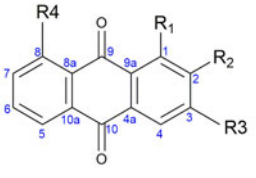
ABSTRACT

Six new anthraquinones named lasianthuoside F (1), G (2), H (3), I (4), J (5), K (6) were isolated from an acetone extract of the root of *Lasianthus acuminatissimus*. Their structures were elucidated by physical and chemical evidence and spectral analysis.



	R_1	R_2	R_3	R_4
1	OH	CH_2OCH_3	O-β -D-glucopyranosyl	H
2	OCH_3	CH_2OCH_3	O-β -D-glucopyranosyl	OH
3	OH	CH_2OCH_3	O-β-D-apiofuranosyl-(1→6) -β-D-glucopyranosyl	H
4	OCH_3	CH_2OCH_3	O-β-D-apiofuranosyl-(1→6)-β-D -glucopyranosyl 2",3"-acetonide	H
5	OCH_3	CH_2OCH_3	O-β-D-apiofuranosyl-(1→6)-β-D -glucopyranosyl 2",3"-acetonide	OH
6	OCH_3	CH_2OH	O-β-D-apiofuranosyl-(1→6)-β-D -glucopyranosyl 2",3"-acetonide	OH

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KEYWORDS
Lasianthus acuminatissimus; anthraquinone; lasianthuoside; acetone extract

1. Introduction

Lasianthus acuminatissimus Merr., a plant of the Rubiaceae family, is used to treat rheumatoid arthritis in traditional Chinese medicine. The research group have made a deep chemical study on the plant previously in which 46 compounds have been isolated and identified from the plant (Li et al. 2006a, 2006b, 2006c, 2007; Huang et al. 2017, 2018a, 2018b). The 46 compounds include eight new anthraquinones, a new furfural glycoside and a new sesquiterpene; among them anthraquinones have been proved to be the bioactive compounds containing anti-inflammatory and anti-tumor activities. In order to find out other bioactive constituents from the plant, the group did the current experimental research in which the acetone extract of the roots was chromatographed. As a result, six new anthraquinone glycosides were isolated and structurally identified, namely lasianthuoside F (1), G (2), H (3), I (4), J (5), K (6).

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2. Results and discussion

Compound **1** was obtained as an orange, amorphous powder. The molecular formula of **1** was deduced as $C_{22}H_{22}O_{10}$ from HR-ESI-MS (*m/z* 469.1107 $[M+Na]^+$, calcd. 469.1111) analysis and its ^1H and ^{13}C-NMR evidence, accounting for 12 indices of hydrogen deficiency. The UV and IR spectrum suggested the presence of a hydroxyanthraquinone. ^1H NMR spectra of **1** showed one isolated aromatic proton at δ_H 7.62 (1H, s, H-4), declaring a penta-substituted aromatic ring which was deduced further from signals in ^{13}C NMR spectra at δ_C 164.4 (C-1), 121.0 (C-2),164.0 (C-3), 107.3 (C-4), 136.3 (C-4a) and 112.9 (C-9a). Four aromatic protons [δ_H 8.26 (1H, dd, $J=7.5$, 2.0 Hz, H-5), 7.86 (1H, br t, $J=7.5$ Hz, H-6), 7.88 (1H, br t, $J=7.5$ Hz, H-7) and 8.32 (1H, dd, $J=7.5$, 2.0 Hz, H-8)] in a symmetrical AA′BB′-type pattern indicated that other aromatic ring in the anthraquinone was unsubstituted. An AB spin system at δ_H 4.71 and 4.74 (each H, d, $J=10.8$ Hz, H-11), a methoxy proton at δ_H 3.40 (s), declaring the existence of a hydroxymethyl and a methoxy. The ^{13}C NMR spectra showed 22 carbon signals, including two carbonyl carbon atoms (δ_C 183.2, 188.8), two benzene rings, a methoxy signals (δ_C58.6) and one hydroxymethyl (δ_C62.6), and a glycosyl section.

The anomeric signals at δ_H 5.20 (1H, d, $J=7.5$ Hz, H-1′) and δ_C 102.0 (C-1′) together with the characteristic signals at δ_C 74.8 (C-2′), 77.9 (C-3′), 71.0 (C-4′), 78.5 (C-5′) and 62.3 (C-6′) were attributed to a glucose group. Acid hydrolysis of **1** afforded a D-glucose, which was determined by GC experiment with an authentic sample. Except for a methoxymethyl signals (δ_H 3.40, 4.74 and 4.71; δ_C 58.6 and 62.6), the left signals at δ_C 188.8 and 183.2 were assigned to two conjugated carbonyl groups. The presence of two carbonyl carbons together with two benzenoid moieties also suggested that**1** was a hydroxyanthraquinone. The aforementioned information suggested that **1** was closely similar to lasianthuoside B (Li et al. 2006c). The only difference between two compounds was a methoxy in lasianthuoside B while a hydroxy in **1** at C-1. The 14 Da difference in molecular weight between them is diagnostic for the current assignment. Furthermore, the HMBC spectrum exhibited correlations from H-11 to C-1 and C-3, which verified that a methoxymethyl group was positioned at C-2. The anomeric proton of glucosyl moiety at δ_H5.20 (1H, d, $J=7.5$ Hz, H-1′) exhibited an HMBC correlation with the aromatic carbon at 164.0 (C-3), confirming that the glucose unit was linked at C-3. All the ^1H and ^{13}C NMR data of **1** were unambiguously assigned by means of the HSQC and HMBC experiments. The glucopyranoside was β-configuration on the ground of the coupling constant of the anomeric proton. Thus, the structure of **1** was established as 1,3-dihydroxy-2-methoxymethylanthraquinone 3-*O*-β-D-glucopyranoside and named lasianthuoside F.

Compound **2** was isolated as a yellow powder. Its molecular formula $C_{23}H_{24}O_{11}$ was deduced from the HR-ESI-MS pseudo-molecular ion at *m/z* 499.1209 ($[M+Na]^+$, calcd. 499.1216). The UV and IR spectrum suggested the presence of a hydroxyanthraquinone. The ^1H NMR showed four aromatic protons at δ_H7.87 (1H, s, H-4), 7.73 (1H, br d, $J=7.5$ Hz, H-5), 7.67 (1H, dd, $J=8.3$, 7.5 Hz, H-6) and 7.30 (1H, br d, $J=8.3$ Hz, H-7), indicating the existence of a 1,2,3-trisubstituted aromatic ring and an unsubstituted aromatic of the hydroxyanthraquinone. The ^1H and ^{13}C NMR spectra of **2** exhibited resonances also similar to those of lasianthuoside B (Li et al. 2006c). Comparing to lasianthuoside B, an additional hydroxy group should be substituted at C-8 in **2**, which

was supported by the HMBC correlations from H-4 and H-5 to C-10 both, declaring there was no group substituted at C-5. The 16 Da difference in molecular weight between them is diagnostic for the current assignment. Therefore, the structure of this new anthraquinone glycoside was established as 3,8-dihydroxy-1-methyoxy-2-methoxymethylanthraquinone3-*O*-β-D-glucopyranoside and named lasianthuoside G.

Compound **3** was obtained as a yellow gum. The molecular formula of **3** was determined to be $C_{27}H_{30}O_{14}$ by HR-ESI-MS at *m/z* 601.1523 $[M+Na]^+$ (calcd. 601.1533). The UV and IR spectrum suggested the presence of an anthraquinone. ^{1}H NMR spectra of **3** showed an isolated aromatic proton at δ_H 7.62 (1H, s, H-4), four aromatic protons [δ_H 8.26 (1H, br d, $J = 7.6$ Hz, H-5), 7.86 (1H, m, H-6), 7.87 (1H, m, H-7) and 8.31 (1H, br d, $J = 7.6$ Hz, H-8)] in a symmetrical AA′BB′-type pattern indicated that one aromatic ring in the anthraquinone was unsubstituted and the other ring was trisubstituted. A methoxy proton at δ_H 3.40 (3H, s) and a hydroxymethyl proton at δ_H 4.71 and 4.74 (each H, d, $J = 10.9$ Hz, H-11), declaring the existence of a hydroxymethyl and a methoxy. The ^{13}C NMR spectra showed 27 carbon signals including two carbonyl carbon atoms (δ_C 183.2, 188.8), two benzene rings, a methoxy signals (δ_C 58.5) and one hydroxymethyl (δ_C 62.6), and two glycosyl sections, which also verified the existence of a hydroxyanthraquinone.

The NMR data of compound **3** were found to be similar to those of compound **1**. Except for, the MS fragmentation pattern and the NMR spectra of **3** were more complex and showed the presence of a series of additional signals at δ_H 4.92, 3.93, 3.76, 4.02, 3.65 and 3.68 in the ^{1}H NMR spectrum and δ_C 111.1, 78.3, 80.7, 75.2, 66.2 in ^{13}C NMR signals, which may be contributed to be a pentose moiety. And the pentose was elucidated as an apiofuranose based on the characteristic chemical shifts, which were fully assigned by the HSQC and HMBC spectra data and the literature data (Huang et al. 2018a). Acid hydrolysis of **3** also afforded a D-glucose and a D-apiose, which was determined by GC with an authentic sample. The configuration of the glycosidic linkage of D-glucose was β on the base of the coupling constant of the anomeric proton at δ_H 5.15 (1H, d, 7.6). The apiose anomeric proton at δ_H 4.92 (1H, d, $J = 1.7$ Hz, H-1″) was identified *via* its HMBC correlation to an oxygenated methylene carbon at δ_C 68.6 (Glc C-6, Supplemental Figure S1), indicated the presence of a β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl moiety. Thus, the structure of compound **3** was established as 1, 3-dihydroxy-2-Methoxymethylanthraquinone-3-O-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, named lasianthuoside H.

Compound **4** was obtained as a yellow gum. The HR-ESI-MS of compound **4** exhibited a pseudo-molecular ion peak at *m/z* 655.1988 $[M+Na]^+$ (calcd. 655.2003), which was consistent with the molecular formula $C_{31}H_{36}O_{14}$, indicating 14 degrees of unsaturation. The UV and IR spectrum suggested the presence of an anthraquinone. ^{1}H NMR spectra of **4** showed one isolated aromatic proton at δ_H 7.81 (1H, s, H-4), declaring a penta-substituted aromatic ring, four aromatic protons [δ_H 8.20 (1H, br d, $J = 7.6$,H-5), 7.78 (1H, br d, $J = 7.6$ Hz, H-6), 7.83 (1H, br d, $J = 7.6$ Hz, H-7) and 8.22 (1H, br d, $J = 7.6$ Hz, H-8)] in a symmetrical AA′BB′-type pattern indicating the other aromatic ring was unsubstituted in the anthraquinone. Two methoxy protons at δ_H3.94 (s), 3.41 (s), a hydroxymethyl proton at δ_H 4.69 and 4.71 (each H, d, $J = 10.4$ Hz, H-12) declaring the existence of two methoxy and a hydroxymethyl. The ^{13}C NMR spectra

showed 31 carbon signals including two carbonyl carbon atoms (δ_C 182.6, 183.8), two benzene rings, two methoxy signals (δ_C63.7, 58.6) and a hydroxymethyl (δ_C 63.5), and two glycosyl sections.

The ^{1}H and ^{13}C NMR data of **4** assigned with the help of its HSQC spectrum suggesting that it was also an anthraquinone glycoside similar to compound **3**. Compared to the spectra of **3**, an additional methoxy signal at δ_H 3.94 (3H, s) and δ_C 63.7, as well as an isopropyl group at δ_H 1.12 (3H, s), 0.88 (3H, s) and δ_C113.9, 27.8 and 27.4 were observed, this was confirmed by the HMBC correlations from the two methyl proton signals to the ketal carbon at δ_C 113.9. The attachment of the isopropyl group was determined to be at C-2″ and C-3″ by the evidence that in ^{13}C NMR spectrum these two carbons obviously downfield shifted (δ_C 87.2 and 93.9) and the presence of an HMBC correlation (Supplemental Figure S1) from the proton δ_H 4.23 (1H, br s, H-2″) to C-1‴at δ_C 113.9 in **4**. Furthermore, a methoxy signal at δ_H 3.94 (3H, s) showed HMBC correlation with C-1 (δ_C163.4), indicating the placement of this group was at C-1. According to the above analysis, compound **4** was established as 3-hydroxy-1-methoxy-2-methoxymethylanthraquinone- 2″, 3″-isopropyl- 3-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, and named as lasianthuoside I.

Compound **5** was also obtained as an orange, amorphous powder. The positive HR-ESI-MS (*m/z* 671.1950, $[M+Na]^+$, calcd. for $C_{31}H_{36}O_{15}Na$, 671.1952) gave the molecular formula as $C_{31}H_{36}O_{15}$, consistent with the complete assignments of ^{1}H and ^{13}C NMR data determined through HSQC and HMBC experiments. The UV and IR spectrum suggested the presence of a hydroxyanthraquinone. The ^{1}H NMR showed four aromatic protons at δ_H 7.78 (1H, s, H-4), 7.70 (1H, br d, $J=7.5$ Hz, H-5), 7.63 (1H, dd, $J=8.3$, 7.5 Hz, H-6), and 7.26 (1H, br d, $J=8.3$ Hz, H-7), indicating that a 1,2,3-trisubstituted aromatic ring and an unsubstituted aromatic ring in the hydroxyanthraquinone. Protons at δ_H 3.95 (s), 3.42 (s) and δ_H 4.67, 4.69 (each H, d, $J=10.4$ Hz, H-12) declared the existence of two methoxy groups and a hydroxymethyl, respectively. The ^{13}C NMR spectrum supported by DEPT experiment revealing 31 carbons, included 11 methines containing seven oxygenated carbons, four oxygenated methylenes, two methyls, two methoxy groups, and 12 quaternary carbons consisting of two conjugated carbonyl groups at δ_C 188.9 (C-9), 183.1 (C-10), and two glycosyl sections. Proton signals at δ_H 1.15(3H, s), 0.88(3H, s) and carbon signals at δ_C 113.9, 27.8, 27.4, declaring an isopropyl group.

Comparison with the NMR data of **4** suggested that structure of compound **5** was quite similar to that of **4**, except for, there was an unsubstituted ring appearance in compound **4**, while there was an additional hydroxy appearance in **5**. In the HMBC spectrum, the protons at δ_H 7.78 (1H, s, H-4) and 7.70 (1H, br d, $J=7.5$ Hz, H-5) were associated with δ_C 183.1 (C-10), confirming that a hydroxy group should be substituted at C-8. Accordingly, the structure of **5** was established as 3, 8- dihydroxy-1-methoxy-2-methoxymethylanthraquinone-2″, 3″-isopropyl-3-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, named lasianthuoside J.

Compound **6** was isolated as a yellow powder. The HR-ESI-MS of **6** showed a molecular ion peak at *m/z* 657.1782 $[M+Na]^+$ (calcd. 657.1795) in accordance with a molecular formula of $C_{30}H_{34}O_{15}$. The ^{1}H NMR showed four aromatic protons at δ_H 7.69 (1H, s, H-4), 7.61 (1H, br d, $J=7.0$ Hz), 7.70 (1H, dd, $J=7.6$, 7.0 Hz) and 7.31 (1H, br d,

$J = 7.6$ Hz), indicating that one aromatic ring was trisubstituted and the other aromatic ring was three unsubstituted. Proton signals at δ_H 3.88 (3H, s) and δ_H 4.67, 4.69 (each H, d, $J = 10.4$ Hz, H-12) declared the existence of a methoxy and a hydroxymethyl, respectively. The ^{13}C NMR spectrum showed 30 carbon signals including two carbonyl carbon atoms (δ_C 186.8, 181.5), two benzene rings, one methoxy(δ_C 62.8) and one hydroxymethyl (δ_C51.8), these signals further indicated the presence of a hydroxyanthraquinone containing a methoxy, a hydroxymethyl and two phenolic hydroxyls. Proton signals at δ_H 1.13(3H, s), 0.98(3H, s) and Carbon signals at δ_C 111.7, 27.4, 26.9, declaring the existence of an isopropyl group.

The NMR spectroscopic data of **6** were very similar to those of **5** although measured in different solvents. The only difference was that a methoxy signal (δ_H 3.42, δ_C 58.7 in **5**) disappeared in **6**, suggesting that in compound **6** a hydroxymethyl was replaced from a methoxymethyl moiety in **5**. The hydroxymethyl carbon signal shifted obviously upfield approximately 11 ppm, also indicated of the absence of the methoxy group. Thus, the structure of compound **6** was established as 3, 8- dihydroxy-1-methoxy-2-hydroxymethylanthraquinone-2″, 3″-isopropyl-3-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, namely lasianthuoside K.

3. Experimental

3.1. General procedures

The optical rotations were taken with a MCP 500 high precision digital rotation. The UV spectra were obtained using a Shimadzu UV-2550 spectrophotometer. The IR spectra were measured on a Perkin Elmer Spectrum Two infra-red spectrometer. The NMR spectra were carried out on a Bruker AVANCE III 600 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany). Chemical shifs (δ) were expressed in ppm with reference to the solvent signals. The HR-ESI-MS were recorded on an Agilent 1100 series LC/MSD Triple TOF5600 + spectrometer. The Preparative HPLC was performed on an ODS column (250 mm × 20 mm, i.d., YMC) with a UV detector (Waters 2489). The GC was conducted using an Agilent7890A instrument. Column chromatography was performed with HPD750 macroporous resin (Cangzhou Baoen Absorption Materials Technology Co. Ltd., Hebei, China), silica gel (200–300 mesh, Qingdao Marine Chemical, Inc, Qingdao, China), Sephadex LH-20 (20–100 μM, Pharmacia), and ODS (50 μM, YMC, Japan). TLC was performed with silica gel GF254 (Qingdao Marine Chemical Industry Factory).

3.2. Plant material

The roots of *Lasianthus acuminatissimus* Merr. were collected from Yushan County of Jiangxi Province in China, during September, 2017. The plant material was identified by Professor Yong Liu (Jiangxi University of Traditional Chinese Medicine). It (voucher specimen number 001703) has been deposited in Herbarium of Jiangxi University of Traditional Chinese Medicine.

3.3. Extraction and isolation

Air-dried and powdered roots of the plants (85.0 kg) were refluxed with 95% EtOH three times, and The EtOH extract was concentrated under reduced pressure to yield 895.0 g of the extract. The total extract (895.0 g) was applied on silica gel CC (2700.0 g) eluting with chloroform, ethyl acetate, acetone, n-butanol, and methanol respectively. The acetone fraction (50.0 g) was applied to a HPD 750 chromatography column and eluted successively with a gradient of C_2H_5OH/H_2O. The 50% Ethanol fraction(10 g) was subjected to a Polyamide column chromatography and eluted with C_2H_5OH/H_2O to give 4 fractions (A1–A4). Fraction A1 (3.0 g) was separated by a ODS eluting with $MeOH/H_2O$ to give six subfractions (A1-1–A1-6). Compound **1** (2 mg) and compound **2** (4 mg) were obtained from subfraction A1-2 (110 mg) by preparative HPLC, eluting with 60% Methanol on a YMC-Pack ODS-A column (250 × 20 mm, 5 μm) at a flow rate of 5 mL/min and UV detection at 264 nm. Subfraction A1-5 (500 mg) was further fractionated to a Sephadex LH-20 (Methanol) chromatography to give seven subfractions (A1-5-1–A1-5-7). Subfraction A1-5-3 (280 mg) was purified by a preparative HPLC and eluted with 60% Methanol at a flow rate of 5 mL/min (264 nm) to obtain compound **3** (10.9 mg), **4** (49.5 mg), **5** (30.1 mg), **6** (4 mg).

3.4. Acid hydrolysis and sugar analysis

Compounds **1** (1 mg), **3** (1 mg) were refluxed with 2 mL of 7% HCl for 2 h to obtain a brown material. The residual material was dissolved in 1.0 mL of pyridine (containing 2.5 g/mL hydroxylaminehydrochloride) and 1.0 mL of TMCS and then reacted for 1 h at 80 °C. Then the derivatives were analysed by GC, and the retentiontimes (tR) were as follows: D-apiose(12.03 min), L-apiose(12.45 min), D-glucose (13.62 min) and L-glucose (13.93 min), (Huang et al. 2018a). The monosaccharides obtained from the acid hydrolysis of compounds **1**and **3**were treated in a similar manner to the authentic monosaccharide samples and were identified as D-apiose (12.03 min) and D-glucose (13.62 min), which were matched to the standard D-apiose and D-glucose.

3.4.1. Lasianthurin F (1)

An orange amorphous powder; $[\alpha]_D^{20}$-54.0 (*c*0.001 in MeOH); UV(MeOH) λ_{max}nm: 264; IR(KBr) cm^{-1}:3354, 2920, 1628, 1586, 1482, 1367, 1272; HR-ESI-MS at *m/z* 469.1108$[M+Na]^+$(calcd For $C_{22}H_{22}O_{10}$469.1111). ^1H NMR (600 MHz,CD_3OD) δ_H: 7.62 (1H, s, H-4), 8.26 (1H, dd, $J=7.5$, 2.0 Hz, H-5), 7.86 (1H, brt, $J=7.5$ Hz, H-6) , 7.88 (1H, brt, $J=7.5$ Hz, H-7),8.32 (1H, dd, $J=7.5$, 2.0 Hz, H-8), 4.71, 4.74 (2H, d, $J=10.8$ Hz, H-11), 3.40 (3H, s, H-11-OMe), 5.20 (1H, d, $J=7.5$ Hz, H-1′), 3.58 (1H, m, H-2′), 3.53 (1H, t, $J=9.1$ Hz, H-3′), 3.47 (1H, t, $J=9.1$ Hz, H-4′), 3.58 (1H, m, H-5′), 3.75, 3.91 (1H, dd, $J=12.3$, 5.2, Hz, H-6′); ^{13}C NMR (150 MHz, CD_3OD) δ_C: 164.4 (C-1), 121.0 (C-2), 164.0 (C-3), 107.3 (C-4), 136.3 (C-4a), 128.2 (C-5), 135.7 (C-6), 135.6 (C-7), 127.9 (C-8), 134.7 (C-8a), 188.8 (C-9), 112.9 (C-9a), 183.2 (C-10), 134.6 (C-10a), 62.6 (C-11), 58.6 (C-11-OMe), 102.0 (C-1′), 74.8 (C-2′), 77.9 (C-3′), 71.0 (C-4′), 78.5 (C-5′), 62.3 (C-6′).

3.4.2. Lasianthurin G (2)

Yellow powder; $[\alpha]_D^{20}$-141.6 (*c* 0.001 in MeOH); UV (MeOH) λ_{max} nm:267; IR (KBr) cm^{-1}:3379, 1666, 1578, 1475, 1347, 1275; HR-ESI-MS at *m/z* 499.1209 $[M+Na]^+$(calcd For $C_{23}H_{24}O_{11}$499.1216). ^1H NMR (600 MHz,CD_3OD) δ_H: 7.87 (1H, s, H-4), 7.73 (1H, brd, $J=7.5$ Hz, H-5), 7.67 (1H, dd, $J=8.3$, 7.5 Hz, H-6) , 7.30 (1H, brd, $J=8.3$ Hz, H-7), 4.68, 4.70 (2H, d, $J=10.2$ Hz, H-11), 3.96 (3H, s, H-1-OMe), 3.42 (3H, s, H-11-OMe), 5.21 (1H, d, $J=7.5$ Hz, H-1′), 3.58 (1H, m, H-2′), 3.53 (1H, t, $J=9.1$ Hz, H-3′), 3.47 (1H, t, $J=9.1$ Hz, H-4′), 3.58 (1H, m, H-5′), 3.75, 3.91 (1H, dd, $J=12.3$, 5.2 Hz, H-6′); ^{13}C NMR (150 MHz, CD_3OD) δ_C: 163.8 (C-1), 129.5 (C-2), 163.2 (C-3),110.7 (C-4), 138.2 (C-4a),119.9 (C-5), 137.1 (C-6), 125.7 (C-7), 163.6 (C-8), 118.0 (C-8a), 188.8 (C-9), 121.5 (C-9a), 183.2 (C-10), 134.1 (C-10a), 63.6 (C-11), 63.9 (C-1-OMe), 58.8 (C-11-OMe), 102.1 (C-1′), 74.8 (C-2′), 77.9 (C-3′), 71.0 (C-4′), 78.5 (C-5′), 62.3 (C-6′).

3.4.3. Lasianthurin H (3)

Yellow gum; $[\alpha]_D^{20}$-86.9 (*c*0.002in MeOH); UV(MeOH) λ_{max} nm: 267; IR(KBr) cm^{-1}: 3356, 2925, 1632, 1589, 1482, 1367, 1297; HR-ESI-MS at *m/z* 601.1523 $[M+Na]^+$ (calcd For $C_{27}H_{30}O_{14}$ 601.1533). ^1H NMR (600 MHz,CD_3OD) δ_H: 7.62 (1H, s, H-4), 8.26 (1H, brd, $J=7.6$ Hz, H-5), 7.86 (1H, m, H-6) , 7.87 (1H, m, H-7), 8.31 (1H, brd, $J=7.6$ Hz, H-8), 4.71, 4.74 (2H, d, $J=10.9$ Hz, H-11), 3.40 (3H, s, H-11-OMe), 5.15 (1H, d, $J=7.6$ Hz, H-1′), 3.57 (1H, m, H-2′), 3.52 (1H, t, $J=9.2$ Hz, H-3′), 3.37 (1H, t, $J=9.2$ Hz, H-4′), 3.73 (1H, m, H-5′), 3.59, 4.06 (1H, dd, $J=11.2$, 6.9 Hz, H-6′), 4.92 (1H, d, $J=1.7$ Hz, H-1″), 3.93 (1H, d, $J=1.7$ Hz, H-2″), 3.76, 4.02 (1H, d, $J=9.7$ Hz,H-4″), 3.65, 3.68 (2H, d, $J=11.5$ Hz, H-5″);^{13}C NMR (150 MHz, CD_3OD) δ_C: 164.4 (C-1), 121.0 (C-2), 164.0 (C-3), 107.5 (C-4), 136.3 (C-4a), 127.8 (C-5), 135.6 (C-6), 135.7 (C-7), 128.3 (C-8), 134.7 (C-8a), 188.8 (C-9),113.0 (C-9a), 183.3 (C-10), 134.6 (C-10a), 62.6 (C-11), 58.5 (C-11-OMe), 101.9 (C-1′), 74.8 (C-2′), 77.9 (C-3′), 71.5 (C-4′), 77.5 (C-5′), 68.6 (C-6′), 111.1 (C-1″), 78.3 (C-2″), 80.7 (C-3″), 75.2 (C-4″), 66.2 (C-5″).

3.4.4. Lasianthurin I (4)

Yellow gum; $[\alpha]_D^{20}$-129.4 (*c*0.001 in MeOH); UV(MeOH) λ_{max} nm: 267; IR(KBr) cm^{-1}:3419, 1668, 1575, 1455, 1311,1282; HR-ESI-MS at *m/z* 655.1991 $[M+Na]^+$ (calcd For $C_{31}H_{36}O_{14}$ 655.2003).^1H NMR (600 MHz,CD_3OD) δ_H: 7.81 (1H, s, H-4), 8.20 (1H, brd, $J=7.6$ Hz, H-5), 7.78 (1H, brt, $J=7.6$ Hz, H-6) , 7.83 (1H, brt, $J=7.6$ Hz, H-7), 8.22 (1H, brd, $J=7.6$, Hz, H-8), 4.69, 4.71 (2H, d, $J=10.4$ Hz, H-11), 3.94 (3H, s, H-1-OMe), 3.41 (3H, s, H-11-OMe), 5.24 (1H, d, $J=7.5$ Hz, H-1′), 3.58 (1H, m, H-2′), 3.54 (1H, t, $J=9.2$ Hz, H-3′), 3.28 (1H, t, $J=9.2$ Hz, H-4′), 3.77 (1H, m, H-5′), 3.57, 3.96 (1H, brd, $J=12.0$ Hz, H-6′), 4.91 (1H, brs, H-1″), 4.23 (1H, brs, H-2″), 3.76, 3.83 (1H, d, $J=10.0$ Hz, H-4″), 3.72 (2H, s, H-5″), 1.12 (3H, s, H-2‴), 0.88 (3H, s, H-3‴); ^{13}C NMR (150 MHz, CD_3OD) δ_C: 163.4 (C-1), 128.9 (C-2),162.1 (C-3), 110.1 (C-4), 138.3 (C-4a), 127.8 (C-5), 134.6 (C-6), 135.6 (C-7), 128.0 (C-8), 136.1 (C-8a), 182.6 (C-9), 121.8 (C-9a), 183.8 (C-10), 134.0 (C-10a), 63.5 (C-11), 63.7 (C-1-OMe), 58.6 (C-11-OMe), 101.0 (C-1′), 74.7 (C-2′), 77.9 (C-3′), 71.9 (C-4′), 78.5 (C-5′), 66.9 (C-6′), 108.9 (C-1″), 87.2 (C-2″), 93.9 (C-3″), 75.3 (C-4″), 65.7 (C-5″), 113.9 (C-1‴), 27.8 (C-2‴), 27.4 (C-3‴).

3.4.5. Lasianthurin J (5)

An orange amorphous powder; $[\alpha]_D^{20}$-126.7 (*c* 0.006 in MeOH); UV(MeOH) λ_{max}nm: 264; IR (KBr) cm^{-1}: 3565, 2987,1671, 1579, 1455,1308, 1233; HR-ESI-MS at *m/z* 671.1952 $[M+Na]^+$ (calcd For $C_{31}H_{36}O_{15}Na$ 671.1952). ^1H NMR (600 MHz,CD_3OD) δ_H: 7.78 (1H, s, H-4), 7.70 (1H, brd, $J=7.5$ Hz, H-5), 7.63 (1H, dd, $J=8.3$, 7.5 Hz, H-6) , 7.26 (1H, brd, $J=8.3$ Hz, H-7), 4.67, 4.69 (2H, d, $J=10.4$ Hz, H-11), 3.95 (3H, s, H-1-OMe), 3.42 (3H, s, H-11-OMe), 5.23 (1H, d, $J=7.5$ Hz, H-1′), 3.59 (1H, m, H-2′), 3.54 (1H, t, $J=9.2$ Hz, H-3′), 3.28 (1H, t, $J=9.2$ Hz, H-4′), 3.76 (1H, m, H-5′), 3.57, 3.96 (1H, dd, $J=11.8$, 1.7 Hz, H-6′), 4.90 (1H, brs, H-1″), 4.22 (1H, brs, H-2″), 3.76, 3.83 (1H, d, $J=10.0$ Hz, H-4″), 3.72 (2H, s, H-5″), 1.15 (3H, s, H-2‴), 0.95 (3H, s, H-3‴); ^{13}C NMR (150 MHz, CD_3OD) δ_C: 163.8 (C-1), 129.3 (C-2), 162.7 (C-3), 110.4 (C-4), 138.3 (C-4a), 119.9 (C-5), 137.1 (C-6), 125.6 (C-7), 163.6 (C-8), 118.0 (C-8a),188.9 (C-9),121.3 (C-9a), 183.1 (C-10), 134.2 (C-10a), 63.5 (C-11), 63.9 (C-1-OMe), 58.7 (C-11-OMe), 101.0 (C-1′), 74.7 (C-2′), 77.9 (C-3′), 71.8 (C-4′), 78.4 (C-5′),66.9 (C-6′), 108.9 (C-1″), 87.2 (C-2″), 93.9 (C-3″), 75.3 (C-4″), 65.8 (C-5″), 113.9 (C-1‴), 27.8 (C-2‴), 27.4 (C-3‴).

3.4.6. Lasianthurin K (6)

Yellow powder; $[\alpha]_D^{20}$-78.4 (*c* 0.001 in MeOH); UV(MeOH)λ_{max} nm: 264; IR(KBr) cm^{-1}: 3355, 2920,1632, 1578, 1455, 1308, 1233; HR-ESI-MS at *m/z* 657.1779 $[M+Na]^+$ (calcd For $C_{30}H_{34}O_{15}$ 657.1795). ^1H NMR (600 MHz,DMSO-d_6) δ_H: 7.69 (1H, s, H-4), 7.61 (1H, brd, $J=7.0$ Hz, H-5), 7.70 (1H, dd, $J=7.6$, 7.0 Hz, H-6) , 7.31 (1H, brd, $J=7.6$ Hz, H-7),4.58, 4.64 (2H, brd, $J=11.0$ Hz, H-11), 3.88 (3H, s, H-1-OMe), 5.15 (1H, d, $J=7.2$ Hz, H-1′), 3.40 (1H, dd, $J=9.2$, 7.2 Hz, H-2′), 3.37 (1H, t, $J=9.2$ Hz, H-3′), 3.11 (1H, t, $J=9.2$ Hz, H-4′), 3.64 (1H, br dd, $J=9.2$, 8.1 Hz, H-5′), 3.45, 3.83 (1H, dd, $J=11.8$, 8.1 Hz, H-6′), 4.88 (1H, brs, H-1″), 4.18 (1H, brs, H-2″), 3.69, 3.76 (1H, d, $J=10.0$ Hz, H-4″), 3.58 (2H, s, H-5″), 1.13 (3H, s, H-2‴), 0.98 (3H, s, H-3‴); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 161.1 (C-1), 131.5 (C-2), 160.8 (C-3), 108.9 (C-4), 135.8 (C-4a), 117.8 (C-5), 135.9 (C-6), 124.9 (C-7), 162.2 (C-8), 116.8 (C-8a), 186.8 (C-9), 120.0 (C-9a), 181.5 (C-10), 132.7 (C-10a), 51.8 (C-11), 62.8 (C-1-OMe), 100.0 (C-1′), 73.1 (C-2′), 75.8 (C-3′), 70.1 (C-4′), 76.6 (C-5′), 65.9 (C-6′), 107.0 (C-1″), 85.3 (C-2″), 92.5 (C-3″), 73.8 (C-4″), 63.8 (C-5″), 111.7 (C-1‴), 27.4 (C-2‴), 26.9 (C-3‴).

4. Conclusions

From an aqueous extract of *Lasianthus acuminatissimus* Merr., six new anthraquinones named lasianthurin F (1), G (2), H (3), I (4), J (5), K (6) were isolated and their structures were elucidated on the basis of the spectroscopic evidence.

Disclosure statement

No potential conflict of interest was reported by the authors.

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