A Novel Phenylethanoid Dimer and Flavonoids from *Jacaranda mimosaefolia*

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A novel phenylethanoid dimer, namely, jacraninoside A (**1**) and the five known constituents *E/Z*-acetoside (**2**), isoacetoside (**3**), cistanoside E (**4**), 6′-acetylacetoside (**5**), and campneoside I (**6**) together with the seven flavonoids isoquercitrin (**7**), scutellarein 7-*O*-β-D-glucuronopyranoside methyl ester (**8**), apigenin 7-*O*-β-D-galacturonopyranoside (**9**), luteolin 7-*O*-β-D-glucuronopyranoside methyl ester (**10**), apigenin 7-*O*-β-D-glucuronopyranoside methyl ester (**11**), luteolin 7-*O*-β-D-glucopyranoside (**12**), and isovitexin (**13**) were isolated from the aqueous methanol extract of *Jacaranda mimosaefolia* D. Don. leaves. All known metabolites have been identified in this genus for the first time except for **2** and **12** which had been isolated once before from the leaves and twigs of *Jacaranda mimosaefolia*. Their structures were elucidated based on chemical evidences and spectroscopic analyses (1D and 2D NMR, HRMS ((–)-ESI)/MS, UV).

Key words: Jacaranda mimosaefolia, Bignoniaceae, Leaves, Acetocide Dimer, Flavone and Flavonol Glycosides

Introduction

The genus *Jacaranda* (Bignoniaceae) is widely distributed in tropical and subtropical areas of the world. *J. mimosaefolia* is native to Brazil and cultivated in Egypt as an ornamental tree. Some species are used in traditional medicine of different countries to cure wounds, ulcers, and as astringent in diarrhea and dysentery [1, 2]. In the previous studies, jacaranone, scutellarein 7-glucuronide [3], verbascoside, phenylacetic β-glucoside, and jacaranose [1] were isolated from the leaves of *J. mimosaefolia*, while 1-hydroxy-4-oxo-2,5-cyclohexadien-1-acetate ethyl ester was isolated from its fruits [3]. In addition, delphinidin 3,5-diglucoside, delphinidin 3-glucoside, apigenin 7-*O*-neohesperidoside and apigenin 7-glucoside were isolated from the flowers of *J. mimosaefolia* and *J. acutifolia* [4]. Also, apigen and its 7-*O*-glucoside and luteolin 7-*O*-glucoside were isolated from *J. mimosaefolia* twigs [2]. The present paper aimed at the isolation of further phenylethanoids with new structural features [5].

Experimental

General

The NMR spectra were recorded at 300, 500 (^{1}H) and 75, 125 (^{13}C) MHz, on Varian Mercury 300 and JEOL-500 NMR spectrometers in [D_6]DMSO or [D_4]MeOH. The δ values are reported in ppm relative to TMS and J values in Hz. HRMS ((–)-ESI) analyses were run on a LTQ-FT-MS spectrometer (Thermo Electron, ISAS-Institute, 44139 Dortmund, Germany). UV/vis analysis of pure isolates was conducted on a Shimadzu UV 240 (P/N 204-58000) spectrophotometer with methanol solutions and with different diagnostic UV shift reagents in case of the flavonoids [6].

Plant material

Leaves of *J. mimosaefolia* D. Don. (Syn. *J. ovalifolia* R. Br.) [3] were collected in May 2004 from the Botanical Garden, Helwan University, Egypt. The identification of the plant was performed by Dr. Wafaa M. Amer, Ass. Prof. of Botany, Botany Dept., Faculty of Science, Cairo University, Giza, Egypt. A voucher sample (J-21) is kept in the Herbarium, Pharmacognosy Department, Faculty of Pharmacy, Helwan University, Egypt.

Table 1. ^{1}H, ^{13}C and HMQC (^2J, ^3J) data of aglycone and caffeoyl moieties in **1**.

No	Monomer A			Monomer B		
	δ_C	δ_H (m, *J* Hz)	HMBC cross peaks	δ_C	δ_H (m, *J* Hz)	HMBC cross peaks
	Aglycone moiety			Aglycone moiety		
1	130.21	–		121.90	–	
2	115.79	6.65 (br s)	C-1, 3, 4, 6, 7	115.72	6.71 (s)	C-1, 3, 4, 6, 7
3	145.50	–		144.77	–	
4	143.31	–		148.23	–	
5	114.97	6.62 (d, *J* = 8.4)	C-1, 3, 4, 6	112.90	7.04 (s)	C-1, 3, 4, 6
6	119.96	6.53 (dd, *J* = 8.4, 2.1)	C-1, 2, 4, 5, 7	151.50	–	
CH_2-7	35.36	2.76 (m)[a]	C-1, 2, 6, 8	35.22	2.76 (m)[a]	C-1, 2, 6, 8
CH_2-8	70.66	3.93, 3.90 (m)[a]	C-1, 7, 1′	70.89	3.93, 3.90 (m)[a]	C-1, 7, 1′
	Caffeoyl moiety			Caffeoyl moiety		
1‴	126.29	–		126.29	–	
2‴	113.80	7.02 (br s)[a]	C-1‴, 3‴, 4‴, 6‴, 7‴	113.86	7.02 (br s)[a]	C-1‴, 3‴, 4‴, 6‴, 7‴
3‴	145.95	–		145.95	–	
4‴	148.46	–		148.46	–	
5‴	115.19	6.76 (d, *J* = 8.4)[a]	C-1‴, 3‴, 4‴, 6‴	115.19	6.76 (d, *J* = 8.4)[a]	C-1‴, 3‴, 4‴, 6‴
6‴	121.98	6.94 (br d, *J* = 7.6)[a]	C-1‴, 2‴, 4‴, 5‴, 7‴	121.98	6.94 (br d, *J* = 7.6)[a]	C-1‴, 2‴, 4‴, 5‴, 7‴
7‴	146.74	7.57 (d, *J* = 16.1)[a]	C-1‴, 2‴, 6‴, 8‴, 9‴	146.74	7.57 (d, *J* = 16.1)[a]	C-1‴, 2‴, 6‴, 8‴, 9‴
8‴	113.01	6.26 (d, *J* = 16.1)[b]	C-1‴, 7‴, 9‴	113.05	6.27 (d, *J* = 16.1)[b]	C-1‴, 7‴, 9‴
9‴	167.01	–		167.01	–	

[a] Signals are centred at the same δ values; [b] signals with exchangeable δ values.

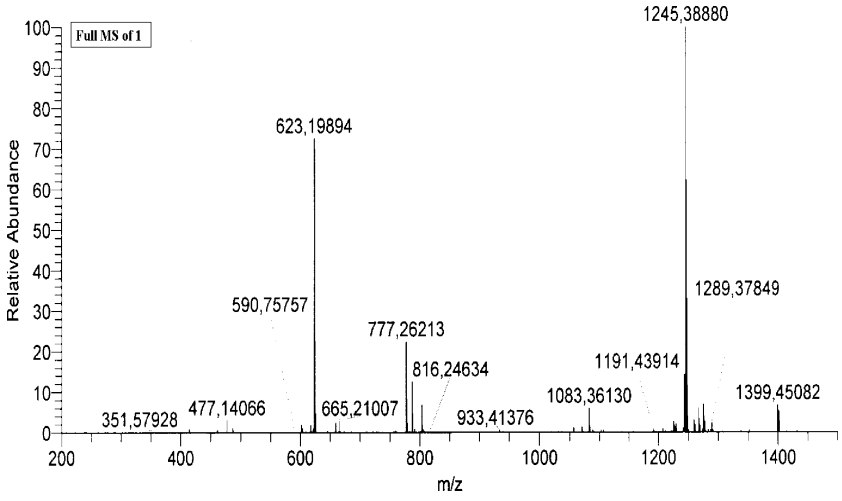
Table 2. ^{1}H, ^{13}C and HMQC (^2J, ^3J) data of rhamnosylglucoside moieties in **1**.

No	Monomer A			Monomer B		
	δ_C	δ_H (m, *J* Hz)	HMBC cross peaks	δ_C	δ_H (m, *J* Hz)	HMBC cross peaks
	Glucopyranoside moiety			Aglycone moiety		
1′	102.84	4.35 (d, *J* = 7.6)[b]	C-2′, 3′, 5′, 8	102.46	4.36 (d, *J* = 7.6)[b]	C-2′, 3′, 5′, 8
2′	74.41	–[c]		74.10	–[c]	
3′	80.40	–[c]		80.40	–[c]	
4′	69.12	4.90 (t-like hidden by [D_4]MeOH signal)[a]	C-2′, 3′, 5′, 9‴	69.12	4.90 (t-like hidden by [D_4]MeOH signal)[a]	C-2′, 3′, 5′, 9‴
5′	74.85	–[c]		74.65	–[c]	
6′	61.00	–[c]		61.00	–[c]	
	Rhamnopyranosyl moiety			Caffeoyl moiety		
1″	101.34	5.16 (br s)[a]	C-3′, 2″, 3″, 5″	101.70	5.16 (br s)[a]	C-3′, 2″, 3″, 5″
2″	70.67	–[c]		70.67	–[c]	
3″	70.80	–[c]		70.80	–[c]	
4″	72.40	–[c]		72.40	–[c]	
5″	68.68	–[c]		68.90	–[c]	
6″-CH_3	17.18	1.08 (br d, *J* = 6)[a]	C-4″, 5″	17.18	1.08 (br d, *J* = 6)[a]	C-4″, 5″

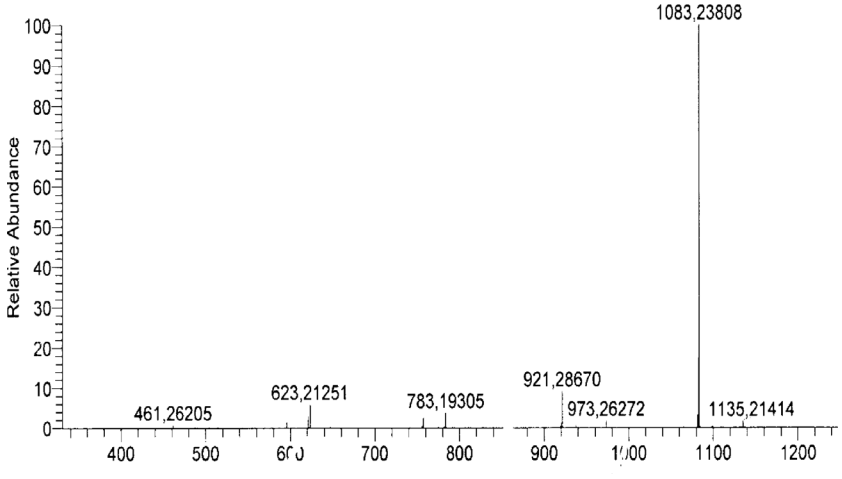
[a] Signals are centred at the same δ values; [b] signals with exchangeable δ values; [c] signals unresolved, m and complex, at δ range of 3.80 – 3.10 ppm.

Extraction and isolation

Air-dried ground leaves (820 g) were extracted with hot 70 % aqueous methanol (4 × 4 L) under reflux (70 °C), then the dry extract was defatted with pet. ether (60 – 80), (5 × 1 L) to afford 107 g dry total extract. Thereafter, it was subjected to a preliminary fractionation on a polyamide S (Flucka) column (C) (300 g, 110 × 10 cm) using a stepwise gradient of H_2O-MeOH 100 : 0 – 0 : 100 for elution to give 40 fractions of 1 L each, which were collected into seven collective fractions (I – VII) monitored by TLC, Comp-PC (systems S_1 and S_2) and UV light detection. Fraction I (4 g) was found to be polyphenolic-free. Fraction II (45 g, 20 – 30 %) was preliminarily separated by desalting with EtOH from its conc. aqueous solution and then taken by EtOAc through liquid-liquid partition from H_2O. Thereafter the residue was subjected to repeated column chromatography (CC) on Sephadex LH-20 (Pharmacia, Uppsala, Sweden) and eluted with MeOH to give pure **2** (32 g) and **3** (0.89 g). Fractionation of fraction III (3 L, 730 mg) on a microcrystalline cellulose (E. Merck, Darmstadt, Germany) column (30 % EtOH, eluent) followed by repeated and separate chromatography on Sephadex C for each of the two major subfractions obtained led to pure **4** (22 mg) and **5** (355 mg). Fraction IV (5.5 L, 3.9 g) was chromatographed on Sephadex C with MeOH for elution to give two major subfractions. The first



1a) MS: 1245.38880 (calcd. 1245.38901 for $C_{58}H_{69}O_{30}$, $[M–H]^-$).

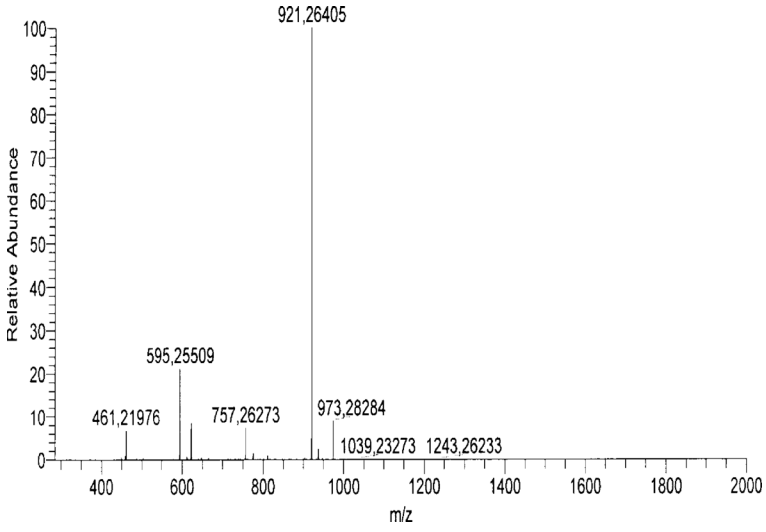


1b) MS^2: 1083.23808 $[M–H–caffeoyl]^-$.

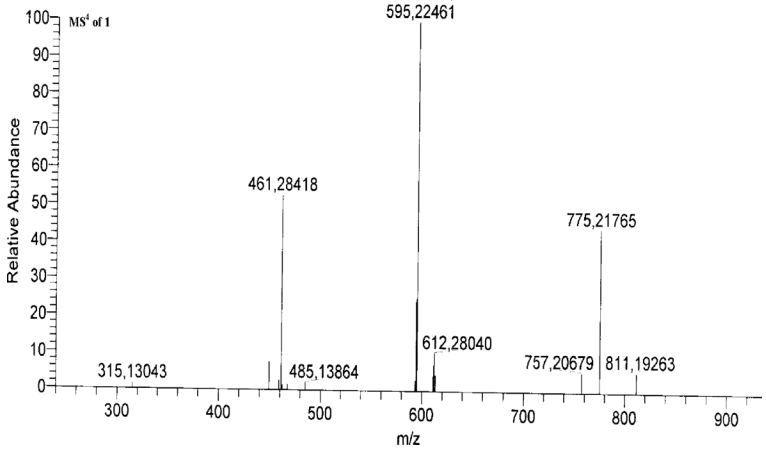
one was applied on cellulose C and eluted with aq. 30 – 50 % MeOH followed by Sephadex C with EtOH for elution to give pure **6** (76 mg) and **7** (31 mg). The second subfraction was applied on Sephadex C with MeOH as an eluent and the major crude product **1** thus obtained was finally purified by precipitation from its conc. aq. solution by excess $CHCl_3$ to give pure **1** (44 mg). Fraction V (3.6 L, 1.7 g) was chromatographed on Sephadex C with 30 – 60 % aq. MeOH to give a crude sample of a major flavonoid, which was then precipitated from its acetone solution to give pure **8** (63 mg). On a cellulose C, fraction VI (5 L, 5.7 g) was separated using aq. 10 – 60 % EtOH to give three main subfractions, each of which was then separately purified on Sephadex C (*n*-BuOH-*i*-PrOH-H_2O BIW, 4 : 1:5, organic layer as an eluent) giving pure **9** (26 mg), **10** (42 mg) and **11** (28 mg). Repeated CC of fraction VII (2.5 L, 2.1 g) on Sephadex twice with BIW followed by MeOH for elution led to pure **12** (43 mg) and **13** (21 mg). The homogeneity of the fractions was tested on Comp-TLC (F_{254} plates 20 × 20 cm, Merck, Darmstadt, Germany, systems S_1, $CHCl_3$-MeOH, 8 : 3), 2D-PC and Comp-PC using Whatmann No. 1 paper (Whatmann ltd., Maidstone, Kent, England, systems S_1 and S_2); S_1: *n*-BuOH-HOAc-H_2O (4 : 1 : 5, top layer) and S_2: 15 % aqueous HOAc. The compounds were visualized by spraying with "naturstoff" (a specific spray reagent for the detection of flavonoids [7], composed of a 1% methanolic solution of diphenylborinic acid ethanol amine complex and a 5 % ethanolic solution of polyethylene glycol 400) and $FeCl_3$ reagents.

*Jacraninoside A (**1**)*

Creamy-white amorphous powder. – R_f = 0.43 (S_1), 0.68 (S_2) on PC. – Blue colour and deep greenish blue fluorescence with $FeCl_3$ and naturstoff spray reagents, respectively. – UV/vis (MeOH): λ_{max} = 219, 302, 328 nm. – ^{1}H NMR (500 MHz, [D_4]MeOH, 25 °C, TMS), ^{13}C NMR (125 MHz, [D_4]MeOH), and HMBC data see Tables 1 and 2. – HRMS ((–)-ESI/MS): *m/z* = 623.19894 $[M–2H]^{2–}$,



1c) MS^3: 921.26405 $[M–H–2caffeoyl]^-$.



1d) MS^4: 775.21765 $[M–H–2caffeoyl–deoxyrhamnosyl]^-$ 595.22461 $[M–H–2caffeoyl–deoxyrhamnosyl–H_2O–deoxyglucosyl]^-$ = A 461.28418 $[A–aglycone\ monomer–H_2O–H_2]^-$.

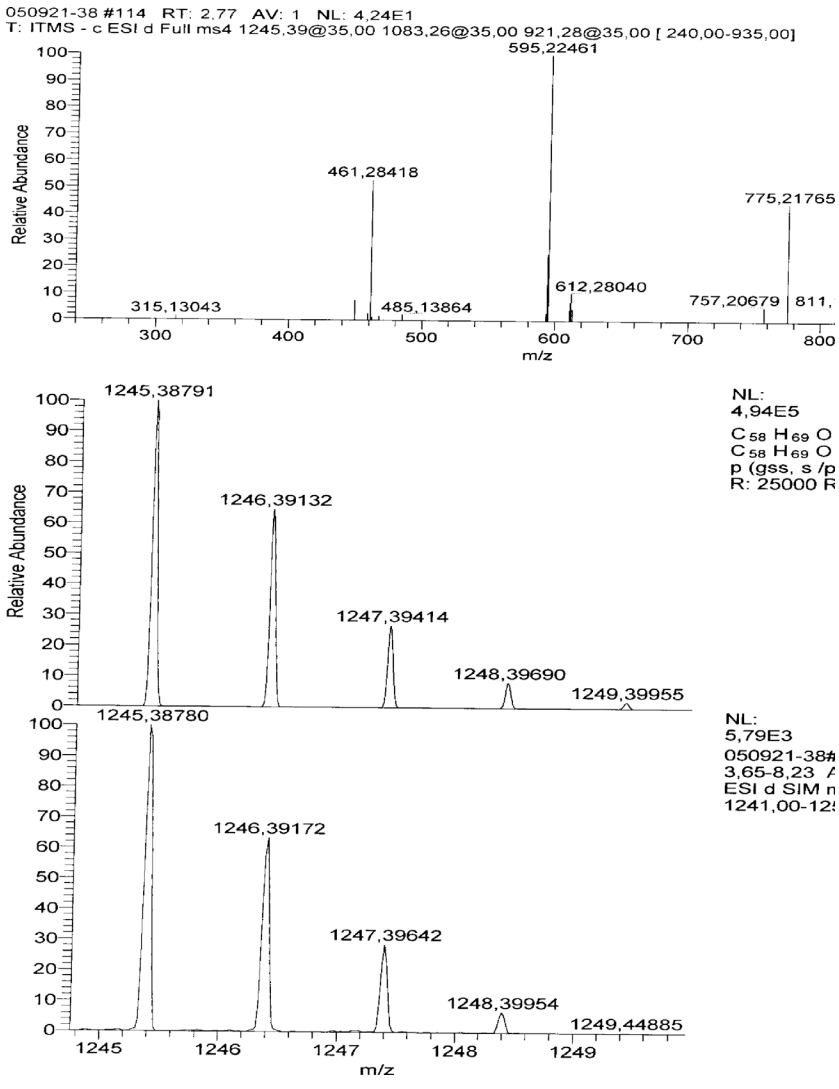
1245.38880 (calcd. 1245.38901 for $C_{58}H_{69}O_{30}$, $[M–H]^-$), MS^2: 1083.23808, MS^3: 921.26405, MS^4: 775.21765, 757.20679, 595.22461, 461.28418, 315.13206, 297.15694, 179.15959, 160.96386, 135.00125. For the assignment of these peaks see Fig. 1 and the discussion below.

Results and Discussion

General

The defatted aqueous methanol extract of *J. memosaefolia* was subjected to sequential column chromatography on polyamide S, microcrystalline cellulose and/or Sephadex LH-20 to yield a novel dimer jacraninoside A (**1**), five known phenylethanoids and seven known flavonoids. The structures of the known compounds were identified by comparative chromatography of their acid hydrolysis products against authentic samples regarding both aglycone (from the organic phase) and sugar moieties (from the aqueous phase). In addition, the structures were confirmed by the assignment of their spectroscopic data [1D and 2D NMR (δ, J values and correlation peaks), HRMS ((–)-ESI)/MS (MWs, MFs) and UV] in comparison to the literature data for *E/Z*-acetoside (**2**), isoacetoside (**3**), cistanoside E (**4**), 6′-acetylacetoside (**5**) and campneoside I (**6**), isoquercitrin (**7**), scutellarein 7-*O*-β-D-glucuronopyranoside methyl ester (**8**), apigenin 7-*O*-β-D-galacturonopyranoside (**9**), luteolin 7-*O*-β-D-glucuronopyranoside methyl ester (**10**), apigenin 7-*O*-β-D-glucuronopyranoside methyl ester (**11**), luteolin 7-*O*-β-D-glucopyranoside (**12**), and isovitexin (**13**) [8 – 13] (Fig. 2).

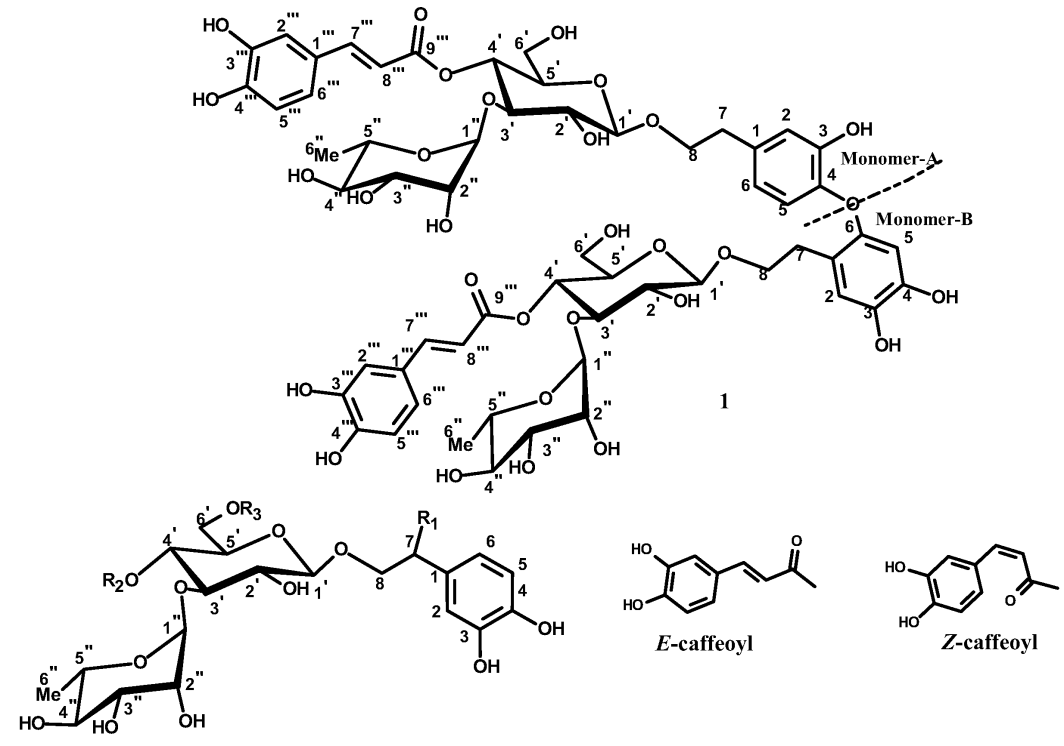
On comparison of its chromatographic behaviour (see Experimental Section) and UV spectral data



1e) $C_{58}H_{69}O_{30}$, $[M–H]^-$

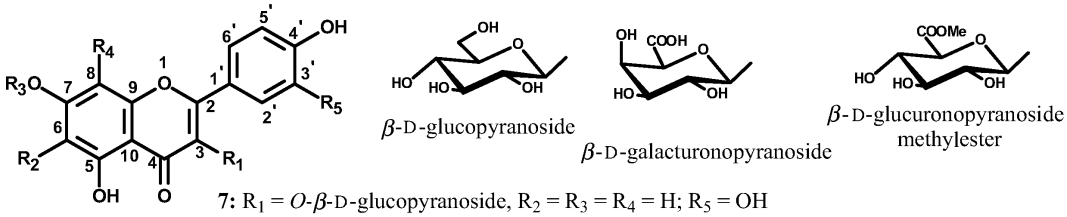
Fig. 1. HR-ESI-MS/MS^4 spectra of jacraninoside A (**1**).

with those of the known acetosides **2** – **6**, **1** was proposed to be an acetoside derivative [9, 12 – 15]. On complete acid hydrolysis, it gave caffeic acid in the organic phase, while D-glucose and L-rhamnose were identified from the aqueous phase as sugar components by GLC analysis of their trimethylsilyl thiazolidine derivatives [16]. The empirical formula was established as $C_{58}H_{70}O_{30}$ on the basis of the complete negative HRMS ((–)-ESI)/MS spectrum (Fig. 1) which showed a doubly charged molecular ion at *m/z* = 623.19894 $[M–2H]^{2-}$, and a molecular ion at 1245.38880 (calcd. 1245.38901 for $C_{58}H_{69}O_{30}$ $[M–H]^-$) diagnostic for an acetoside dimer through an oxidative coupling (loss of H_2, 2 mu). This evidence was further corroborated by a series of informative sequential fragments obtained at 1083.23808 $[M–H–caffeoyl]^-$, MS^3: 921.26405 $[M–H–2caffeoyl]^-$, MS^4: 775.21765 $[M–H–2caffeoyldeoxyrhamnosyl]^-$, 757.20679 $[M–H–2caffeoyl–deoxyrhamnosyl–H_2O]^-$, 595.22461 $[M–H–2caffeoyl–deoxyrhamnosyl–H_2O–deoxyglucosyl]^-$ = A, 461.28418 [A–aglycone monomer–H_2O–H_2]$^-$ = B, 315.13206 [B–deoxyrhamnosyl]$^-$, 297.15694 [B–deoxyrhamnosyl–H_2O]$^-$, 179.15959 [caffeate]$^-$, 160.96386 [caffeate–H_2O]$^-$, 135.00125 [aglycone–H–H_2O]$^-$, which were recorded in the MS^2, MS^3 and MS^4 spectra of the molecular ion at 1245.38880 (Fig. 1). This order of the fragmentation pattern



2: $R_1 = R_3 = H$; R_2 = *Z*- or *E*-caffeoyl **3:** $R_1 = R_2 = H$; R_3 = *E*-caffeoyl **4:** $R_1 = R_2 = R_3 = H$

5: $R_1 = H$; R_2 = *E*-caffeoyl; R_3 = acetyl (CH_3CO-) **6:** $R_1 = -OCH_3$; R_2 = *E*-caffeoyl; $R_3 = H$



7: R_1 = *O*-β-D-glucopyranoside, $R_2 = R_3 = R_4 = H$; $R_5 = OH$

8: $R_1 = R_4 = R_5 = H$; $R_2 = OH$; R_3 = β-D-glucuronopyranoside methylester

9: $R_1 = R_2 = R_4 = R_5 = H$; R_3 = β-D-galacturonopyranoside

10: $R_1 = R_2 = R_4 = H$; R_3 = β-D-glucuronopyranoside methylester; $R_5 = OH$

11: $R_1 = R_2 = R_4 = R_5 = H$; R_3 = β-D-glucuronopyranosidelmethylester

12: $R_1 = R_2 = R_4 = H$; R_3 = β-D-glucopyranoside; $R_5 = OH$

13: $R_1 = R_3 = R_4 = R_5 = H$; R_2 = *C*-β-D-glucopyranoside; $R_5 = OH$

Fig. 2. Structural formulae of the isolated compounds **1** – **13**. (The two monomeric units of jacraninoside A (**1**), referred to in the text and in the atom designators, are arbitrarily labelled A and B as shown below).

was a strong evidence for a dimeric acetoside structure formed by an ether linkage through dehydrogenation.

The ^{1}H NMR spectrum of **1** showed two overlapping ABX and two AX spin-spin coupling systems typical for 1,3,4-trisubstituted phenyl and *E*-olefinic protons of two caffeoyl esters, respectively, having very similar chemical and magnetic environments (see Table 1) [17]. Also, a third ABX system was assigned in the aromatic region at δ = 6.65 (br s, 1H, 2A-H), 6.62 (d, J = 8.4 Hz, 5A-H), 6.53 (dd, J = 8.4, 2.1 Hz, 6A-H), and two singlets at δ = 7.04 (1H, 5B-H) and

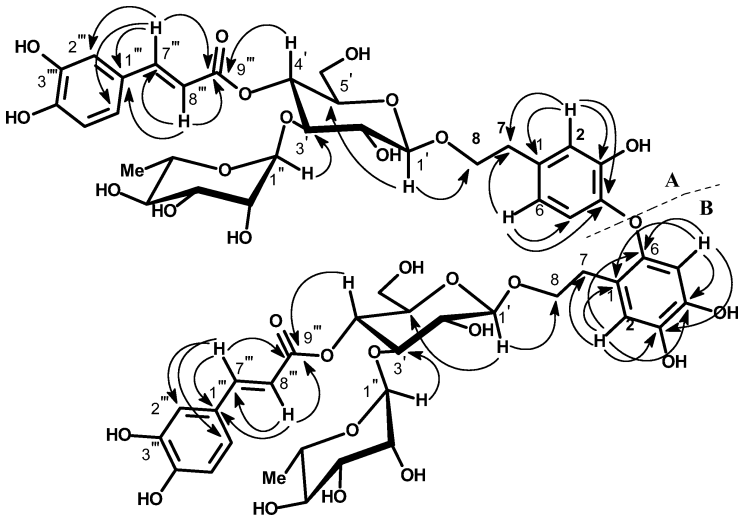


Fig. 3. Significant ^2J and ^3J HMBC correlations of jacraninoside A (**1**).

6.71 (1H, 2B-H) were attributed together with the two pairs of methylene protons at δ = 3.93, 3.90 (m, 2H each, 8A-, 8B-H) and 2.76 (m, 4H, 7A-, 7B-H) to two 3,4-dihydroxyphenylethanoid aglycones connected through an oxidative coupling between 4A-OH and 6B-H. This structural feature was deduced on the basis of the disappearance of a 6B-H aglycone and the appearance of both 2B-H and 5B-H units as two singlets instead of *meta* and *ortho* doublets, respectively, taken as those corresponding in the aglycone moiety of monomer A (Fig. 2). In the aliphatic region, four anomeric resonances were indicative of two α-L-rhamnosyl-(1→3)-β-D-glucoside residues in the structure of **1** [δ = 5.16 (br s, 2H, 2 × 1″rh-Hα), 4.36, 4.35 (d, J = 7.6 Hz, 1H each, 2 × 1′gl-Hβ)] [9, 13, 17]. The two caffeoyl units were found to be located at C-4′ of the two glucose moieties suggested by the strong deshielding of both H-4′-glucose resonances at δ = 4.90 (2H, t-like). The two interglycosidic linkages were confirmed to be of the *O*-α-L-rhamnosyl-(1→3)-β-D-glucoside-type on the basis of the splitting pattern of their anomeric signals (br s of α-1″-H-rhamnosyl and d, J_{12} = 7.6 for β-1′-glucoside configuration), characteristic downfield shifts (∼ 5.1, 4.3) and the strong α-downfield effect of the two C-3′ glucose carbons at δ = 82.40 (∼ Δ = −4.5 ppm) in the ^{13}C NMR spectrum (Table 2).

All ^{1}H and ^{13}C resonances of **1** were confirmed (Experimental Part, Tables 1 and 2) by the aid of ^{1}H,^{1}H-COSY, HMQC and HMBC experiments and by comparison with the literature on the acetoside compounds to suggest the complete structure as that of an acetoside dimer connected by a C_4–*O*–C_6 ether linkage (Fig. 3). This was clear from the characteristic strong downfield shifts of C-6B at δ = 151.50 (∼ Δ = +30 ppm) and C-4B at 148.23 (∼ Δ = +4 ppm) and from the upfield shifts of C-1B to δ = 121.90 (∼ Δ = −10 ppm) and C-5B to 112.90 in comparison of the reported corresponding values of the acetosides **2**–**6** at about 121.3, 144.6, 131.5, and 116.3 ppm [17], respectively. This connection between the two aglycone moieties was finally confirmed by the two bond HMBC correlation peaks of 5B-H at δ = 7.04 (s) with C-6B at 151.50 and C-4B at 148.23 and 2B-H at 6.71 (s) with C-1B at 121.90, as well as through three bond correlations of 5B-H with C-1B and 2B-H with C-4B and C-6B (Fig. 3, Table 1). Important H-C long range correlations (Fig. 3), reflecting inter-residues conjugation, were observed between H-1′gl (δ_H = 4.36, 4.35), H-1″rh (δ_H = 5.16, br s) and H-4′gl (δ_H = 4.90, t-like) with C-8A,B (δ_C = 70.66, 70.89), C-3′A,B (δ_C = 80.40) and C-9A,B (carbonyl, δ_C = 167.01) [17] (Tables 1 and 2).

The above-mentioned signals in the NMR spectra of **1** were paired by a series of weaker signals, which could be ascribed to the presence of a *Z*-isomer with regard to the configuration of the olefinic bonds of the caffeoyl group ($J_{7''',8'''}$ = 11.5 Hz, instead of 16 Hz). Finally, the $^4C_1$ and $^1C_4$ pyranoses of the glucoside and rhamnosyl moieties were established on the basis of J values of the vicinally coupled protons, especially the $J_{1,2}$ and δ_C values of the sugar moieties in both ^{1}H and ^{13}C NMR spectra (Table 2). Thus, **1** was identified as

a novel dimer of acetoside or jacraninoside A (Fig. 2).

Acknowledgement

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