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Acylated Iridoid Glycosides from *Verbascum lasianthum*

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From the roots of *Verbascum lasianthum* Boiss. ex Bentham 4 catalpol derivatives, 6-*O*-(α-L-rhamnopyranosyl)-catalpol (**1**), verbascoside A [= 6-*O*-(4″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol] (**2**), pulverulentoside I [= 6-*O*-(3″-*O*-acetyl-2″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol] (**3**), and buddlejoside A_5 [= 6-*O*-(2″-*O*-acetyl-3″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol] (**4**), as well as aucubin (**5**) and an aucubin derivative, unduloside III [= 6-*O*-(3″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylaucubin] (**6**), were isolated and characterized. The structure elucidation of the compounds was established on the basis of spectroscopic evidence. Buddlejoside A_5 (**4**) was found for the first time in the genus *Verbascum*.

Key Words: *Verbascum lasianthum* Boiss. ex Bentham, Scrophulariaceae, iridoid glycosides, 6-*O*-(α-L-rhamnopyranosyl)-catalpol, verbascoside A, pulverulentoside I, buddlejoside A_5, aucubin, unduloside III

Introduction

The genus *Verbascum* (Scrophulariaceae) is represented by 228 species in the Turkish flora. *Verbascum lasianthum* is a biennial herb widespread in Turkey[1]. Some *Verbascum* species are used an as expectorant and mucolytic in folk medicine[2]. The iridoid glycosides are widely distributed in the genus *Verbascum* and it is well known for its variety of iridoids, which are of value for the taxonomic evaluation of this genus[3]. Phytochemical studies of European *Verbascum* species have revealed the presence of iridoids[4], phenylethanoids[5], lignans[5], saponins[6], flavonoids[7] and sterols[8]. In a previous paper, Ulubelen et al.[8] described the isolation of steroidal compounds and hydrocarbons from the aerial parts of *V. lasianthum.* However, there has been no report on the iridoids of the title plant.

In the present study, we report on the isolation and structure elucidation of 6 iridoid glycosides, 6-*O*-(α-L-rhamnopyranosyl)-catalpol (**1**), verbascoside A (**2**), pulverulentoside I (**3**), buddlejoside A_5 (**4**), aucubin (**5**) and unduloside III (**6**), using 1D and 2D NMR techniques. All of the aforementioned compounds were isolated from *V. lasianthum* for the first time.

Experimental General Experimental Procedures: The UV spectra (λ_{max}) were recorded on a Hitachi HP 8452 A spectrophotometer. The IR spectra (υ_{max}) were determined on an ATI Mattson Genesis Series FT-IR spectrophotometer. LC-ESIMS were recorded on a Bruker BioApex FT-MS in ESI mode. NMR measurements in DMSO-d_6 were recorded on a Bruker Avance DRX 300 and a 500 FT spectrometer operating at 300 or 500 MHz for ^{1}H NMR and 75 or 125 MHz for ^{13}C NMR. ^{1}H, ^{13}C NMR, DQF-COSY, HMQC and HMBC experiments were recorded by employing conventional pulse sequences. Reverse-phase material (Sepralyte 40 μm, C_{18}) was used for vacuum liquid chromatograpy (VLC) and open column chromatography (CC). Polyamide (ICN) and silica gel 60 (0.063-0.200 mm, Merck) were used for open column chromatography (CC). Medium pressure liquid chromatography (MPLC) separations were performed on a Labomatic glass column packed with LiChroprep RP-18 (Merck), using a Lewa M5 peristaltic pump. TLC analyses were carried out on precoated silica gel 60 F_{254} aluminum sheets (Merck). Compounds were detected by UV fluorescence and spraying with 1% vanillin/H_2SO_4 reagent followed by heating at 105 ^{o}C for 1-2 min.

Plant Material: *Verbascum lasianthum* Boiss. ex Bentham (Scrophulariaceae) was collected at florescence from İzmir in August 1999. A voucher specimen has been deposited in the Herbarium of the Pharmacognosy Department, Faculty of Pharmacy, Hacettepe University, Ankara, Turkey (HUEF 99130).

Extraction and Isolation: The air-dried and powdered roots of *Verbascum lasianthum* (333.9 g) were extracted twice with MeOH (2 x 2 L) at 40 °C. The combined extracts were evaporated under reduced pressure and the crude extract (36.7 g) was partitioned between $CHCl_3$ and H_2O. The aqueous phase was freeze-dried (16.0 g) and subjected to polyamide (100 g) CC, eluting with H_2O and mixtures of H_2O-MeOH, to afford 5 fractions (Fr. A-E). Fr. A (4.3 g) was subjected to C_{18}– VLC (350 g) using gradient H_2O-MeOH mixtures (0-100%) to afford aucubin (**5**) (201.3 mg). Fr. B (1.54 g) was subjected to C_{18}– MPLC using gradient H_2O-MeOH mixtures (2.5-90%) to afford 5 fractions (Fr. B_1-B_5). Separation of B_2 (159.2 mg) was carried out on C_{18}-column using gradient H_2O-MeOH mixtures (0-35%) to give 6-*O*-(α-L-rhamnopyranosyl)-catalpol (**1**) (10.5 mg). Fr. B_3 (273.6 mg) was rechromatographed over silica gel (100 g) and eluted with $CHCl_3$-MeOH mixtures (95:5, 90:10, 85:15, 80:20), and $CHCl_3$-MeOH-H_2O mixtures (80:20:2, 80:20:1) to yield buddlejoside A_5 (**4**) (2.9 mg), pulverulentoside I (**3**) (16.3 mg), unduloside III (**6**) (25.1 mg) and verbascoside A (**2**) (19.3 mg).

Results

6-*O*-(α-L-rhamnopyranosyl)-catalpol (**1**): UV (MeOH) λ_{max} 206 nm, IR (KBr) υ_{max} 3600 (OH), 1654 (C=C) cm^{-1}, LC-ESIMS m/z 531 [M+Na]$^+$ (calc. for $C_{21}H_{32}O_{14}$), ^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data (see Tables 1 and 2).

Verbascoside A [= 6-*O*-(4″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L- rhamnopyranosylcatalpol] (**2**): UV (MeOH) λ_{max}230, 318 nm, IR (KBr) υ_{max} 3600 (OH), 1708 (C=O), 1654 (C=C), 1604, 1515, 1385 (aromatic ring) cm^{-1}, LC-ESIMS m/z 691 [M+Na]$^+$ (calc. for $C_{31}H_{40}O_{16}$). ^{1}H NMR (300 MHz, DMSO-d_6) and ^{13}C NMR (75 MHz, DMSO-d_6) data (see Tables 1 and 2).

Pulverulentoside I [= 6-*O*-(3″-*O*-acetyl-2″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol]

(**3**): UV (MeOH) λ_{max}216, 292 (sh) nm, IR (KBr) υ_{max} 3600 (OH), 1708 (C=O), 1654 (C=C), 1604, 1546, 1363 (aromatic ring) cm^{-1}, LC-ESIMS m/z 733 $[M+Na]^+$ (calc. for $C_{33}H_{42}O_{17}$). ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data (see Tables 1 and 2).

Buddlejoside A$_5$[= 6-*O*-(2″-*O*-acetyl-3″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol] (**4**): UV (MeOH) λ_{max} 212, 232, 298 (sh) nm, IR (KBr) υ_{max} 3600 (OH), 1708 (C=O), 1654 (C=C), 1527, 1363 (aromatic ring) cm^{-1}, LC-ESIMS m/z 733 $[M+Na]^+$ (calc. for $C_{33}H_{42}O_{17}$). ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data (see Tables 1 and 2).

Aucubin (**5**): UV (MeOH) λ_{max}204 nm, IR (KBr) υ_{max} 3629 (OH), 1666 (C=C) cm^{-1}, LC-ESIMS m/z 368 $[M+Na]^+$ (calc. for$C_{21}H_{32}O_{13}$). ^1H NMR (300 MHz, DMSO-d_6) and ^{13}C NMR (75 MHz, DMSO-d_6) data (see Tables 1 and 2) are superimposable with those reported in the literature[9].

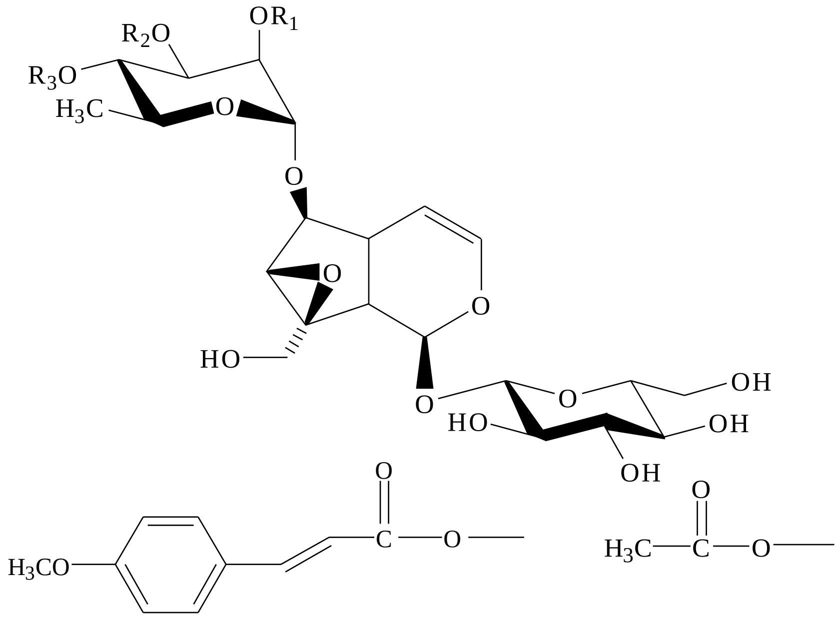
Unduloside III [= 6-*O*-(3″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylaucubin] (**6**): UV (MeOH) λ_{max}218, 232 nm, IR (KBr) υ_{max} 3600 (OH), 1706 (C=O), 1654 (C=C), 1533, 1363 (aromatic ring) cm^{-1}, LC-ESIMS m/z 675 $[M+Na]^+$ (calc. for $C_{31}H_{40}O_{15}$). ^1H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) data (see Tables 1 and 2).

Discussion

The water-soluble extract obtained from the methanolic extract of the roots of *V. lasianthum* was fractionated on polyamide, followed by open CC on silica gel and/or C_{18}-VLC as well as C_{18}-MPLC to yield compounds **1-6** (see Figure).

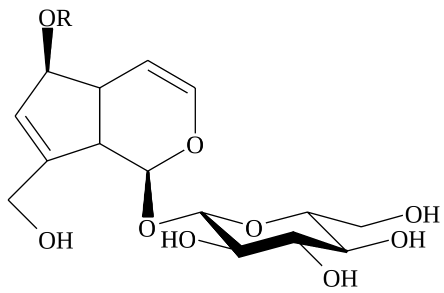
Compound **1** was obtained as an amorphous powder. The LC-ESIMS spectrum of **1** showed a molecular ion peak at m/z 531 suggesting a molecular formula of $C_{21}H_{32}O_{14}$.The ^1H and ^{13}C NMR and DEPT-135 data of **1** (see Tables 1 and 2) indicated the presence of a C-4 non-substituted iridoid skeleton and 2 sugar units. The ^1H and ^{13}C NMR data of **1** showed a close relationship with those of catalpol[10]. In the ^1H NMR spectrum of compound **1**, additional an anomeric proton signal was observed at δ 4.83 (*br s*), which was attributed to a α-rhamnopyranosyl moiety. A proton resonance at δ 1.14 (*d*, J= 6.2 Hz) also verified the presence of the rhamnopyranosyl unit. As the signals for the glucose portion were superimposable with those of catalpol[10], the signals for the aglycone moieties showed slight differences. The site of the rhamnopyranosyl unit was found to be C-6 due to the downfield shift of C-6 resonance (δ 81.5) in comparison to that reported for catalpol (δ 75.3)[10]. These results were in good accordance with those reported for 6-*O*-(α-L-rhamnopyranosyl)-catalpol[11].

Compound **2** was obtained as an amorphous powder. The molecular formula of **2** was determined to be $C_{31}H_{40}O_{16}$due to the LC-ESIMS molecular ion peak at m/z 691 together with ^1H and ^{13}C NMR data. Comparison of the ^1H and ^{13}C NMR spectral data of **2** with those of **1** indicated that **2** was a monoacyl derivative of **1** (see Tables 1 and 2). The signals of 2 *trans* olefinic protons (δ 6.49 and 7.61, *d*, J= 16.0 Hz), as well as 2 pairs of *ortho*-coupled aromatic protons (δ 7.66 and 6.95, *d*, J= 8.4 Hz) and 1 aromatic methoxy group (δ 3.77, *s*) in the ^1H NMR spectrum, showed clearly that the acyl moiety was a *trans*-*p*-methoxycinnamoyl unit. ^{13}C NMR and DEPT-135 spectra of **2** confirmed the presence of *p*-methoxycinnamic acid. The site of esterification was determined to be the C-4″ position of the rhamnopyranosyl moiety based on the chemical shifts of C-3″, C-4″ and C-5″ ($\Delta\delta$ -1.3, +2.6 and -1.5 ppm, resp.). In the ^1H NMR spectrum, the proton signal of H-4″ (δ 4.93) was shifted downfield by ca. 1.67 ppm, supporting the acylation site, by comparison with that of **1** (see Table 1). In conclusion, the structure of **2** was determined to be verbascoside A [= 6-*O*-(4″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol][11].



trans-p-methoxycinnamoyl　　　　acetyl

	R_1	R_2	R_3
1	H	H	H
2	H	H	*trans-p*-methoxycinnamoyl
3	*trans-p*-methoxycinnamoyl	acetyl	H
4	acetyl	*trans-p*-methoxycinnamoyl	H



	R
5	H
6	3”-*O*-*trans*-*p*-methoxycinnamoyl-α-L-rhamnopyranosyl

Figure. Iridoid glycosides isolated from *Verbascum lasianthum*

Table 1. ^{1}H NMR (500 MHz, DMSO-d_6) data of compounds **1-6**.

	1		2*		3		4		5*		6	
Position	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
Aglycone												
1	4.96 d	9.5	5.19 d	2.7	5.01 †	-	4.97 †	-	4.98 d	6.0	5.14 d	5.9
3	6.41 dd	1.8/6.0	6.40 d	5.5	6.43 d	5.7	6.38 d	5.8	6.27 d	6.0	6.36 dd	1.6/6.0
4	4.95 d	6.3	5.10 d	4.4	5.12 d	4.9	5.07 d	4.3	4.81 d	6.7	4.94 d	7.1
5	2.25 m	-	2.28 m		2.31 m	-	2.26 m	-	2.92 m	-	2.82 m	-
6	3.88 d	7.6	3.91 d	7.5	3.95 d	7.7	3.90 d	7.6	4.70 m	-	4.47 brs	-
7	3.60 brs	-	3.73 brs	-	3.68 brs	-	3.63 brs	-	5.62 brs	-	5.89 brs	-
9	2.38 dd	9.4/7.8	2.40 m	-	2.43 m	-	2.36 m	-	2.92 m	-	2.90 d	7.2
10a	3.70 d	11.5	3.68 †	-	3.66 †	-	3.66 †	-	3.94 d	16.0	4.15 d	15.2
10b	3.91 d	11.5	3.89 †	-	3.90 d	16.0	3.87 †	-	4.14 d	16.0	4.39 d	15.7
β- D-Glucose												
1′	4.59 d	7.9	4.59 d	7.5	4.59 d	7.8	4.55 d	7.8	4.48 d	7.7	4.69 d	7.8
2′	3.04 d	9.1	3.00 †	-	3.03 †	-	3.05 †	-	3.12 d	8.3	3.23 d	8.2
3′	3.14 †	-	3.09-3.15 †	-	3.16 †	-	3.13 †	-	3.41 †	-	3.38 d	8.3
4′	3.03 †	-	3.00 †	-	3.01 †	-	3.05 †	-	2.98 dd	8.1/9.5	3.27 †	-
5′	3.20 m	-	3.09-3.15 †	-	3.14 †	-	3.13 †	-	3.35 m	-	3.30 m	-
6′a	3.45 †	-	3.64 †	-	3.43 †	-	3.41 †	-	3.64 d	11.3	3.63 dd	6.0/14.1
6′b	3.68 d	11.5	3.86 †	-	3.73 †	-	3.73 †	-	3.90 †	-	3.92 dd	6.1/13.7
α- L-Rhamnose												
1″	4.83 brs	-	5.02 brs	-	5.00 brs	-	4.98 brs	-	-	-	4.89 brs	-
2″	3.91 †	-	3.86 †	-	5.22 †	-	5.35 †	-	-	-	3.91 †	-
3″	3.50 †	-	3.36 †	-	4.98 †	-	4.96 †	-	-	-	5.06 d	9.6
4″	3.26 †	-	4.93 †	-	3.46 †	-	3.45 †	-	-	-	3.60 †	-
5″	3.45-3.58 †	-	3.73 †	-	3.78 †	-	3.74 †	-	-	-	3.78 †	-
6″	1.14 d	6.2	1.05 d	5.8	1.24 d	6.0	1.06 d	6.2	-	-	1.19 d	6.6
Acyl moiety												
2‴	-	-	7.66 d	8.4	7.73 d	8.7	7.69 d	8.7	-	-	7.60 d	8.7
3‴	-	-	6.95 d	8.4	6.97 d	8.7	6.93 d	8.7	-	-	6.98 d	8.7
5‴	-	-	6.95 d	8.4	6.97 d	8.7	6.93 d	8.7	-	-	6.98 d	8.7
6‴	-	-	7.66 d	8.4	7.73 d	8.7	7.69 d	8.7	-	-	7.60 d	8.7
α	-	-	6.49 d	16.0	6.56 d	16.0	6.54 d	15.9	-	-	6.45 d	16.0
β	-	-	7.61 d	16.0	7.65 d	16.0	7.61 d	15.7	-	-	7.68 d	16.0
OC<u>H</u>3	-	-	3.77 s	-	3.80 s	-	3.76 s	-	-	-	3.84 s	-
OCOC<u>H</u>3	-	-	-	-	1.94 s	-	2.02 s	-	-	-	-	-

† unclear due to overlapping

* 300 MHz

Table 2. ^{13}C NMR (125 MHz, DMSO-d_6) data of compounds 1-6.

		1	2*	3	4	5*	6
Position	C_{Atom}	δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)
Aglycone							
1	CH	93.2	94.0	94.0	94.0	97.5	97.0
3	CH	140.9	141.8	142.0	142.0	141.0	141.1
4	CH	102.5	103.1	103.0	103.0	105.9	104.7
5	CH	35.7	36.4	36.3	36.3	46.1	43.3
6	CH	81.5	82.8	83.0	83.0	82.0	88.3
7	CH	57.5	58.3	58.2	59.5	130.7	126.2
8	C	65.3	66.2	66.3	67.0	147.9	148.8
9	CH	41.9	42.8	42.8	42.8	47.9	47.3
10	CH_2	58.9	59.6	59.5	59.5	61.0	60.5
β- D-Glucose							
1′	CH	97.9	98.7	98.7	98.7	100.6	99.1
2′	CH	73.5	74.2	74.3	74.3	75.1	74.0
3′	CH	77.4	78.3	77.3	77.3	78.8	77.4
4′	CH	70.6	71.1	71.1	71.1	71.6	71.7
5′	CH	76.4	77.2	78.3	78.3	78.5	77.8
6′	CH_2	61.4	62.1	62.2	62.2	62.6	61.7
α- L-Rhamnose							
1″	CH	98.9	99.7	96.7	102.8	-	100.3
2″	CH	70.7	71.5	72.4	70.1	-	70.8
3″	CH	70.3	69.0	70.2	72.5	-	74.6
4″	CH	71.9	74.5	70.1	70.1	-	70.6
5″	CH	68.9	67.4	69.6	67.0	-	69.3
6″	CH_3	17.9	18.4	18.5	18.3	-	17.2
Acyl moiety							
1‴	C	-	127.5	127.3	127.0	-	127.4
2‴	CH	-	131.0	131.3	131.3	-	130.2
3‴	CH	-	115.3	115.3	115.3	-	114.6
4‴	C	-	162.0	162.2	162.0	-	162.4
5‴	CH	-	115.3	115.3	115.3	-	114.6
6‴	CH	-	131.0	131.3	131.3	-	130.2
α	CH	-	116.4	115.4	115.4	-	115.4
β	CH	-	145.3	146.3	146.0	-	145.4
C=O	C	-	168.0	162.7	162.5	-	167.6
O<u>C</u>H3	CH_3	-	56.1	56.2	56.2	-	55.1
O<u>C</u>OCH3	C	-	-	170.8	170.8	-	-
OCO<u>C</u>H3	CH_3	-	-	21.6	21.8	-	-

∗ 75 MHz

Compounds **3** and **4** were obtained as amorphous powders. The LC-ESIMS spectra of 2 substances showed a molecular ion at m/z 733 suggesting that they have a very similar molecular formula to that of $C_{33}H_{42}O_{17}$. Their ^{13}C NMR spectra were also very similar, showing 6 typical signals for β-glucopyranose and 6 signals for di-substituted α-L-rhamnopyranose. The presence of these sugar units was confirmed by ^{1}H NMR spectrum. Among the remaining 21 carbon signals, 10 signals were identical with those reported for *p*-methoxycinnamoyl ester[11], as well as 2 signals for acetyl groups[4]. The rest of the ^{13}C NMR signals showed the presence of a double bond, an acetal, 2 –CH<, 2 >CHO-, a >CO- and a -CH_2OH. These indicated that compounds **3** and **4** were iridoid derivatives. The ^{13}C NMR signals of catalpol[10] and compounds **3** and **4** were identical (see Table 1). However, the ^{13}C NMR of **3** and **4** showed additional signals for rhamnosyl, acetyl and *p*-methoxycinnamoyl moieties. The signals for the glucose portion were superimposable on those of catalpol[10], while the signals for the aglycone moieties showed slight differences. Thus, rhamnose appeared to be attached to the C-6 hydroxyl group of the aglycone. This was also supported by an HMBC spectrum. The comparison of ^{1}H and ^{13}C NMR spectra of **3** and **4** with those of 6-O-(α-L-rhamnopyranosyl)-catalpol (**1**) suggested that compounds **3** and **4** were positional isomers in which the *p*-methoxycinnamoyl and acetyl group are esterified to different hydroxyl groups of the rhamnose moiety. To determine the acylation position of the rhamnosyl moiety, the substitution shift regularity of the esterified sugar was considered[12]. When the ^{13}C NMR chemical shifts of the rhamnose moiety (C-1″-C-6″) of **3** were compared with those of **1**, the C-2″ signal was seen to be significantly shifted downfield by 1.7 ppm and the C-1″ signal was shifted upfield by 2.2 ppm.

This established that the position of the *p*-methoxycinnamoyl ester of compound **3** is the C-2″ of rhamnose[12,13]. An HMBC experiment established the attachment site of the acetyl group at C-3″ and the *p*-methoxycinnamoyl group at C-2″ of the rhamnose. In compound **4**, the 2.2 ppm downfield shift of C-3″ and 1.8 ppm upfield shift of C-4″ suggested that *p*-methoxycinnamoyl must be at C-3″. The site of esterification was confirmed by the HMBC spectrum on the basis of correlations between the carbonyl carbon of the *p*-methoxycinnamoyl group (δ_C 162.5) and the H-3″ (δ_H 4.96) of the rhamnose, as well as the acetyl group (δ_C 170.8) and the H-2″ (δ_H 5.35) of the rhamnose. Therefore, the structures of compounds **3** and **4** were elucidated to be pulverulentoside I [= 6-*O*-(3″-*O*-acetyl-2″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol][14]and buddlejoside A_5 [= 6-*O*-(2″-*O*-acetyl-3″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylcatalpol][15], respectively.

Compound **5** was obtained as an amorphous powder. Its structure was identified as aucubin[9] by comparing its ^{1}H and ^{13}C NMR data with previously published data and by direct comparison with an authentic sample on a TLC plate.

Compound **6** was obtained as an amorphous powder. The LC-ESIMS spectrum showed a molecular ion peak at m/z 675 suggesting a molecular formula of $C_{31}H_{40}O_{15}$. The ^{1}H, ^{13}C NMR and DEPT-135 data of compound **6** (see Tables 1 and 2) showed signals very similar to those of aucubin (**5**) with similar additional signals arising from a *trans*-*p*-methoxycinnamic acid as well as α-L-rhamnopyranosyl moieties after comparing with compound **2**. The location of the α-L-rhamnopyranosyl group was determined to be at the C-6 position in the aucubin unit from the HMBC spectrum. The site of esterification by the *trans*-*p*-methoxycinnamoyl group was determined to be the C-3″ position in the rhamnopyranosyl moiety, because, in the ^{1}H NMR spectrum, the signal of the H-3″ was shifted downfield (δ_H 5.06 ppm) in comparison with 6-*O*-(α-L-rhamnopyranosyl) aucubin (= Sinuatol)[9]. The site of esterification was confirmed as the C-3″ position of the rhamnose unit from the HMBC spectrum, where a long-range coupling was observed between the signal at δ_C 167.6 (carbonyl of *trans-p*-methoxycinnamoyl group) and the signal at δ_H 5.06 (H-3″). Accordingly, the structure of **6** was determined to be unduloside III [= 6-*O*-(3″-*O*-*trans*-*p*-methoxycinnamoyl)-α-L-rhamnopyranosylaucubin][16].

Conclusion

Concerning the iridoid glycosides of the genus *Verbascum*, the isolation of aucubin (**5**)[9], 6-*O*-(α-L-rhamnopyranosyl)-catalpol (**1**)[11,17], verbascoside A (**2**)[4,11] and pulverulentoside I (**3**) [4,14,18,19] from several other *Verbascum* species has been reported previously. It is well known that aucubin is one of the most common iridoid glucosides in the genus *Verbascum* and family Scrophulariaceae[20]. Buddlejoside A_5(**4**) was previously reported from *Buddleja japonica* (Buddlejaceae)[15], and this is the first report the isolation of this compound from a *Verbascum* species. To our knowledge, unduloside III (**6**) has only been previously reported from *V. undulatum*[16].

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