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# Iridoid glycosides from *Gmelina arborea*

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ABSTRACT

Three iridoid glycosides 6-*O*-(3″-*O*-benzoyl)-α-L-rhamnopyranosylcatalpol (**1a**), 6-*O*-(3″-*O*-*trans*-cinnamoyl)-α-L-rhamnopyranosylcatalpol (**2a**) and 6-*O*-(3″-*O*-*cis*-cinnamoyl)-α-L-rhamnopyranosylcatalpol (**3a**) were isolated from aerial parts of *Gmelina arborea* and structures were elucidated by spectral analysis. Additionally a known iridoid 6-*O*-(3″, 4″-*O*-dibenzoyl)-α-L-rhamnopyranosylcatalpol (**4**) was also isolated and identified.



## 1. Introduction

Iridoid glycosides are a large group of naturally occurring monoterpenoids with a glucose moiety attached to C-1 in the pyran ring (Song et al., 2006). These occupy an important position in the field of natural product chemistry and biology, as they provide a structural link between terpenoids and indole alkaloids and display a broad spectrum of biological activities (Sticher, 1977).

*Gmelina arborea* Roxb. (Verbenaceae), a popular commercial timber grows naturally in the warm temperate regions of Mediterranean and South Asia. The plant is commonly found in abundance on the hills and in the Andaman Islands of India. Folklore use for the treatment of liver disorders, loosening phlegm, as a diuretic, an appetite stimulant and a galactogogue has been reported (Hosny and Rosazza, 1998). It is an important ingredient of well known "Dashamul" used in Indian traditional system of medicine as a unique combination of herbs that nourishes and rejuvenates the tissue, maintains healthy reproductive system and removes toxins from blood (Joy et al., 1998). Phytochemical investigations had led to the isolation of few iridoid glycosides from leaves of *G. arborea* viz.-Gmelinosides A-L, 6-*O*-(3″-*O*-*trans*-feruloyl)-α-L-rhamnopyranosylcatalpol, 6-*O*-(2″*O*-acetyl 3″,4″-*O* di-*trans*-cinnamoyl)-α-L-rhamnopyranosylcatalpol (Hosny and Rosazza, 1998).

During detailed chemical investigations of plant only one iridoid glycoside 6-*O*-(3″, 4″-*O*-dibenzoyl)-α-L-rhamnopyranosylcatalpol (**4**) has been isolated even by preparative HPLC. Recently, it had been mentioned that some catalpol derivatives are unstable and could not be isolated in pure form (Cogne et al., 2005). We therefore, acetylated the iridoid mixtures to isolate and characterize three new iridoid glycosides (**1a**), (**2a**) and (**3a**) as their acetylated derivatives by preparative HPLC (Fig. 1).

## 2. Results and discussion

Compound **1b**, obtained as viscous mass, showed UV spectrum-232, 278 nm for an iridoid system with a benzoyl chromophore (Hosny and Rosazza, 1998). Its IR spectrum also revealed presence of acetyl groups, unsaturated bonds, and aromatic system. Its positive ESI mass spectra showed a quasimolecular ion peak at *m*/*z* 929 $[M + Na]^+$ suggesting the molecular formula as $C_{42}H_{50}O_{22}$ which was further confirmed by $^{13}C$ NMR and DEPT spectra. The $^1H$ and $^{13}C$ NMR spectroscopic data were consistent with a C-6 iridoid monoglucoside moiety (Helfrich and Rimpler, 2000). The complete and unambiguous assignment of all protons and carbon resonances were based on the use of $^1H$–$^1H$ correlation spectroscopy (COSY), heteronuclear multiple bond correlation spectroscopy (HMBC) and heteronuclear single quantum coherence experiments (HSQC) via direct coupling.

The proton and carbon NMR values of isolated compounds have been assigned in Tables 1 and 2.

The $^1H$ NMR spectrum (300 MHz, $CDCl_3$) of compound (**1b**) showed a broad singlet for H-7 at δ 3.59 due to small coupling between H-7 and H-6 and confirmed C-8 to be quarternary. A characteristic doublet for acetal proton (H-1) arisen at δ 4.77 ($J$ = 9.6 Hz) (Kalpoutzakis et al., 1999); the large coupling constant demonstrated the dihedral angle to be 180° between vicinally coupled

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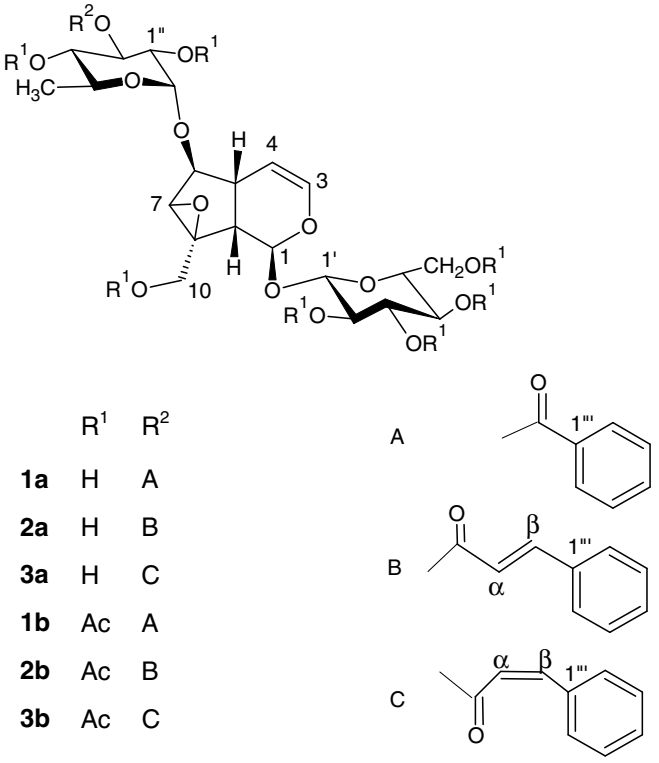



**Fig. 1.** Chemical structures of compounds **1a**–**3b**.

protons (H-1 and H-9) (Gousiadou et al., 2007). H-9 gave a double doublet (δ 2.65, $J$ = 9.6, 8 Hz) due to coupling with H-5 and H-1. Appreciable coupling with H-5 indicated a dihedral angle of 0° and thus revealed that the stereochemistry of pyran and cyclopentane ring fusion was *cis* (Gousiadou et al., 2007). A double doublet (δ 6.32, $J$ = 6, 1.5 Hz.) suggested a characteristic enol ether signal for H-3 of iridoids (Domìnguez et al., 2007) which was further confirmed by an intense signal in COSY between H-3 and H-4 and a very weak for H-3 and H-5. A doublet ($J$ = 8.1 Hz) arisen in $^1$H NMR spectra for glucosyl anomeric proton (H-1′) at δ 4.97 and showed a long range coupling with H-1 in HMBC spectra; thus confirmed the usual C-1 attachment of glucose (Kalpoutzakis et al., 1999). Coupling constant ($J_{aa}$ = 8.1 Hz) indicated a dihedral angle of 180°, a diaxial relationship between H-1′ and H-2′ vicinal protons and thus confirmed the natural β attachment of glucose with aglycon (Zhou et al., 2007). On quite contrary to it, the rhamnose anomeric proton gave a broad singlet at δ 4.96 showing a dihedral angle of 60° ($\theta_{ae}$) and confirmed rhamnose as α isomer. Location of α-rhamnopyranosyl group was determined to be at the C-6 position of the catalpol unit from HMBC spectrum as H-6 showed a long range connectivity with C-1″ of rhamnopyranose.

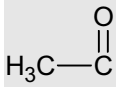
The $^{13}$C NMR spectrum (75 MHz, $CDCl_3$) also suggested the presence of a benzoyl group, an α-rhamnopyranosyl unit and a catalpol moiety (Hosny and Rosazza, 1998). Seven methyl carbons of the acetate groups appeared as overlapped signals (δ 20.8–21.2) due to hepta acetylation of compound **1b** and confirmed single benzoyl esterification. The cyclopentane ring carbons involved in the epoxide ring formation resonated at δ 58.5 and δ 67.0 corresponding to C-7 and C-8. The signal at δ 67.0 disappeared in DEPT 135° and gave no connectivity in HSQC with any proton signal. The downfield signal at δ 94.7 appeared for acetal carbon (C-1) of pyran ring and judged direct attachment of two oxygen atoms. In HMBC spectrum C-1 correlated with the proton signal at δ 6.32 ($J$ = 6, 1.5 Hz) which had HSQC connectivity with carbon signal at δ 141.5. The signal at δ 141.5 was characteristic of an enol ether carbon (Cogne et al., 2005), thus there is a double bond between C-3 and C-4. $J$ values of H-3 and H-4 gave support for the presence of a *cis* double bond (Silverstein et al., 1991). Moreover the signal at δ 35.9 gave HMBC correlations with proton signal at δ 5.11 (H-4), δ 3.95 (H-6), δ 2.65 (H-9) which was possible if it was a ring junction carbon. C-4 (δ 102.8) is the double bonded carbon of pyran ring. The downfield signal (δ 84.2) of C-6 judged the rhamnopyranosyl attachment through an ether linkage (Hosny and Rosazza, 1998) so the only possibility for another ring junction carbon is C-9 (δ 42.3). H-9 was a double doublet which again confirmed C-8 to be quarternary and epoxide ring carbons to be C-7 and C-8. The HMBC correlation shown between acetate bearing methylene carbon at δ 62.6 (C-10) and proton signal at δ 2.65 and δ 3.59 corresponding to C-7 and C-9 enabled to decide the position of $CH_2OAc$ at C-8 (δ 67.0). Characteristic signals of diacetylated single benzoyl esterified α linked rhamnose moiety and β glucose tetra acetate were observed in its $^{13}$C NMR spectra (Faizi et al., 1995; Watanabe et al., 1989). The site of benzoyl esterification was determined to be the C-3″ position of rhamnopyranosyl moiety because the $^1$H NMR signal of H-3″ (δ 5.60, $J$ = 9.6, 3.6 Hz) was shifted downfield in comparison with 6-*O*-α-L-rhamnopyranosylcatalpol (Hosny and Rosazza, 1998). Thus, on the basis of above discussion compound **1b** was characterized as 6-*O*-(3″-*O*-benzoyl)-α-L-rhamnopyranosylcatalpol.

Compound **2b**, viscous mass, also showed UV absorption at 218, 223, 282 nm for an iridoid unit bearing a cinnamoyl moiety (Miyase and Mimatsu, 1999). The molecular formula was determined to be $C_{44}H_{52}O_{22}$ on the basis of positive ESI mass which showed quasimolecular ion peaks at 955 $[M + Na]^+$ and at 971 $[M + K]^+$. Structure elucidation strategy was similar to compound **1b**. The $^1$H and $^{13}$C NMR data were very much similar to **1b** except the signals of benzoyl esterification. Two characteristic doublets (δ 6.38 and δ 7.68) of 16 Hz judged the presence of two *trans* olefinic protons (Kalpoutzakis et al., 1999; Silverstein et al., 1991). $^{13}$C NMR spectrum gave signals at δ 117.4 (C-α) and at δ 146.8 (C-β) for a double bond in conjugation with a benzene ring (Cogne et al., 2005). Five aromatic protons resonated at δ 7.53 [H-2‴, H-6‴, *d*, $J$ = 8.2 Hz), δ 7.40 (H-3‴, H-5‴, *t*, $J$ = 8.2 Hz), δ 7.34 (H-4‴, m)] suggesting no substitution in benzene ring whereas 6 aromatic carbon appeared at δ 128.9 (C-2‴,6‴), δ 129.5 (C-3‴,5‴), δ 130.9 (C-4‴), δ 134.5 (C-1‴) confirming the cinnamoyl group (Kalpoutzakis et al., 1999).

Similar to compound **1b**, it also showed characteristic signals of iridoid system containing an epoxide ring (Kalpoutzakis et al., 1999). The signals of sugar moieties appeared between δ 67.6 and 72.9. Rhamnose methyl appeared at δ 17.8 and glucose $CH_2OAc$ at δ 61.6. Assignment of protons and carbons was further confirmed by HMBC, HSQC and COSY experiments. The site of cinnamoyl esterification was revealed by direct comparison of downfield shifts with 6-*O*-α-L-rhamnopyranosylcatalpol (Hosny and Rosazza, 1998). Based upon the data mentioned above the structure of **2b** was assigned as 6-*O*-(3″-*O*-*trans*-cinnamoyl)-α-L-rhamnopyranosylcatalpol.

Compound **3b**, viscous mass obtained in traces and possessed UV absorption at 215, 225, 285 nm. Its IR spectrum revealed a similar structure to **2b**. Its ESI mass gave quasimolecular ion peaks at 955 $[M+Na]^+$ and 971 $[M+K]^+$ which suggested that compound **3b** has same molecular formula as **2b**, i.e. $C_{44}H_{52}O_{22}$ and **3b** is an isomer of **2b**. A similar $^1$H NMR spectrum was observed except the signals of olefinic protons of cinnamoyl group. In $^1$H NMR spectrum, instead of two doublets at δ 6.38 and δ 7.68 of 16 Hz, two doublets arisen at δ 5.90 and δ 7.02 of 12.6 Hz. These data judged the stereochemistry of cinnamoyl double bond to be *cis* (Silverstein et al., 1991). The $^1$H NMR spectrum also showed a characteristic singlet at δ 3.54 for H-7, a double doublet at δ 6.31 for H-3 and glucose and rhamnose anomeric protons at δ 4.94 (*d*, $J$ = 8.1 Hz, H-1′) and δ 4.92 (*brs*, H-1″), respectively (Kalpoutzakis et al., 1999). A doublet for protons 10a, 10b at δ 3.94 and δ 4.86 of 12.6 Hz and a double doublet for protons 6a, 6b at δ 4.21 ($J$ = 12.3, 3.9 Hz)

**Table 1**
$^1$H NMR shifts in δ for compounds **1b-3b** (in $CDCl_3$)

| Position | Compound **1b** δ H (m, *J* in Hz) | Compound **2b** δ H (m, *J* in Hz) | Compound **3b** δ H (m, *J* in Hz) | COSY |
|---|---|---|---|---|
| *Aglycon* | | | | |
| 1 | 4.77 (1H, *d*, *J* = 9.6) | 4.77 (1H, *d*, *J* = 9.6) | 4.74 (1H, *d*, *J* = 9.6) | H-9 |
| 3 | 6.32 (1H, *dd*, *J* = 6, 1.5) | 6.32 (1H, *dd*, *J* = 6, 1.5) | 6.31 (1H, *dd*, *J* = 6, 1.5) | H-4, H-5, |
| 4 | 5.11 (1H, *dd*, *J* = 6, 4.8) | 5.09 (1H, *dd*, *J* = 6, 4.8) | 5.04 (1H, *dd*, *J* = 4.8) | H-3, H-5, H-6 |
| 5 | 2.57 (1H, m) | 2.50 (1H, m) | 2.51 (1H, m) | H-3, H-4, H-6 |
| 6 | 3.95 (1H, *dd*, *J* = 8.5, 1.8) | 3.93 (1H, *dd*, *J* = 8.5, 1.8) | 3.95 (1H, *dd*, *J* = 8.5, 1.5) | H-1″, H-5, H-7 |
| 7 | 3.59 (1H, *brs*) | 3.57 (1H, *brs*) | 3.54 (1H, *brs*) | H-6 |
| 8 | – | – | – | – |
| 9 | 2.65 (1H, *dd*, *J* = 9.6, 8) | 2.61 (1H, *dd*, *J* = 9.6,8) | 2.61 (1H, *dd*, *J* = 9.6, 8) | H-1 |
| 10a | 3.98 (1H, *d*, *J* = 12.6) | 3.96 (1H, *d*, *J* = 12.6) | 3.94 (1H, *d*, *J* = 12.6) | H-10b |
| 10b | 4.82 (1H, *d*, *J* = 12.6) | 4.80 (1H, *d*, *J* = 12.6) | 4.86 (1H, *d*, *J* = 12.6) | H-10a |
| *Glucosyl* | | | | |
| 1′ | 4.97 (1H, *d*, *J* = 8.1) | 4.96 (1H, *d*, *J* = 8) | 4.94 (1H, *d*, *J* = 8.1) | H-2′ |
| 2′ | 5.27 (1H, *dd*, *J* = 9.5, 8) | 5.19 (1H, *dd*, *J* = 9.5, 8) | 5.21 (1H, *dd*, *J* = 9.5, 8) | H-1′ |
| 3′ | 4.95 (1H, t, *J* = 9.6) | 4.96 (1H,t, *J* = 9.6) | 4.96 (1H, t, *J* = 9.6) | H-4′ |
| 4′ | 5.22 (1H, t, *J* = 9.5) | 5.15 (1H, t, *J* = 9.6) | 5.18 (1H, t, *J* = 9.5) | H-3′, H-5′ |
| 5′ | 3.69 (1H, m) | 3.68 (1H, m) | 3.69 (1H, m) | H-6′a,b, H-4′ |
| 6′a | 4.15 (1H, *dd*, *J* = 12.3, 3.9) | 4.15 (1H, *d*, *J* = 12.3, 3.9) | 4.21 (1H, *dd*, *J* = 12.3, 3.9) | H-5′, H-6′b |
| 6′b | 4.34 (1H, *dd*, *J* = 12.3, 2.4) | 4.32 (1H, *dd*, *J* = 12.3, 2.4) | 4.30 (1H, *dd*, *J* = 12.3, 2.4) | H-5′, H-6′a |
| *Rhamnosyl* | | | | |
| 1″ | 4.96 (1H, *brs*) | 4.96 (1H, *brs*) | 4.92 (1H, *brs*) | H-2″ |
| 2″ | 5.34 (1H, *dd*, *J* =3.5, 1.7) | 5.32 (1H, *dd*, *J* = 3.5, 1.7) | 5.31(1H, *dd*, *J* = 3.5, 1.7) | H-1″, H-3″ |
| 3″ | 5.60 (1H, *dd*, *J* = 9.6, 3.6) | 5.42 (1H, *dd*, *J* = 9.6, 3.6) | 5.41 (1H, *dd*, *J* = 9.6, 3.6) | H-2″, H-4″ |
| 4″ | 5.36 (1H, t, *J* = 9.6) | 5.22 (1H, t, *J* = 9.6) | 5.28 (1H, t, *J* = 9.6) | H-3″, H-5″ |
| 5″ | 4.08 (1H, *dd*, *J* = 9.8, 6.3) | 4.00 (1H, *dd*, *J* = 9.8, 6.3) | 3.98 (1H, *dd*, *J* = 9.8, 6.3) | H-4″, H-6″ |
| 6″ | 1.26 (3H, *d*, *J* = 6.3) | 1.24 (3H, *d*, *J* = 6.3) | 1.27 (3H, *d*, *J* = 6.3) | H-5″ |
| *Ester* | | | | |
| α | – | 6.38 (1H, *d*, *J* = 16) | 5.90 (1H, *d*, *J* = 12.6) | H-β |
| β | – | 7.68 (1H, *d*, *J* = 16) | 7.02 (1H, *d*, *J* = 12.6) | H-α |
| 1‴ | – | – | – | – |
| 2‴,6‴ | 8.00 (2H, *dd*, *J* = 8.7, 1.5) | 7.53 (2H, *d*, *J* = 8.2) | 7.58 (2H, *d*, *J* = 8.2) | H-2″, H-3″, H-4″ |
| 3‴,5‴ | 7.46 (2H, t, *J* = 7.8) | 7.40 (2H, t, *J* = 8.2) | 7.38(2H, t, *J* = 8.2) | H-2″, H-4″, H-6″ |
| 4‴ | 7.58 (IH, tt, *J* = 7.5) | 7.34 (1H, m) | 7.35(1H, m) | H-2″, H-3″ |
| *Acetyl* | | | | |
|  | 1.89, 2.04, 2.05, 2.07, 2.13, 2.15, 2.19,s | 1.93, 1.94, 1.96, 1.97, 2.03, 2.05, 2.07,s | 2.01, 2.07, 2.10, 2.16, 2.18, 2.20, 2.23,s | |

and δ 4.30 (*J* = 12.3, 2.4 Hz) were also observed for geminally coupled protons (Silverstein et al., 1991). All the glucose and rhamnose protons were similar to compound **2b**. Thus, the structure of compound **3a** was assigned as 6-*O*-(3″-*O*-*cis*-cinnamoyl)-α-L-rhamnopyranosylcatalpol.

Compound **4** was obtained after chromatography on silica gel column followed by preparative HPLC and characterized as 6-*O*-(3″, 4″-*O*-dibenzoyl)-α-L-rhamnopyranosylcatalpol by comparison of spectral data to reported one (Hosny and Rosazza, 1998).

On contrary to earlier report (Hosny and Rosazza, 1998), we were unable to isolate any acetate from the crude extract which may be due to the non-occurence of iridoid acetates in the plant collected from Lucknow, as observed by the absence of any acetate methyl signal in NMR spectrum of crude extract in the region 1.8–2.5 ppm. HPLC analysis (mobile solvent: MeOH: water; 70:30, PDA detection: 220 nm, flow rate: 1 ml/ min, column: Spherisorb ODS2, 10 μm, 250 × 4.6 mm, Waters) also revealed absence of **1b**, **2b** and **3b** in the plant as such. Occurrence of acetates in earlier report may be specific to plant origin. However, similar to earlier report occurrence of novel iridoids in *G. arborea* may be of chemotaxonomic importance.

## 3. Experimental

### 3.1. General experimental procedures

The 300 MHz NMR spectra were recorded in $CDCl_3$ with tetramethyl silane (TMS) as internal standard on Bruker Avance instrument. $^{13}$C NMR and DEPT spectras were recorded at 75 MHz. The DEPT experiments were used to determine multiplicities of carbon atoms. Chemical shifts are given in parts per million. COSY, HSQC and HMBC were performed using standard Bruker pulse programs. IR spectras were obtained on a Perkin–Elmer spectrum BX spectrophotometer. ESI mass spectra were measured on a Shimadzu ESI-MS spectrometer (70 ev). Optical rotations were measured on a HORIBA polarimeter (SEPA-300). Preparative HPLC was performed on a Shimadzu LC-8A semipreparative HPLC using reverse phase Si gel column (RP-18, Supelcosil); 25 cm × 21.2 mm, 12 μm (particle size). Column chromatography was performed using Si gel (60–120 mesh, Merck, India).

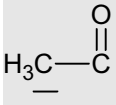
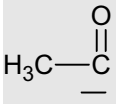
### 3.2. Plant material

Aerial parts of *G. arborea* were collected locally from Lucknow in the month of February, 2007. Botanical identification was performed by Botany and Pharmacognosy Department of institute and a voucher specimen (CIMAP No.-7656) has been deposited in the herbarium of this institute.

### 3.3. Extraction and isolation

Air dried and finely powdered aerial parts of the plant (1.45 kg) were exhaustively extracted at room temperature (25 ± 5°) with methanol (5 liter × 4 times) and the methanolic extract was concentrated in vacuo to give a residue (243 g). Water (250 ml) was added and it was then partitioned with *n*-hexane, chloroform

**Table 2**
$^{13}C$ NMR shifts in δ for compounds **1b, 2b** (in $CDCl_3$)

| Position | Compound **1b** δ C | Compound **2b** δ C | HMBC C → H |
|---|---|---|---|
| *Aglycon* | | | |
| 1 | 94.7 | 94.7 | H-9, H-1′, H-3′ |
| 3 | 141.5 | 141.7 | H-4 |
| 4 | 102.8 | 102.9 | H-3, H-6 |
| 5 | 35.9 | 35.9 | H-3, H-4, H-6, H-7 |
| 6 | 84.2 | 83.9 | H-5, H-9, H-7, H-1″ |
| 7 | 58.5 | 58.5 | H-5, H-9, H-6, H-10a, H-10b |
| 8 | 67.0 | 67.0 | H-9, H-10a |
| 9 | 42.3 | 42.1 | H-6, H-10a, H-1 |
| 10 | 62.6 | 62.8 | H-9, H-7 |
| *Glucosyl* | | | |
| 1′ | 97.1 | 97.1 | H-1 |
| 2′ | 73.0 | 72.9 | H-3′ |
| 3′ | 71.2 | 71.0 | H-2′, H-4′ |
| 4′ | 68.8 | 68.7 | – |
| 5′ | 72.8 | 72.7 | H-4′ |
| 6′ | 61.6 | 61.6 | H-5′ |
| *Rhamnosyl* | | | |
| 1″ | 97.0 | 97.1 | H-6″, H-6, H-2″ |
| 2″ | 70.7 | 70.4 | H-1″ |
| 3″ | 69.2 | 69.1 | H-1″, H-2″ |
| 4″ | 72.1 | 71.4 | H-6″, H-3″ |
| 5″ | 67.7 | 67.6 | H-6″, H-3″, H-1″ |
| 6″ | 17.8 | 17.8 | H-5″ |
| *Ester* | | | |
| α | – | 117.4 | H-β |
| β | – | 146.8 | H-α, H-2‴, H-6‴ |
| 1‴ | 129.8 | 134.5 | H-2‴, H-6‴ |
| 2‴,6‴ | 130.2 | 128.9 | H-3‴, H-5‴ |
| 3‴,5‴ | 128.9 | 129.5 | H-2‴, H-6‴, H-4‴ |
| 4‴ | 133.8 | 130.9 | H-3‴, H-5‴ |
| C=O | 166.1 | 166.2 | H-2‴, H-6‴ |
| *Acetyl* | | | |
|  | 20.8, 20.9, 20.9, 21.2 | 20.8,,20.9, 21.1 | |
|  | 169.3, 169.5, 170.1, 170.3, 170.5, 170.8, 170.9 | 169.2, 169.4, 170.1 170.3, 170.4, 170.7, 170.8 | |

and *n*-butanol soluble fractions. The *n*-butanol extract (68 g) was subjected to column chromatography on silica gel (1 kg). Elution was carried out in varying percentage of MeOH in chloroform. Fractions (145–150) eluted with chloroform–methanol (90:10) were subjected to reverse phase preparative HPLC chromatography which afforded compound 4 (RT-11 min). Later fractions (170–196) of chloroform: methanol (90:10) were pooled (2 g), dissolved in pyridine (30 ml) and 30 ml of $Ac_2O$ was added. The mixture was left overnight at room temperature, diluted with cold water (100 ml) and extracted with ether (5 × 50 ml). The ether extract was washed successively with dil. HCl (3 × 50 ml), $H_2O$ (3 × 50 ml), $NaHCO_3$ solution (3 × 50 ml) and $H_2O$ (3 × 50 ml) and dried over anhydrous $Na_2SO_4$. Removal of solvent gave acetylated iridoid mixture (2.1 g). 100 mg of acetylated iridoid mixture was subjected to preparative HPLC using MeOH: $H_2O$ (65:35) as mobile solvent and 15 ml/min flow rate. Detection was carried out at 220 nm which afforded three compounds **1b** (28.07 min, 10 mg), **2b** (43.30 min, 7.5 mg) min and **3b** (19.0 min, 3.5 mg).

### 3.4. 6-O-(3″-O-benzoyl)-α-L-rhamnopyranosylcatalpol heptaacetate (*1b*)

Viscous mass; $\alpha_D^{28}$ = −17.7° (c 0.08, $CHCl_3$); UV $\lambda_{max:}$ 232, 278 nm; IR $\nu_{max}^{KBr}cm^{-1}$: 2956, 2925, 1759, 1654, 1637, 1560, 1544, 1510, 1422, 1375, 1080, 1066, 980; for $^1H$ and $^{13}C$ NMR, spectroscopic data, see Tables 1 and 2; ESIMS (positive) *m*/*z* 929 $[MNa]^+$.

### 3.5. 6-O-(3″-O-trans-cinnamoyl)-α-L-rhamnopyranosylcatalpol heptaacetate (*2b*)

Viscous mass; $\alpha_D^{28}$= −14.2° (c 0.16, $CHCl_3$); UV $\lambda_{max}$: 218, 223, 282 nm; IR $\nu_{max}^{KBr}cm^{-1}$: 2957, 2927, 1750, 1654, 1636, 1560, 1543, 1510, 1426, 1373, 1080, 1044, 982; for $^1H$ and $^{13}C$ NMR, spectroscopic data, see Tables 1 and 2; ESIMS (positive) *m*/*z* 955 $[MNa]^+$, 971 $[MK]^+$.

### 3.6. 6-O-(3″-O-cis-cinnamoyl)-α-L-rhamnopyranosylcatalpol heptaacetate (*3b*)

Viscous mass; $\alpha_D^{28}$= −10.4° (c 0.14, $CHCl_3$); UV $\lambda_{max}$: 215, 225, 285 nm; IR $\nu_{max}^{KBr}cm^{-1}$: 2957, 2926, 1749, 1653, 1637, 1560, 1543, 1509, 1437, 1373, 1080, 1043, 981; for $^1H$ NMR, spectroscopic data, see Table 1; ESIMS (positive) *m*/*z* 955 $[MNa]^+$, 971 $[MK]^+$.

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