Carbohydrate Research 363 (2012) 66–72

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

First total chemical synthesis of natural acyl derivatives of some phenolglycosides of the family *Salicaceae*

Maxim L. Belyanin [a], Elena V. Stepanova [a,*], Vladimir D. Ogorodnikov [b]

[a] National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk 634050, Russia
[b] The Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Science, 4 Akademichesky Avenue, 634021 Tomsk, Russia

ARTICLE INFO

Article history:
Received 8 June 2012
Received in revised form 3 October 2012
Accepted 5 October 2012
Available online 13 October 2012

Keywords:
Phenolic glycosides
Glycosylation
Salireposide
Populosides A, B, C
Protective group cleavage

ABSTRACT

The total synthesis of certain natural phenolglycosides of the family *Salicaceae*, namely: salireposide, populosides A, B, and C and not occurring in plants desoxysalireposide (2-(β-D-glucopyranosyloxy)-benzylbenzoate) and per-acetate of *iso*-salireposide (2-(β-D-glucopyranosyloxy)-5-benzoyloxy benzyl alcohol), starting from readily available phenols and glucose was accomplished. A simple method for the synthesis of phenolglycosides derivatives of 2-acyloxy salicyl and gentisyl alcohol was developed. The key step of these natural products' synthesis is a selective removal of acetyl groups in the presence of other acyl groups.

1. Introduction

Phenolglycoside derivatives of 2-acyloxy salicyl alcohol are widespread in plants of the family *Salicaceae*. Most phenolglycosides of this family contain salicin moiety (2-(β-D-glucopyranosyloxy)-benzyl alcohol). These natural compounds cover a large spectrum of biological activity. Phenolic glycosides are some of the most abundant secondary metabolites known in plant tissues, and play an important role as anti-herbivore defenses in the *Salicaceae*.[1,2] Salireposide (**1**) has antiviral activity,[3] and antitumor activity.[4,5] It could be useful for arthritis therapy[5] and shows an inhibitory activity against snake-venom phosphodiesterase.[6] Populosides A (**2**), B (**3**), and C (**4**) exhibit antioxidant activity.[7] These compounds are also potential candidates for acute or chronic opisthorchiasis treatment.

Salireposide was found out in many plants.[8–13] Populosides A, B, and C were first isolated from *Populus davidiana* in 2006,[7] and populoside A was also isolated from *Populus ussuriensis*.[14]

However, despite the fact that phenolglycosides, derivatives of 2-acyloxy salicyl alcohol are well-known as natural compounds, there is no mentioning on the synthesis of these glycosides in the literature to date. Thus, the present work's aim is to synthesize some phenolglycosides inaccessible from natural sources (Fig. 1).

It was found that salireposide (**1**) cannot be selectively obtained by direct benzoylation of salirepin (2-(β-D-glucopyranosyloxy)-5-hydroxy benzyl alcohol), since a mixture of acylated products was formed. In addition, it is known that benzoylation of glycosides firstly goes to the C-6 hydroxy group of the glucose residue[15,16] rather than alcohol hydroxyl of the aglycone.

The present paper reports on the first synthesis of salireposide and 2-acyl analogs of salicin and salirepin: populosides A, B, C, desoxysalireposide and *per*-acetate of artificial *iso*-salireposide–4-benzoyloxy-salicin. The suggested method allows to obtain phenolglycosides, derivatives of 2-acyloxy salicyl alcohol in a selective way.

2. Results and discussion

Salicylic aldehyde (**5**) or 4-*O*-acetyloxy salicylic aldehyde (**6a**) and 4-*O*-benzoyloxy salicylic aldehyde (**6b**) were used as initial substrates (Scheme 1). Aldehydes **6a**, **6b** were obtained by selective formylation of monoacyl-hydroquinone (**7a**,**7b**), which in turn can be easily obtained by hydroquinone acylation.[17]

α-D-Acetobromglucose (**ABG**) was employed as a donor of a carbohydrate residue in the glycosylation reaction. Glycosylation of **5** was carried out under Koennigs–Knorr conditions in aqueous acetone with an equimolar amount of NaOH[18] to produce glycoside **8**. Unfortunately, this method proved to be unsuited for **6a** and **6b** glycosylation, since acyl group of the aglycone was removed and, consequently, several isomeric glycosides were formed. Therefore, for **6a** and **6b** glycosylation another way of the Koennigs–Knorr method was applied. This method avoids the aquatic environment, using quinoline and silver oxide. Although

* Corresponding author. Tel.: +7 83822 56 38 61; fax: +7 83822 56 36 37.
E-mail address: eline_m@mail.ru (E.V. Stepanova).

0008-6215/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carres.2012.10.006

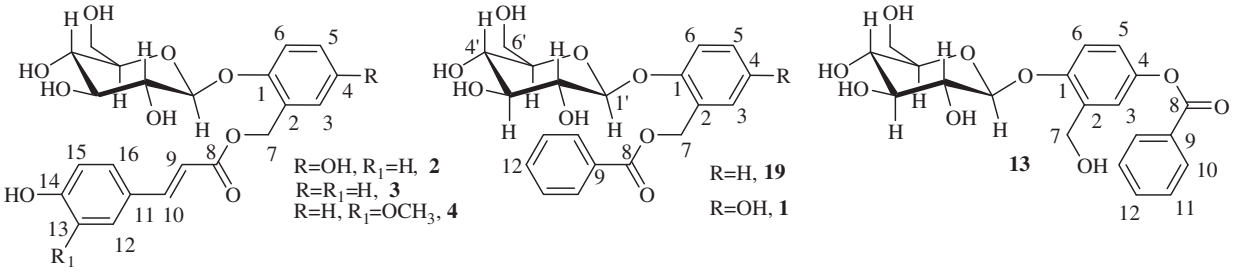
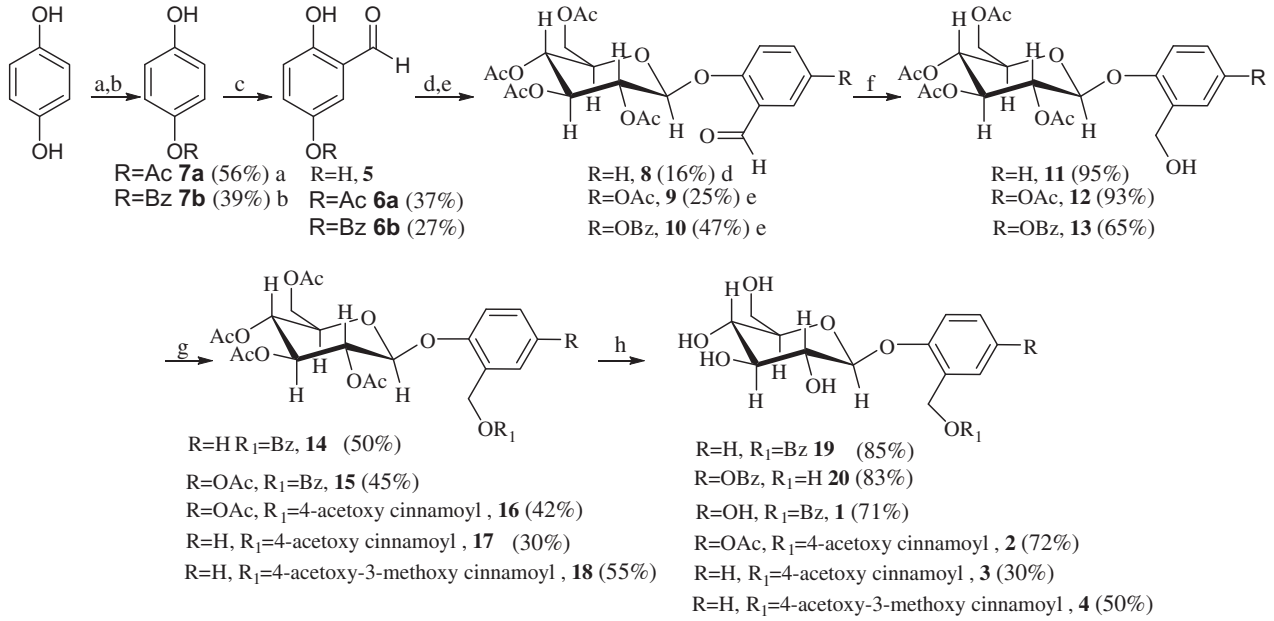


Figure 1. Structure of synthesized phenolglycosides.



Scheme 1. Synthesis of 2-acyl phenolglycosides. Reagents and conditions: (a) Ac_2O, AcOH, 2 h, 110 °C; (b) BzCl, NaOH, H_2O 1 h 40 min, 5 °C; (c) CF_3COOH, hexamethylentetramine, 1 h, 80 °C; (d) acetobromglucose, NaOH, acetone 24 h, 20 °C; (e) acetobromglucose, Ag_2O, quinoline, 1 h, 20 °C; (f) $NaBH_4$, CTMABr, $CHCl_3$, H_2O, 2 h, 20 °C; (g) acyl chloride of proper acid (benzoyl chloride, 4-acetoxy cinnamoyl chloride or 4-acetoxy-3-methoxy cinnamoyl chloride), pyridine, $CHCl_3$, 24 h, 20 °C; (h) 36% HCl, $CHCl_3$, EtOH (1:1:3), 24–48 h, 20 °C.

a number of side-reactions take place,[19] glycosides **9** and **10**, respectively, were obtained by higher yields rather than employing aqueous acetone. Both methods produce glycosides of β-configuration.

Further aldehyde groups of glycosides **8**, **9,** and **10** were reduced by sodium borohydride using cetyltrimethylammonium bromide (CTMABr) as a phase transfer catalyst in chloroform–water system.[20] The reaction proceeds at ambient temperature with almost quantitative yields. The best results were obtained when using CTMABr in quantities of 1% mol of the substrate.[21] Sodium borohydride in water or alcohol solvents without any phase transfer catalysis condition[22] was found to be unsuited, because complete removal of acetyl groups takes place, which, as a result, requires re-acetylation.

Reduced glycosides **11** and **12** were subjected to acylation with benzoylchloride in pyridine to produce desoxysalireposide tetraacetate **14** and salireposide pentaacetate **15**, respectively.

Glycosides **16**, **17**, and **18**, were synthesized in the same way, applying acylation of compounds **11** and **12** with the acyl chloride of convenient acid.[23]

Selective cleavage of acetyl groups in the presence of benzoyl is possible if the H_2SO_4–acetone[24] system is applied, but cleavage of benzoyl group is still significant. The best results were obtained by using HBF_4–MeOH[25] and HC1–MeOH[26,27] systems. However, the application of these systems is limited for compounds containing acid-labile acyl groups instead of benzoyl one. Thus, for selective removal of acetyl groups in presence of benzoyl we applied the following system: HCl (aqueous solution, ρ = 1.18 g/mL)–EtOH (96%)–chloroform in a molar ratio of HCl–glycoside 54:1 and the concentration of HCl in ethanol–chloroform mixture (volume ratio 3:1) 2.4 mol/L at the ambient temperature for 48 h.

The reaction at the ambient temperature resulted in a successful cleavage of protective acetyl groups not only for glycoside **13**, **14,** and **15**, containing benzoyl group, but also for **16**, **17,** and **18**, containing 4-acetoxy cinnamoyl and 4-acetoxy-3-methoxy cinnamoyl groups, respectively, without significant cleavage of these groups and without breaking the glycosidic bond. Yet, it was observed that benzoyl group has a high resistance to hydrolysis under these conditions, as compared to 4-acetoxy cinnamoyl and 4-acetoxy-3-methoxy cinnamoyl groups. Also, when monitoring the reaction by HPLC, ethyl esters of 4-acetoxy-3-methoxy cinnamic and 4-acetoxy cinnamic acids were detected. The formation of benzoic acid or ethylbenzoate in the case of substances **13, 14,** and **15** was not significant.

It was established that glycosides' anomerization and configuration change did not occur under the described conditions. Chemical shifts of anomeric carbon atoms for both glycosides (101.4–104.1 ppm, depending on the solvent), and their per-acetates

(97.0–99.8 ppm) in ^{13}C NMR spectrum correspond to chemical shifts of anomeric carbon atoms for glycosides of β-configuration.[28] Phenolglycosides **1–4** are identical with naturally-occurring glycosides according to published data.[29,7] Also compound **1** was isolated from *Populus tremula* bark using the method described in literature,[7] and physicochemical characteristics of natural and synthetic samples were identical.

We found out that the selective deacetylation reaction does not cause acyl groups migration, as it corresponds to the base conditions.[32] To prove this, synthetic glycosides were re-acetylated to yield compounds with physicochemical characteristics identical to original acetates.[30,31]

In conclusion, we have developed a simple synthetic pathway for some natural phenolglycosides derivatives of salicyl and gentisyl alcohols involving simple and readily accessible starting materials such as glucose and hydroquinone or salicylic aldehyde. The developed scheme allows obtaining glycosides of β-configuration regioselectively. Also investigation of these latter issues is currently in progress.

3. Experimental

3.1. General experimental procedures

Melting points, which are uncorrected, were determined using a Kofler hot stage apparatus. UV spectroscopic data were obtained with SF-102 spectrophotometer. IR spectra were recorded with IR Fourier spectrophotometer Spectrum BX II using KBr disks. The ^1H and ^{13}C NMR spectra were recorded on Bruker-300 MMX spectrometer at 300 and 75.5 MHz, respectively, in $CDCl_3$, DMSO-d_6 and MeOD-d_4 with TMS as an internal standard and Cr(*acac*)$_3$ as a relaxant. The chemical shifts are given in δ (ppm) and the spin–spin coupling constants (J) in hertz. GC–MS analysis was performed using Aligent 7890A/5975C GC/MSD instrument, electron energy 70 eV. The ion source temperature was 230 °C, with the quadrupole temperature 150 °C and evaporator temperature 315 °C, employing a 30.000 × 0.25 mm × 0.25 μm HP-5MS fused-silica capillary column. Helium was used as carrier gas at a constant flow of 1 mL/min and an inlet temperature of 315 °C. The column temperature mode: 2 min at 150 °C, 150–315 °C (20 °C/min), and 25 min at 315 °C. TLC was performed using plates Silufol-UV 254 and Sorbfil-UV 254 using benzene–ethanol 9:1 (method A) or chloroform–methanol 4:1 (B) mixtures as eluents. HPLC analysis was carried out with the liquid chromatographer Agilent Compact LC with column 150 × 4.6 Exlips Plus C-18 (5 μm). Analysis was performed using 0.1% trifluoroacetic acid in H_2O–CH_3CN as mobile phase, at gradient elution (from 0% to 100% CH_3CN in 20 min) at a flow rate of 1 mL/min. Probe volume was 20 μL. UV detection was performed at 220 nm. Accurate mass measurement was performed on an Agilent 1200 series LC system coupled with an Agilent 6210 TOF mass spectrometer. Silica gel MN Kieselgel 60 0.04–0.063 mm was used for column chromatography. Commercially available solvents were used after drying with $CaCl_2$.

3.2. 2-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyloxy)bromide (ABG)

Was obtained according to the method described, in lit.[3] and additionally recrystallized from Et_2O. Yield 58%, mp 88 °C.

3.3. Monoacetylhydroquinone (7a)

Was obtained according to the method[17] by acetylation of hydroquinone with acetic anhydride. Yield 56%; mp 49–50 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.28 (3H, s, $COCH_3$); 6.67 (2H, d, J = 7.8 Hz, H-2, H-6); 6.86 (2H, d, J = 8.1 Hz, H-3, H-6). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 21.1 (CH_3, $COCH_3$); 116.4 (C-2, C-6); 122.3 (C-3, C-5); 143.7 (C-4); 153.7 (C-1); 171.2 (C, $COCH_3$). MS *m/z* 152 $[M]^+$ (19), 110 (100), 43 (55).

3.4. Monobenzoylhydroquinone (7b)

To 11.44 g (0.104 mol) of hydroquinone dissolved in 120 mL 0.43 n. NaOH (0.052 mol) cooled to 5 °C. Six milliliters of (0.052 mol) benzoylchloride was drop-added for 1 h while agitating the solution at 5 °C. The mixture was stirred at this temperature for 40 min. The precipitate was filtered, washed with saturated solution of $NaHCO_3$ and water. Recrystallization from toluene gave light brown crystals, yield 4.34 g (39%); mp 162–163 °C, lit.[33] 163 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.80 (2H, d, H-6, J = 8.7 Hz, H-2); 7.03 (2H, d, J = 8.7 Hz, H-3, H-5); 7.51 (2H, m, H-10, H-12); 7.64 (1H, m, H-11); 8.19 (2H, d, J = 8.1 Hz, H-9, H-13). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 116.8 (C-2, C-6); 122.7 (C-5, C-3); 128.7 (C-10, C-12); 130.3 (C-8, C-9, C-13); 133.80 (C-11); 144.2 (C-4); 153.9 (C-1); 165.9 (C-7).

3.5. 2-Hydroxy-5-acyloxy benzaldehyde (6a, 6b). General method

To 0.01 mol of monoacylhydroqinone (**7a** or **7b**), dissolved in 20 mL trifluoroacetic acid, 0.04 mol of hexamethylenetetramine was added, and the mixture was stirred at temperature 80 °C for 1 h. The reaction mixture was diluted with 60 mL 0.35% HCl and extracted with $CHCl_3$ (3 × 30 mL). The extracts were combined, washed with saturated NaCl, water, dried over Na_2SO_4, subjected to flash column chromatography, and evaporated.

3.5.1. 2-Hydroxy-5-acetyloxy benzaldehyde (6a)

Recrystallization from water gave (**6a**) as white needles (37%): mp 78–79 °C. IR (KBr, ν_{max}/cm^{-1}): 3075 (OH); 1766 (C=O); 1674 (HC=O) 1587 (Ar); 1488 (Ar); 1373 (C–H); 1224 (C–O–C); 1142, 1015(C–O); 913 (C–H); 834 (Ar), 710 (Ar). ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.30 (3H, s, $COCH_3$); 6.97 (1H, d, J = 8.7 Hz, H-6,); 7.22 (1H, dd, J = 2.7, 9.0 Hz, H-5,); 7.31 (1H, d, J = 2.7 Hz, H-3); 9.83 (1H, s, CHO). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.9 (CH_3, $COCH_3$); 118.7(C-2); 120.1(C-6); 125.4(C-3); 130.66(C-5); 142.93(C-4); 159.18(C-1); 169.46(C, $COCH_3$); 195.80(CHO). MS *m/z* 180 $[M]^+$ 180 (10), 138 (100), 120 (7), 92 (8), 43 (19).

3.5.2. 2-Hydroxy-5-benzoyloxy benzaldehyde (6b)

Recrystallization from water gave (**6b**) as white needles (27%): mp 109–110 °C. IR (KBr, ν_{max}/cm^{-1}): 3063 (OH); 2863 (CH); 1734 (CO); 1665 (HC=O) 1627, 1587 (Ar); 1479, 1451 (Ar); 1371 (C–H); 1231 (C–O–C); 1061(C–O); 911 (CH); 714 (Ar). ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.04 (1H, d, J = 8.7 Hz, H-6); 7.37 (1H, dd, J = 8.7, 2.4 Hz, H-5); 7.46 (1H, d, J = 2.4 Hz, H-3); 7.50 (2H, m, H-10, H-12); 7.64, (1H, m, H-11); 8.18, (2H, m, H-9, H-13); 9.88 (1H, s, COH). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 118.8 (C-2); 120.3 (C-6); 125.6 (C-3); 128.7 (C-10, C-12); 129.0 (C-5); 130.2 (C-9, C-13); 130.9 (C-8); 133.9 (C-11); 143.3 (C-4); 159.4 (C-1); 165.3 (C7); 195.8 (CHO). MS *m/z* 242 $[M]^+$ (5), 105 (100), 77 (35).

3.6. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-benzaldehyde (helicin tetraacetate) (8)

Was obtained from (**5**) according to the method described.[18] Yield 16%, mp 142–143 °C. IR (KBr, ν_{max}/cm^{-1}): 2964, 2777 (C–H); 1762 (C=O), 1685 (HC=O); 1602 (Ar) 1484 (Ar); 1378, 1367 (C–H); 1234 (C–O) 1071, 1041 (C–O); 909 (C–H); 764 (Ar). ^1H NMR

(DMSO-d_6, 300 MHz) δ: 1.99, 2.01, 2.02 (4 × 3H, s, $COCH_3$); 4.09 (1H, m, H-5′); 4.20–4.32 (2H, m, H-6′a, H-6′b); 5.02 (1H, m, H-4′); 5.16 (1H, m, Hz, H-3′); 5.43 (1H, t, J = 9.3 Hz, H-2′); 5.70 (1H, d, J = 7.8 Hz, H-1′,); 7.20 (2H, m, H-4, H-6); 7.72 (2H, m, H-3, H-5); 10.15 (1H, s, CHO). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 20.3 (4 × $COCH_3$); 61.5 (C-6′); 67.9 (C-4′); 70.5 (C-2′); 70.9 (C-5′); 71.5(C-3′); 97.2(C-1′); 115.9(C-6); 123.1(C-4); 124.9(C-2); 127.5 (C-3); 136.3(C-5); 158.3(C-1); 169.3, 169.5, 169.9(4 × $COCH_3$); 189.1(CHO).

3.7. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5-acyloxy benzaldehyde (9,10). General method

To a mixture of 7 mmol compound **6a** or **6b** and 7 mmol ABG in 3 mL quinoline was added 7 mmol Ag_2O, and the mixture was stirred until thickening and kept for 1 h under room temperature. The reaction mixture was diluted with 20 mL $CHCl_3$, centrifuged (10 min, 1500 rpm), $CHCl_3$ was separated, washed with 0.1 M H_2SO_4 (3 × 5 mL), water, dried over Na_2SO_4, subjected to flash column chromatography, and evaporated.

3.7.1. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5-acetyloxy benzaldehyde (9)

Recrystallization from ethanol gave (**9**) as white needles (25%), mp 144–146 °C. IR (KBr, ν_{max}/cm^{-1}): 3484 (C–H); 2948, 2903 (CH_3); 1760, 1690 (C=O); 1607 (Ar) 1489 (Ar); 1379 (C–H); 1236 (C–O); 1072, 1041 (C–O); 908 (C–H). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.03, 2.04, 2.05, 2.06 (4 × 3H, s, $COCH_3$); 2.29 (3H, s, $COCH_3$); 3.85 (1H, m, H-5′); 4.14–4.31 (2H, m, H-6′a, H-6′b); 5.13–5.38 (4H, m, H-1′, H-2′, H-3′, H-4′); 7.12 (1H, d, J = 9.0 Hz, H-6); 7.26 (1H, dd, J = 3.0, 9.0 Hz, H-5); 7.54 (1H, d, J = 2.7 Hz, H-3); 10.29 (1H, s, CHO). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.5 (CH_3, $COCH_3$); 20.9 (4 × CH_3, $COCH_3$); 61.7 (C-6′); 68.0 (C4′); 70.8 (C-2′); 72.3(C-3′, C-5′); 99.4(C-1′); 117.5(C-6); 120.9(C-3); 127.0(C-2); 128.8(C-5); 146.3(C-4); 156.2(C-1); 169.3; 170.1; 170.4(5 × C, $COCH_3$); 188.2(CHO). HRESIMS Calcd for $C_{23}H_{26}O_{13}$ 533,12656 [M+Na]$^+$. Found 533,12428 [M+Na]$^+$.

3.7.2. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5-benzoyloxy benzaldehyde (10)

Recrystallization from ethanol gave (**10**) as white needles (47%), mp 124–125 °C. IR (KBr, ν_{max}/cm^{-1}): 3484 (C–H); 3074, 2887 (CH_3); 1749, 1687 (C=O); 1611 (Ar) 1490 (Ar); 1379 (C–H); 1221 (C–O); 1063, 1036 (C–O); 906 (C–H); 707 (Ar). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.04, 2.05, 2.07 (4 × 3H, s, $COCH_3$); 3.88 (1H, m, H-5′); 4.15 (2H, m, H-6′a, H-6′b); 5.17–5.41 (4H, m, H-1′, H-2′, H-3′, H-4′); 7.18 (1H, d, J = 9.3 Hz, H-6); 7.40 (1H, dd, J = 3.0, 9.0 Hz, H-5); 7.48 (2H, m, H-10, H-12); 7.62 (1H, d, J = 7.5 Hz, H-11); 7.67 (1H, d, J = 2.7 Hz, H-3); 8.16 (2H, d, J = 7.8 Hz, H-9, H-13); 10.30 (1H, s, CHO). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.5 (CH_3, $COCH_3$); 61.7 (C-6′); 68.0 (C-4′); 70.8 (C-2′); 72.3(C-3′, C-5′); 99.4(C-1′); 117.6 (C-6); 121.0 (C-3); 122.6 (C-5); 127.1(C-2); 128.6(C-10, C-12); 128.8(C-8); 129.0 (C-9); 130.13(C-13); 133.9(C-11); 146.6(C-4); 156.2 (C-1); 165.0(C-7); 169.1; 169.3; 170.0; 170.4(4 × C, $COCH_3$); 188.0(CHO). HRESIMS Calcd for $C_{28}H_{28}O_{13}$ 595,14221 [M+Na]$^+$. Found 595,14412 [M+Na]$^+$.

3.8. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy) benzyl alcohol (11, 12, 13). General method

To a solution of glycoside (**8**–**10**) (0.7 mmol) in 5 mL $CHCl_3$, was added a solution of $NaBH_4$ (0.7 mmol) in 2 mL water and 0.0025 g (1% mol) CTMABr. The reaction mixture was stirred at room temperature until TLC showed complete conversion of starting material (2 h). $CHCl_3$ was separated, washed with 0.1 M HCl (3 × 5 mL), water, dried over Na_2SO_4, evaporated, and recrystallized from ethanol.

3.8.1. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-benzyl alcohol (salicine tetraacetate) (11)

Yield 95%, mp 117–119 °C. IR (KBr, ν_{max}/cm^{-1}): 3479 (OH); 2970 (CH_3); 1754 (C=O); 1610 (Ar) 1490 (Ar); 1385, 1365 (C–H); 1240 (C–O); 1068, 1037 (C–O); 910 (C–H); 759 (Ar). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 1.98, 2.02, 2.02, 2.04 (4 × 3H, s, $COCH_3$); 4.07 (1H, d, J = 9.9 Hz, H-5′); 4.21 (1H, m, H-6′b); 4.39 (1H, m, H-6′a); 4.24 (1H, m, H-7b), 4.39 (1H, m, H-7a); 4.97 (1H, m, H-4′); 5.06 (1H, m, H-3′); 5.39–5.47 (2H, m, H-2′, H-1′); 7.03 (2H, m, H-6, H-4); 7. 21 (1H, m, H-5); 7.41 (1H, d, J = 6.9 Hz, H-3). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 20.4 (4 × CH_3, $COCH_3$); 57.3 (C-7); 61.6 (C-6′); 68.1 (C-4′); 70.5 (C-2′); 70.7 (C-5′); 71.7(C-3′); 97.5(C-1′); 114.3(C-6); 122.6(C-4); 127.1(C-3); 127.5(C-5); 131.4(C-2); 153.1(C-1); 169.1; 169.3, 169.5 169.6 (4 × C, $COCH_3$).

3.8.2. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranozyloxy)-5-acetyloxy benzyl alcohol (12)

Yield 93%, mp 110–111 °C. IR (KBr, ν_{max}/cm^{-1}): 3547 (OH); 2982 (C-H); 1758 (C=O); 1507, 1490 (Ar); 1374 (C–H); 1227, 1194 (C–O–C); 1065, 1043(C–O); 911 (C–H); 826, 706 (Ar). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 1.98, 2.01, 2.02, 2.05 (4 × 3H, s, $COCH_3$); 2.25 (3H, s, $COCH_3$); 4.08 (1H, d, J = 9.9 Hz, H-5′); 4.21, (1H, m, H-6′b); 4.23 (1H, m, H-7b); 4.38 (2H, m, H-6′a, H-7a); 4.98 (1H, m, H-4′,); 5.06 т (1H, t, J = 9.0 Hz,H-3′); 5.39–5.46 (2H, m, H-2′, H-1′); 6.97 (1H, d, J = 8.4 Hz, H-5); 7. 05 д (1H, d, J = 8.7 Hz, H-6); 7.14 (1H, s, H-3). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 20.4 (4 × CH_3, $COCH_3$); 20.7 (CH_3, $COCH_3$); 57.1 (C-7); 61.6 (C-6′); 68.1 (C-4′); 70.5 (C-2′); 70.8 (C-5′); 71.7(C-3′); 97.8(C-1′); 115.3(C-6); 120.2(C-5); 120.4(C-3); 133.0(C-2); 145.7(C-4); 150.4(C-1); 169.1; 169.3, 169.4, 169.5, 169.9(5 × C, $COCH_3$). HRESIMS Calcd for $C_{23}H_{28}O_{13}$ 535,14221 [M+Na]$^+$. Found 535,16732 [M+Na]$^+$.

3.8.3. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranozyloxy)-5-benzoyloxy benzyl alcohol (*iso*-salireposide tetraacetate) (13)

Yield 65%, mp 84–86 °C. IR (KBr, ν_{max}/cm^{-1}): 3526 (OH); 2925 (C–H); 1750 (C=O); 1507, 1497 (Ar); 1375 (C–H); 1227 (C–O–C); 1067(C–O); 908 (C–H); 803, 706 (Ar). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.05, 2.07, 2.11 (4 × 3H, s, $COCH_3$); 3.85 (1H, m, H-5′); 4.15–4.31 (2H, m, H-6′a, H-6′b); 4.51 (1H, d, J = 13.5 Hz, H-7b); 4.67 (1H, d, J = 13.2 Hz, H-7a); 5.09–5.33 (4H, m, H-1′, H-2′, H-3′, H-4′); 7.05 (2H, m, H-5, H-6); 7.23 (1H, m, H-3); 7.48 (2H, m, H-10, H-12); 7.61 (1H, m, H-11); 8.17 (2H, d, J = 7.2 Hz, H-9, H-13). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.3 (4 × CH_3, $COCH_3$); 60.3 (C-7); 61.5 (C-6′); 67.9 (C-4′); 70.8 (C-2′); 71.8 (C-5′); 72.1(C-3′); 99.7 (C-1′); 116.5(C-6); 121.5(C-3); 122.2(C-5); 128.4(C-11, C-13); 129.0(C-9); 129.9 (C-10,C-14); 132.8 (C-2); 133.5(C-12); 146.4(C-4); 151.7(C-1); 165.0(C, C=O); 169.1; 169.3; 169.9; 170.3(4 × C, $COCH_3$). HRESIMS Calcd for $C_{28}H_{30}O_{13}$ 597,15786 [M+Na]$^+$. Found 597,16006 [M+Na]$^+$.

3.9. Acylation of glycosides (11, 12). General method

To a solution of glycoside (**11** or **12**) (0.2 mmol) in 1 mL $CHCl_3$, was added chloroanhydride of acid (benzoylchloride, 4-acetyloxycynnamic acid chloroanhydride or 3-methoxy-4-acetyloxycynnamic acid chloroanhydride) (0.22 mmol) and 0.26 mmol of pyridine. The reaction mixture was kept at room temperature for 24 h and diluted with 20 mL $CHCl_3$. The solution was washed with 0.1 M H_2SO_4, sat. Na_2CO_3, water, dried over Na_2SO_4, and evaporated. The residue was recrystallized from ethanol.

3.9.1. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-benzylbenzoate(desoxysalireposide tetraacetate) (14)

Was obtained from glycoside (**11**) and benzoylchloride. Yield 50%, mp 82–83 °C. IR (KBr, ν_{max}/cm^{-1}): 3071, 2960 (C-H); 1753 (C=O); 1507, 1457 (Ar); 1377 (C–H); 1235 (C–O–C); 1070,

1046(C–O); 908 (C–H); 761 (Ar). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.03, 2.04, 2.05, 2.08 (4 × 3H, s, $COCH_3$, at 2′, 3′, 4′, and 6′); 3.86 (1H, m, H-5′); 4.15–4.32 (2H, m, H-6′b, H-6′a); 5.10–5.45 (4H, m, H1′, H-2′, H-3′, H-4′); 5.30 (2H, m, H-7a, H-7b); 7.09 (2H, m, H-4, H-6); 7.27 (1H, m, H-5); 7.42 (3H, m, H-3, H-11, H-13); 7.54 (1H, m, H-12); 8.06 (2H, dd, J = 1.5, 8.4 Hz, H-10, H-14). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.6(4 × CH_3, $COCH_3$); 61.3 (C-7); 61.8 (C-6′); 68.2(C-4′); 70.9(C-2′); 72.0(C-5′); 72.6(C-3′); 99.4(C-1′); 115.9(C-6); 123.6(C-4); 126.4(C-2); 128.4(C-11, C-13); 129.3(C-3); 129.6(C-5, C-10, C-14); 130.0(C-9); 133.1 (C-12);154.4(C-1); 166.2(C-8); 169.3, 170.2, 170.5(4 × C, $COCH_3$). HRESIMS Calcd for $C_{28}H_{30}O_{12}$ 581,16295 $[M+Na]^+$. Found 581,19996 $[M+Na]^+$.

3.9.2. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5-acetyloxy benzylbenzoate (salireposide pentaacetate) (15)

Was obtained from glycoside (**12**) and benzoylchloride. Yield 45%, mp 127–128 °C. UV λ_{max} (EtOH)/nm: 225, 274. IR (KBr, ν_{max}/cm^{-1}): 2940 (C-H); 1752 (C=O); 1603 (Ar) 1498 (Ar); 1375 (C–H); 1232 (C–O–C); 1085, 1043 (C–O); 908 (C–H); 708 (Ar). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.03, 2.05, 2.07, 2.08 (4 × 3H, s, $COCH_3$); 2.28 (3H, s, $COCH_3$); 3.83 (1H, m, H-5′); 4.15–4.31м (2H, m, H-6′a, H-6′b); 5.04–5.41м (4H, m, H-1′, H-2′, H-3′, H-4′); 5.28 (2H, m, H-7a, H-7b); 7.00 (1H, dd, J = 3.0, 9.0 Hz, H-5); 7.11 (1H, d, J = 8.7 Hz, H-6); 7.16 (1H, d, J = 2.7 Hz, H-3); 7.43 (2H, m, H-11, H-13); 7.55 (1H, m, H-12); 8.06 (2H, d, J = 7.2 Hz, H-10, H-14). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.6 (4×CH_3, $COCH_3$); 21.1 (CH_3, $COCH_3$); 60.9 (C-7); 61.8 (C-6′); 68.2(C-4′); 70.9(C-2′); 72.0(C-5′); 72.5(C-3′); 99.8(C-1′); 117.2(C-6); 122.0(C-5); 122.1(C-3); 128.0(C-2); 128.4(C-11, C-13); 129.7(C-9, C-10, C-14); 133.1(C-12); 146.3(C-4); 151.8(C-1); 166.1(C-8); 169.3, 169.6, 170.2, 170.5(5 × C,$COCH_3$).

3.9.3. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5-acetyloxy benzyl (4-acetoxy) cinnamoate (populoside A hexaacetate) (16)

Was obtained from glycoside (**12**) and 4-acetyloxycynnamoyl chloride. Yield 42%, mp 113–114 °C. UV λ_{max} (EtOH)/nm: 218, 283. IR (KBr, ν_{max}/cm^{-1}): 2940 (C–H); 1752(C=O); 1640, 1603 (Ar) 1508 (Ar); 1373 (C–H); 1222 (C–O–C); 1037 (C–O); 907 (C–H); 838 (Ar). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.03, 2.04, 2.07, 2.11 (4 × 3H, s, $COCH_3$); 2,28 (3H, s, $COCH_3$); 2.30 (3H, s, $COCH_3$); 3.84 (1H, m, H-5′); 4.16–4.30 (2H, m, H-6′a, H-6′b); 5.03–5.31 (4H, m, H-1′, H-2′, H-3′, H-4′); 5.29 (2H, m, H-7a, H-7b); 6.40 (1H, d, J = 16.2 Hz, H-9,); 6.98 (1H, dd, J = 2.7, 8.7 Hz, H-5); 7.10 (4H, m, H-3, H-6, H-13,H-15); 7.53 (2H, d, J = 8.7 Hz, H-12, H-16); 7.67 (1H, d, J = 15.9 Hz, H-10). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20. 6 (4 × CH_3, $COCH_3$); 21.1(2 × CH_3, $COCH_3$); 60.5(C-7); 61.8(C-6′); 68.2(C-4′); 70.9(C-2′); 72.0(C-5′); 72.6(C-3′); 99.8(C-1′); 117.2 (C-9); 117.7(C-6); 122.1(C-3, C-5, C-13, C-15); 127.9(C-2); 129.3(C-12, C-16); 132.0(C-11); 144.2(C-4, C-10); 146.3(C-1); 151.9(C-14); 166.3(C-8); 169.1, 169.3, 169.6, 170.2, 170.5(6 × C, $COCH_3$). HRESIMS Calcd for $C_{34}H_{36}O_{16}$ 723,18956 $[M+Na]^+$. Found 723,18345 $[M+Na]^+$.

3.9.4. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-benzyl (4-acetoxy) cinnamoate (populoside B pentaacetate) (17)

Was obtained from glycoside (**11**) and 4-acetyloxycynnamoyl chloride. Yield 30%, mp 123–124 °C. UV λ_{max} (EtOH)/nm: 283. IR (KBr, ν_{max}/cm^{-1}): 2963 (C–H); 1748, 1714 (C=O); 1641, 1603 (Ar) 1509, 1495 (Ar); 1373 (C–H); 1230 (C–O); 1068, 1036 (C–O); 910 (C–H); 763(Ar). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.04, 2.04, 2.07, 2.10 (4 × 3H, s, $COCH_3$); 2,31 (3H, s, $COCH_3$); 3.88 (1H, m, H-5′); 4.17–4.32 (2H, m, H-6′a, H-6′b); 5.09–5.32 (4H, m, H-1′, H-2′, H-3′, H-4′); 5.27 (2H, m, H-7a, H-7b); 6.41 (1H, d, J = 15.9 Hz, H-9); 7.08 (4H, m, H-4, H-6, H-13, H-15); 7.29 (1H, m, H-3); 7.39 (1H, d, J = 7.2 Hz, H-5); 7.53 (2H, d, J = 8.4 Hz, H-12, H-16); 7.67 (1H, d, J = 15.9 Hz, H-10). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.6 (4 × CH_3, $COCH_3$); 21.1(CH_3, $COCH_3$); 61.0(C-7); 61.9(C-6′); 68.3(C-4′); 71.0(C-2′); 72.0(C-5′); 72.6(C-3′); 99.4(C-1′); 115.9(C-6); 118.0(C-9); 122.1(C-13, C-15); 123.6(C-4); 126.3(C-2); 129.2(C-5); 129.4(C-3); 129.5(C-12, C-16); 132.1(C-11); 144.0(C-10); 152.1(C-1); 154.5(C-14); 166.5(C-8); 169.1, 169.4, 170.2, 170.5(5 × C, $COCH_3$). HRESIMS Calcd for $C_{32}H_{34}O_{14}$ 665,18408 $[M+Na]^+$. Found 665,17862 $[M+Na]^+$.

3.9.5. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-benzyl (4-acetoxy-3-methoxy) cinnamoate (populoside C pentaacetate) (18)

Was obtained from glycoside (**11**) and 3-methoxy-4-acetyloxycynnamoyl chloride. Yield 55%, mp 91–92 °C. UV λ_{max} (EtOH)/nm: 281. IR (KBr, ν_{max}/cm^{-1}): 3019, 2941 (C-H); 1762, 1718 (C=O); 1643, 1602 (Ar) 15.15, 1496 (Ar); 1373 (C–H); 1284, 1228 (C–O–C); 1036 (C–O); 908 (C–H); 760(Ar). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.03, 2.04, 2.06, 2.09 (4 × 3H, s, $COCH_3$); 2,31 (3H, $COCH_3$); 3.85 (4H, s, OCH_3; 1H, H-5′); 4.17–4.31 (2H, m, H-6′a, H-6′b); 5.09–5.31 (4H, m, H-1′, H-2′, H-3′, H-4′); 5.27 (2H, m, H-7a, H-7b); 6.40 (1H, d, J = 15.9 Hz, H-9); 7.02 (2H, m, H-4, H-6); 7.10 (3H, m, H-12, H-15, H-16); 7.29 (2H, m, H-3, H-5); 7.64 (1H, d, J = 15.9 Hz, H-10). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 20.6 (5 × CH_3, $COCH_3$); 55.9 (OCH_3); 61.1(C-7); 61.9(C-6′); 68.3(C-4′); 71.0(C-2′); 72.0(C-5′); 72.6(C-3′); 99.4(C-1′); 111.3 (C-12); 115.9(C-6); 118.1(C-9); 121.3(C-16); 123.3(C-4); 123.6 (C-15); 126.3 (C-2,); 129.5(C-5); 129.6(C-3); 133.3(C-11); 141.5 (C-14); 144.4(C-10); 151.4(C-1); 154.6(C-13); 166.4(C-8); 168.7, 169.4, 170.2, 170.5(5 × C, $COCH_3$). HRESIMS Calcd for $C_{33}H_{36}O_{15}$ 695,19464 $[M+Na]^+$. Found 695,19193 $[M+Na]^+$.

3.10. Selective acetyl group cleavage. General method

To a glycoside (**14**, **15**, **17**–**19**) (0.15 mmol) in a mixture of 96%-ethanol and $CHCl_3$ in proportion 1.5–0.5 mL was added 0.5 mL 36% HCl. The reaction mixture was stirred and then kept at room temperature for a 24–48 h. The reaction mixture was neutralized with 20%-solution of Na_2CO_3 until pH 7, evaporated to dryness and product was isolated employing column chromatography by gradient elution using chloroform and chloroform–ethanol mixture (from ratio 9:1 to 4:1). Analytical samples were purified by recrystallization from ethanol.

3.10.1. Desoxysalireposide (19)

Yield 85% mp 149–150 °C. IR (KBr, ν_{max}/cm^{-1}): 3361 (OH); 2930, 2890 (C–H); 1716 (C=O); 1635, 1604 (Ar) 1495, 1457 (Ar); 1381 (C–H); 1282, 1247 (C–O); 1094, 1046 (C–O); 712 (C–O–C). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 3.18–3.45 (4H, m, H-2′, H-3′, H-4′, H-5′); 3.48 (1H, m, H-6′b); 3.72 (1H, m, H-6′a); 4.88 (1H, m, H-1′); 5.38 (1H, d, J = 12.9 Hz, H-7b), 5.44 (1H, d, J = 13.2 Hz, H-7a); 7.03 (1H, m, H-4); 7.18 (1H, d, J = 7.8 Hz, H-6); 7.31 (1H, m, H-5); 7.39 (1H, d, J = 7.2 Hz, H-3); 7.51 (2H, t, J = 7.2 Hz, H-11, H-13); 7.64 (1H, d, J = 7.2 Hz, H-12); 8.01 (2H, d, J = 7.2 Hz, H-10, H-14). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 60.7 (C-7) 61.7(C-6′); 69.7(C-4′); 73.3(C-2′); 76.5(C-3′); 77.1 (C-5′); 101.0 (C-1′); 115.1 (C-6); 121.9(C-4); 124.9(C-2); 128.8 (C-11, C-13, C-3); 129.3 (C-10, C-14); 129.4 (C-5); 129.7 (C-9); 133.4(C-12); 155.2 (C-1); 165.7 (C-8). HRESIMS Calcd for $C_{20}H_{22}O_8$ 413.12069 $[M+Na]^+$. Found 413.12362 $[M+Na]^+$.

3.10.2. *iso*-Salireposide (20)

Yield 83%, mp 168–171 °C. UV λ_{max} (EtOH)/nm: 228, 273. ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 4.46 (1H, dd, J = 12.6, 6.0 Hz, H-6′a); 4.64 (2H, m, H-6′a, H-7b); 4.78 (1H, d, J = 8.0 Hz, H-7a); 5.06 (1H, d, J = 7.5 Hz, H-4′); 5.13 (1H, m, H-3′); 5.18 (1H, t, J = 7.5 Hz, H-2′);5.42 (1H, d, J = 6.0 Hz, H-1′); 7.16 (1H, dd, J = 12.0, 1.5 Hz, H-

5); 7.14 (1H, m, H-3); 7.21 (1H, m, H-6); 7.58 (2H, t, J = 7.5 Hz, H-11, H-13); 7.72 (1H, d, J = 7.5 Hz, H-12); 8.11 (2H, d, J = 7.2 Hz, H-10, H-14). Not specified a signal of a proton H-5′, overlapped by signal of the solvent. ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 57.8 (C-7); 60.9(C-6′); 69.9(C-4′); 73.1(C-2′); 76.1(C-3′); 77.0 (C-5′); 101.7 (C-1′); 115.5 (C-6); 120.0(C-3); 120.5(C-5); 129.1 (C-11, C-13); 129.8 (C-10, C-14); 131.8 (C-2); 133.0 (C-9); 134.1(C-12); 145.1 (C-4); 152.0 (C-1); 165.0 (C-8). HRESIMS Calcd for $C_{20}H_{22}O_9$ 429.12632 $[M+Na]^+$. Found 429.12852 $[M+Na]^+$.

3.10.3. Salireposide (1)

Yield 71%, mp 206–207 °C, lit.[6] 206–207 °C. UV λ_{max} (H_2O)/nm: 226, 284. IR (KBr, ν_{max}/cm^{-1}): 3370 (OH); 2931, 2890 (C–H); 1709 (C=O); 1602 (Ar) 1453, 1478 (Ar); 1382 (C–H); 1284 (C–O); 1214 (C–O); 1084, 1049 (C–O); 907 (C–H); 711 (C–O–C). The infrared spectrum coincides with the infrared spectrum of salireposide isolated from *P. tremula*. ^{1}H NMR (MeOD-d_4, 300 MHz) δ: 3.31–3.47 (4H, m, H-2′, H-3′, H-4′, H-5′); 3.60–3.89 (2H, m, H-6′a, H-6′b); 5.39 (2H, m, H-7a, H-7b); 6.75 (1H, d, J = 7.2 Hz, H-5); 6.88 (1H, s, H-3); 7.11 (1H, d, J = 8.7 Hz, H-6); 7.49 (2H, d, J = 7.8 Hz, H-10, H-13); 7.60 (1H, d, J = 7.5 Hz, H-12); 8.04 (2H, J = 7.5 Hz, H-10, H-14). Not specified a signal of a proton H-1′, overlapped by signal of the solvent. ^{13}C NMR (MeOD-d_4, 75.5 MHz) δ: 62.4 (C-7) 63.2(C-6′); 71.0(C-4′); 74.8(C-2′); 77.8 (C-3′, C-5′); 103.1 (C-1′); 116.1 (C-3); 117.0(C-5); 119.1(C-6); 128.5 (C-2); 129.7(C-11, C-13); 130.5 (C-10, C-14); 131.1(C-9); 134.3(C-12); 149.7(C-1); 154.0 (C-4); 168.7(C-8). The data agree well with those given in.[6]

3.10.4. Populoside A (2)

Yield 72%, mp 162–163 °C, lit.[7] 162–163 °C. UV λ_{max} (H_2O)/nm: 226, 314 nm. IR (KBr, ν_{max}/cm^{-1}): 3400 (OH); 2925, 2887 (C-H); 1678 (C=O); 1606 (C=C Ar) 1515 (Ar); 1464 (C–H); 1210 (C–O); 1079, 1043 (C–O); 979 (HC=CH); 870 (C–H); 830 (C–O–C). ^{1}H NMR (MeOD-d_4, 300 MHz) δ: 3.31–3.48 (4H, m, H-2′, H-3′, H-4′, H-5′); 3.63 (1H, m, H-6′b); 3.86 (1H, d, J 12.0 Hz, H-6′a); 5.24 (1H, d, J = 12.9 Hz, H-7b); 5.34 (1H, d, J = 12.6 Hz, H-7a); 6.36 (1H, d, J = 15.9 Hz, H-9); 6.73 (1H, dd, J = 1.5, 8.4 Hz, H-5); 6.82 (1H, d, J = 2.7 Hz, H-3); 6.84 (2H, m, H-13, H-15); 7.10 (1H, d, J = 8.4 Hz, H-6); 7.46 (2H, d, J = 8.4 Hz, H-12, H-16); 7.64 (1H, d, J = 15.9 Hz, H-10). Not specified a signal of a proton H-1′, overlapped by signal of the solvent. ^{13}C NMR (MeOD-d_4, 75.5 MHz) δ: 62.4(C-7, C-6′); 71.2(C-4′); 74.8(C-2′); 77.8(C-3′, C-5′); 104.1(C-1′); 115.0 (C-3, C-5; C-9); 116.9 (C-13, C-15); 119.1 (C-6); 127.1 (C-11); 128.6 (C-2); 131.3 (C-12, C-16); 147.0 (C-10); 149.8 (C-1); 153.6 (C-4); 161.0 (C-14); 169.4 (C-8). HRESIMS Calcd for $C_{22}H_{24}O_{10}$ 471.12617 $[M+Na]^+$. Found 471.12447 $[M+Na]^+$. The data agree well with those given in.[7]

3.10.5. Populoside B (3)

Yield 30%, mp 187–188 °C, lit.[7] 187–188 °C. UV λ_{max} (H_2O)/nm: 314 nm. IR (KBr, ν_{max}/cm^{-1}): 3388 (OH); 2927 (C–H); 1686 (C=O); 1605 (Ar) 1586 (Ar); 1241 (C–O); 1078 (C–O); 833 (C–O–C). ^{1}H NMR (MeOD-d_4, 300 MHz) δ: 3.31 (4H, m, H-2′, H-3′, H-4′, H-5′); 3.69 (1H, m, H-6′b); 3.88 (1H, d, J = 12.0 Hz, H-6′a,); 5.28 (2H, d, J = 12.9 Hz, H-7a, H-7b); 6.35 (1H, d, J = 15.9 Hz, H-9); 6.84 (2H, d, J = 8.4 Hz, H-13, H-15); 7.25 (1H, t, J = 7.2 Hz, H-4); 7.21 (1H, m, H-6); 7.30 (1H, m, H-5); 7.35 (1H, m, H-3); 7.46 (2H, d, J = 8.4 Hz, H-12, H-16); 7.64 (1H, d, J = 15.9 Hz, H-10). ^{13}C NMR (MeOD-d_4, 75.5 MHz) δ: 58.0 (C-7); 62.8 (C-6′); 71.2(C-4′); 75.0(C-2′); 77.9(C-3′, C-5′); 103.9(C-1′); 114.7 (C-9); 116.5 (C-6); 117.0(C-13, C-15); 123.5 (C-4); 127.0(C-11); 130.2 (C-3); 130.5(C-5); 131.2(C-12, C-16); 147.0 (C-10); 156.9(C-1); 161.9 (C-14); 169.9(C-8). HRESIMS Calcd for $C_{22}H_{24}O_9$ 455.14205 $[M+Na]^+$. Found 455.13659 $[M+Na]^+$. The data agree well with those given in.[7]

3.10.6. Populoside C (4)

Yield 50%, mp 107–109 °C, lit.[7] 109–111 °C. UV λ_{max} (H_2O)/nm: 234, 327 nm. IR (KBr, ν_{max}/cm^{-1}): 3370 (OH); 2927 (C–H); 1688 (C=O); 1615 (Ar) 1589, 1522, 1450 (Ar); 1285, 1241, 1185 (C–O); 1079 (C–O); 980 (C–O -C), 751 (Ar). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 3.20–3.39 (4H, m, H-2′, H-3′, H-4′, H-5′); 3.69, 3.75 (2H, m, H-6′a, H-6′b); 3.81 (3H, s, OCH_3); 4.86 (1H, m, H-1′); 5.28 (2H, m, H-7a, H-7b); 6.53 (1H, d, J = 15.9 Hz, H-9); 6.78 (1H, d, J = 7.5 Hz, H-15); 7.03 (1H, m, H-16); 7.12 (2H, m, H-4, H-6); 7.33 (3H, m, H-3, H-5, H-12); 7.58 (1H, d, J = 15.6 Hz, H-10). ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ: 56.1 (OCH_3); 60.7 (C-7, C-6′); 69.7(C-4′); 73.3(C-2′); 76.5(C-3′); 77.1(C-5′); 101.0(C-1′); 111.2 (C-12); 114.4 (C-9); 115.0(C-6); 115.5(C-15); 121.8 (C-4); 123.3(C-16); 125.2 (C-2); 125.6(C-11); 128.7(C-3); 129.3(C-5); 145.3 (C-10); 147.9(C-14); 149.4(C-13); 155.2(C-1); 166.6(C-8). HRESIMS Calcd for $C_{23}H_{26}O_{10}$ 485.14182 $[M+Na]^+$. Found 485.13927 $[M+Na]^+$. The data agree well with those given in.[7]

Acknowledgements

We would like to thank Head of the Laboratory of Petrochemical Synthesis, NIOST LLC (Tomsk), Kolesnik Vasiliy Dmitrievich and operator Zamanova Margarita Karimovna for assistance in obtaining spectral data of certain compounds. This work was supported by the scientific program "Nauka" N 3060.2012.

Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra of compounds **1–4**, **6a**, **6b**, **8–19**, IR spectra of Salireposide (**1**) isolated from *P. tremula* bark and obtained by synthetic means and UV spectra of selected compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.10.006.

References

1. Babst, B. A.; Harding, S. A.; Tsai, C. J. *J. Chem. Ecol.* **2010**, *36*, 286.
2. Boeckler, G. A.; Gershenzon, J.; Unsicker, S. B. *Phytochemistry* **2011**. http://dx.doi.org/10.1016/j.phytochem.2011.01.038.
3. Van Hoof, J.; Torre, J.; Corthout, L. A. *J. Nat. Prod.* **1989**, *2*, 875.
4. Lee, K. H.; Yang, M. C. *Molecules* **2008**, *13*, 41.
5. Choudhary, M. I.; Fatima, N.; Abbasi, M. A.; Jalil, S.; Ahmad, V. U.; Atta-ur-Rahman *Bioorg. Med. Chem.* **2004**, *12*, 5793.
6. Ahmad, V. U.; Abbasi, M. A.; Zubair, M.; Fatima, N.; Farooq, U.; Choudhary, M. I. *Helv. Chim. Acta* **2004**, *87*, 67.
7. Zhang, X. F.; Thuong, P. T.; Min, B. S. *J. Nat. Prod.* **2006**, *69*, 1370.
8. Rabate, M. J. *Bull. Soc. Chim. Biol.* **1935**, *17*, 328.
9. Wattiez, M. N. *Bull. Soc. Chim. Biol.* **1931**, *13*, 658.
10. Pearl, A.; Darling, S. F. *J. Org. Chem.* **1959**, *24*, 1616.
11. Ekabo, O. A.; Farnsworth, N. R.; Santisuk, T.; Reutrakul, V. *Phytochemistry* **1993**, *32*, 747.
12. Ahmad, V. U.; Abbasi, M. A.; Hussain, H.; Akhtar, M. N.; Farooq, U.; Fatima, N.; Choudhary, M. I. *Phytochemistry* **2003**, *63*, 217.
13. Abbasi, M. A.; Ahmad, V. U.; Zubair, M.; Fatima, N.; Farooq, U.; Hussain, S.; Lodhi, M. A.; Choudhary, M. I. *Planta Med.* **2004**, *70*, 1189.
14. Si, C. L.; Kim, J. K.; Bae, Y. S.; Li, S. M. *Planta Med.* **2009**, *75*, 1165.
15. Thieme, H.; Benecke, R. *Pharmazie* **1970**, *25*, 492.
16. Richtmyer, N. K.; Yeakel, E. H. *J. Am. Chem. Soc.* **1934**, *56*, 2495.
17. Lee, Y. S.; Kim, B. T. U.S. Patent 20040260114A1, 2001, KR.
18. Furuya, T.; Ayabe, S.; Kobayashi, M. U.S. Patent 4089606, 1978, US.
19. Giam, C. S.; Goldschmid, H. R.; Perlin, A. S. *Can. J. Chem.* **1963**, *39*, 2025.
20. Brown, H. C.; Mead, E. J.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1955**, *77*, 6209.
21. Raber, D. J.; Guida, W. C. *J. Org. Chem.* **1976**, *41*, 690.
22. Chaikin, S. W.; Brown, W. G. *J. Am. Chem. Soc.* **1955**, *77*, 6209.
23. Zakis, G. F. *Synthesis of Modeled Lignin Compounds*; Zinatne: Riga, 1980. 288.
24. Josephson, K. *Chem. Ber.* **1929**, *62*, 317.
25. Pozsgay, V. *J. Am. Chem. Soc.* **1995**, *117*, 6673.
26. Corey, E. J.; Clark, D. A.; Goto, G.; Marfat, A.; Mioskowski, C.; Samuelsson, B.; Hammarstroem, S. *J. Am. Chem. Soc.* **1980**, *102*, 1436.
27. Byramova, N. E.; Ovchinnikov, M. V.; Backinowsky, L. V.; Kochetkov, N. K. *Carbohydr. Res.* **1983**, *124*, C8.
28. Beier, R. C.; Mundy, B. P.; Strobel, G. A. *Can. J. Chem.* **1980**, *58*, 2800.
29. Thieme, H.; Benecke, R. *Die Pharmazie.* **1970**, *25*, 780.

30. Pearl, I. A.; Darling, S. F. *J. Org. Chem.* **1959**, *24*, 731.
31. Mizuno, M.; Kato, M.; Misu, C.; Iinuma, M.; Tanaka, T. *J. Nat. Prod.* **1991**, *54*, 1447.
32. Pearl, I. A.; Darling, S. F. *Arch. Biochem. Biophys.* **1963**, *102*, 33.
33. Buess, Ch. M.; Giudici, T.; Kharasch, N.; King, W.; Lawson, D. D.; Saha, N. N. J. *Med. Chem.* **1965**, *8*, 469.