

Simplified stereoselective synthesis of triterpene 3-*O*-2-deoxy- $\alpha$ -D-glycosides

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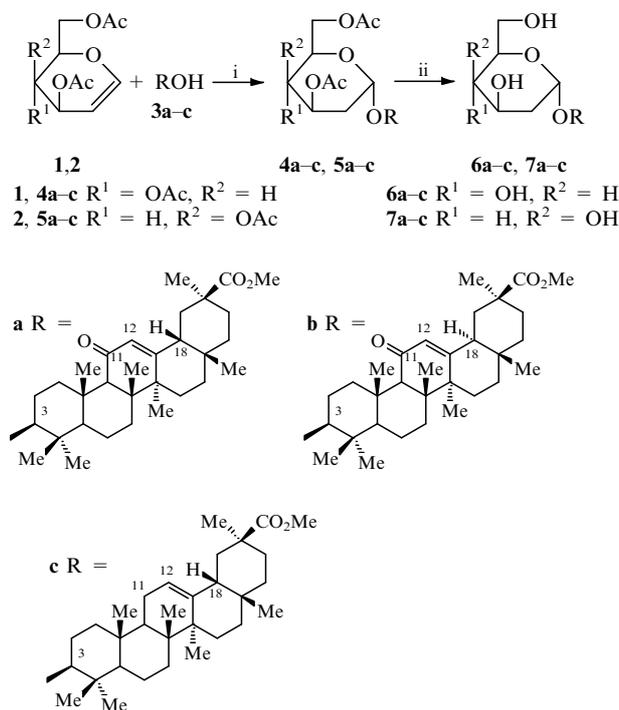
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3-*O*-2-Deoxy- $\alpha$ -D-glycosides of glycyrrhetic acid derivatives are stereoselectively synthesized *via* electrophilic glycosylation of triterpene alcohols by D-glucal and D-galactal acetates in the presence of anhydrous sulfonic acid cation exchange resins and lithium bromide.

Triterpene glycosides are widely distributed in nature and are known for their diverse biological activity.<sup>1</sup> The synthesis of glycoside analogues from medicinal plants (ginseng, licorice *etc.*) has attracted a great deal of attention over the last few years and compounds of improved pharmacological properties were obtained.<sup>2–4</sup> Earlier<sup>5,6</sup> we carried out an enantiospecific synthesis of the oleanane type triterpene 3-*O*-2-deoxy- $\alpha$ -D-glycosides from biologically active triterpene alcohols and D-glucal acetate in the presence of iodine containing activators *N*-iodosuccinimide (NIS) and di(sym-collidine)iodonium perchlorate (IDCP). The shortcomings of this method are that it is multistage and that it gives unsatisfactory yields since the glycosylation of complex alcohols occurs *via* the formation of 2-deoxy-2-iodo-glycoside intermediates.

Here we report the direct syntheses of triterpene 3-*O*-2-deoxy- $\alpha$ -D-glycosides from triterpene alcohols and acylated glycals in the presence of anhydrous sulfonic acid cation exchange resins and lithium bromide *via* a simplified route without the need to obtain 2-deoxy-2-iodo-glycosides and hence to deiodinate them *via* catalytic hydrogenolysis. The complex biologically active triterpene 2-deoxy- $\alpha$ -D-glycosides were synthesised by the method used by Sabesan and Neira<sup>7</sup> to synthesise 2-deoxy-sugars. 3,4,6-Tri-*O*-acetyl-D-glucal **1** and D-galactal **2** were used as glycosyl donors and the biologically active triterpenoids of licorice root extract, 18 $\beta$ - and 18 $\alpha$ -glycyrrhetic acids **3a** and **3b**, 11-deoxo analogue **3c** as methyl esters were used as the alcohol components. The glycosylation was carried out in methylene dichloride–acetonitrile (1:1, v/v) with an equimolecular mixture of glycals **1,2** and triterpene alcohols **3a–c** in the presence of cation exchange resins (KU-2-8, DOWEX-50) in the H<sup>+</sup>-form with lithium bromide and anhydrous molecular sieves (4A) at room temperature. Glycosides **4a–c**, **5a–c**<sup>†</sup> were formed after 2–3 h in a 76.9–79.8% yield after chromatographic purification. Deacetylation with a 5% methanolic solution of KOH led to the triterpene 3-*O*-2-deoxy- $\alpha$ -D-glycosides **6a–c**, **7a–c**<sup>‡</sup> in 86.7–88.4% yields (Scheme 1).

The glycoside structures were assigned by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker AM-300 spectrometer at 300 and 75.5 MHz) by comparison with literature data for aglycons<sup>8–10</sup> 2-deoxy- $\alpha$ -glycosides.<sup>7,11,12</sup> The chromatographic mobility and physico-chemical properties of the newly synthesized compounds were



**Scheme 1** Reagents: i, cation exchange resin, LiBr, CH<sub>2</sub>Cl<sub>2</sub>, MeCN; ii, 5% KOH/MeOH.

<sup>†</sup> Selected data for **4a**: C<sub>43</sub>H<sub>64</sub>O<sub>11</sub>, decomp. 217–219 °C; [α]<sub>D</sub><sup>20</sup> +87±3° (c 0.04, CHCl<sub>3</sub>); UV (MeOH), λ<sub>max</sub>/nm: 248.6 (lg ε 3.62); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 21.8 (C2), 82.8 (C3), 200.3 (C11), 128.6 (C12), 169.3 (C13), 177.0 (C30), 51.9 (C31), 93.2 (C1'), 35.7 (C2'), 69.1 (C3'), 68.3 (C4'), 69.3 (C5'), 62.5 (C6'), 170.1, 170.3, 170.8 (OCOCH<sub>3</sub>), 20.8, 20.9, 21.1 (OCOCH<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, J/Hz): 0.80, 0.85, 1.01, 1.12, 1.14, 1.35 (s, 7CH<sub>3</sub>), 1.20–1.95 (m, CH<sub>2</sub>, CH of aglycone), 1.80–2.25 (m, 2H, H2'), 2.01, 2.03, 2.08 (s, 3Ac), 2.32 (s, 1H, H9), 2.82 (d, 1H, H18, J 13.8), 3.19 (dd, 1H, H3, J<sub>3,2e</sub> 4.7, J<sub>3,2a</sub> 11.7), 3.68 (s, 3H, OCH<sub>3</sub>), 4.00–4.10 (m, 2H, H6'), 4.26 (dd, 1H, H5', J<sub>4',5'</sub> 9.7, J<sub>5',6'</sub> 6.0), 4.99 (t, 1H, H4', J<sub>3',4'</sub> = J<sub>4',5'</sub> 9.7), 5.16 (br. s, 1H, H1'), 5.22–5.38 (m, 1H, H3'), 5.66 (s, 1H, H12).

For **4b**: C<sub>43</sub>H<sub>64</sub>O<sub>11</sub>, decomp. 168–170 °C; [α]<sub>D</sub><sup>20</sup> +98±3° (c 0.09, CHCl<sub>3</sub>); UV (MeOH), λ<sub>max</sub>/nm: 245.6 (lg ε 4.21); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 21.8 (C2), 82.9 (C3), 199.7 (C11), 124.5 (C12), 165.7 (C13), 178.0 (C30), 51.9 (C31), 93.3 (C1'), 35.7 (C2'), 69.2 (C3'), 68.4 (C4'), 69.3 (C5'), 62.5 (C6'), 169.9, 170.2, 170.7 (OCOCH<sub>3</sub>), 20.8, 20.9, 21.1 (OCOCH<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, J/Hz): 0.71, 0.78, 0.84, 0.89, 0.96, 1.12, 1.20 (s, 7CH<sub>3</sub>), 1.20–2.00 (m, CH<sub>2</sub>, CH of aglycone), 1.60–2.00 (m, 2H, H2'), 2.01, 2.03, 2.08 (s, 3Ac), 2.15 (s, 1H, H9), 2.70 (d,

1H, H18, J 13.6), 3.14 (dd, 1H, H3, J<sub>3,2e</sub> 3.8, J<sub>3,2a</sub> 11.2), 3.69 (s, 3H, OCH<sub>3</sub>), 4.03–4.12 (m, 2H, H6'), 4.22 (dd, 1H, H5', J<sub>4',5'</sub> 9.7, J<sub>5',6'</sub> 6.1), 4.99 (t, 1H, H4', J<sub>3',4'</sub> = J<sub>4',5'</sub> 9.7), 5.16 (br. s, 1H, H1'), 5.20–5.28 (m, 1H, H3'), 5.57 (s, 1H, H12).

For **4c**: C<sub>43</sub>H<sub>66</sub>O<sub>10</sub>, mp 223–225 °C; [α]<sub>D</sub><sup>20</sup> +78±3° (c 0.04, CHCl<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 21.9 (C2), 83.0 (C3), 23.5 (C11), 122.5 (C12), 144.5 (C13), 177.7 (C30), 51.5 (C31), 93.3 (C1'), 35.8 (C2'), 69.3 (C3'), 68.4 (C4'), 69.7 (C5'), 62.6 (C6'); 169.7, 169.9, 170.8 (OCOCH<sub>3</sub>), 20.8, 20.9, 21.1 (OCOCH<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, J/Hz): 0.71, 0.76, 0.88, 0.91, 0.94, 1.05, 1.40 (s, 7CH<sub>3</sub>), 1.20–2.00 (m, CH<sub>2</sub>, CH of aglycone), 1.60–2.15 (m, 2H, H2'), 1.94, 1.98, 2.02 (s, 3Ac), 3.12 (dd, 1H, H3, J<sub>3,2e</sub> 3.7, J<sub>3,2a</sub> 11.5), 3.68 (s, 3H, OCH<sub>3</sub>), 3.98–4.06 (m, 2H, H6'), 4.21 (dd, 1H, H5', J<sub>4',5'</sub> 9.8, J<sub>5',6'</sub> 6.1), 4.92 (t, 1H, H4', J<sub>3',4'</sub> = J<sub>4',5'</sub> 9.8), 5.12 (d, 1H, H1', J<sub>1',2'e</sub> 1.4), 5.22–5.31 (m, 1H, H3'), 5.26 (br. s, 1H, H12).

For **5a**: C<sub>43</sub>H<sub>64</sub>O<sub>11</sub>, decomp. 239–241 °C; [α]<sub>D</sub><sup>20</sup> +80±3° (c 0.06, CHCl<sub>3</sub>); UV (MeOH), λ<sub>max</sub>/nm: 248.2 (lg ε 3.66); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 21.8 (C2), 82.6 (C3), 200.3 (C11), 128.6 (C12), 169.4 (C13), 177.0 (C30), 51.8 (C31), 93.6 (C1'), 30.7 (C2'), 66.5 (C3'), 66.8 (C4'), 67.0 (C5'), 62.6 (C6'), 170.2, 170.4, 170.6 (OCOCH<sub>3</sub>), 20.8, 20.9, 21.0

also compared with those of glycosides obtained earlier using NIS- and IDCP-methods.<sup>5,6</sup>

The reaction results in  $\alpha$ -glycosides which seems bound by steric factors caused by bulk aglycons.  $\beta$ -Anomers were not observed by TLC and NMR.  $^{13}\text{C}$  NMR spectra of the aglycone fragments of synthesized glycosides were similar to those of the initial triterpenes. In the  $^{13}\text{C}$  NMR spectra of 2-deoxy-glycosides **4–7** signals due to carbinol atoms at C-3 were observed at 81.7–83.0 ppm. On going from alcohols **3a–c** to the glycosides **4a–c**, **5a–c** the C-3 signal is shifted to a lower field (3.9–4.7 ppm). The introduction of carbohydrate fragments in triterpenoid molecules also shifted the signals of the  $\alpha$ -carbon atoms in aglycon.

The signals of the C-2 atoms of glycosides **4–7** were shifted to a higher field (5.1–5.7 ppm). The anomeric carbon atoms at C-1' of the pyranose residues in the spectra of compounds **4–7** resonate at 93.2–93.6 ppm, which provides evidence for the formation of  $\alpha$ -glycoside linkages and the axial position of aglycons.<sup>13,14</sup> The  $\alpha$ -configuration of glycoside linkages and the diequatorial location of H-1' and H-2' protons in glycoside molecules **4a–c**, **5a–c** were confirmed by the presence of a doublet of anomeric protons (H-1') at a low field (5.12–5.18 ppm) with a small spin–spin coupling constant (SSCC) ( $J_{1',2'}$  1.3 Hz **4b**, 1.4 Hz **4c** and 1.2 Hz **5b**) or by broad singlets for **4a**, **5a,c**. Protons H-2' of glycosides **4a–c**, **5a–c** resonate at 1.60–2.30 ppm. SSCC values for compounds **4a–c** [ $J_{3',4'} = J_{4',5'}$  9.7 (9.8),  $J_{5',6'}$  6.0 (6.1) Hz] demonstrate the axial position of protons H-3', H-4' and H-5'. The chemical shifts of protons H-1'–H-6' and their mutual location in glycosides **4a–c** confirm the  $\alpha$ -D-arabinohexopyranose configuration and  $^4\text{C}_1$  (D)-conformation for the carbohydrate rings of these compounds.

The chemical shifts of the protons and their SSCC values [ $J_{4',5'} = J_{5',6'}$  6.2 (6.3) Hz] in the  $^1\text{H}$  NMR spectra of **5a–c** (protons H-4'–H-5' are equatorial–axial) confirm the  $\alpha$ -D-lixohexopyranose configuration and  $^4\text{C}_1$  (D)-conformation of these compounds.

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## References

- 1 Th. Schopke and K. Hiller, *Pharmazie*, 1990, **45**, 313.

(OCOCH<sub>3</sub>);  $^1\text{H}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm, J/Hz): 0.80, 0.82, 1.01, 1.13, 1.16, 1.35 (s, 7CH<sub>3</sub>), 1.25–1.95 (m, CH<sub>2</sub>, CH of aglycone), 1.70–2.30 (m, 2H, H<sub>2'</sub>), 1.99, 2.04, 2.14 (s, 3Ac), 2.31 (s, 1H, H<sub>9</sub>), 2.83 (d, 1H, H<sub>18</sub>, J 13.6), 3.20 (dd, 1H, H<sub>3</sub>,  $J_{3,2e}$  4.5,  $J_{3,2a}$  11.3), 3.69 (s, 3H, OCH<sub>3</sub>), 4.07–4.12 (m, 2H, H<sub>6'</sub>), 4.27 (t, 1H, H<sub>5'</sub>,  $J_{4',5'} = J_{5',6'}$  6.3), 5.17 (br. s, 1H, H<sub>1'</sub>), 5.22–5.33 (m, 1H, H<sub>3'</sub>), 5.36 (br. s, 1H, H<sub>4'</sub>), 5.66 (s, 1H, H<sub>12</sub>).

For **5b**: C<sub>43</sub>H<sub>64</sub>O<sub>11</sub>, decomp. 185–187 °C;  $[\alpha]_{\text{D}}^{20} + 125 \pm 4^\circ$  (c 0.06, CHCl<sub>3</sub>); UV (MeOH),  $\lambda_{\text{max}}/\text{nm}$ : 246.4 (lg  $\epsilon$  4.23);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 22.0 (C<sub>2</sub>), 82.8 (C<sub>3</sub>), 200.0 (C<sub>11</sub>), 124.2 (C<sub>12</sub>), 166.0 (C<sub>13</sub>), 178.9 (C<sub>30</sub>), 51.9 (C<sub>31</sub>), 93.5 (C<sub>1'</sub>), 30.9 (C<sub>2'</sub>), 66.6 (C<sub>3'</sub>), 66.9 (C<sub>4'</sub>), 67.1 (C<sub>5'</sub>), 62.4 (C<sub>6'</sub>), 169.9, 170.2, 170.3 (OCOCH<sub>3</sub>), 20.8, 20.9, 21.1 (OCOCH<sub>3</sub>);  $^1\text{H}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm, J/Hz): 0.70, 0.87, 0.96, 1.12, 1.19, 1.36 (s, 7CH<sub>3</sub>), 1.15–2.00 (m, CH<sub>2</sub>, CH of aglycone), 1.60–2.00 (m, 2H, H<sub>2'</sub>), 1.98, 2.05, 2.11 (s, 3Ac), 2.21 (s, 1H, H<sub>9</sub>), 2.69 (d, 1H, H<sub>18</sub>, J 13.7), 3.17 (dd, 1H, H<sub>3</sub>,  $J_{3,2e}$  4.0,  $J_{3,2a}$  11.3), 3.69 (s, 3H, OCH<sub>3</sub>), 4.07–4.11 (m, 2H, H<sub>6'</sub>), 4.28 (t, 1H, H<sub>5'</sub>,  $J_{4',5'} = J_{5',6'}$  6.2), 5.18 (d, 1H, H<sub>1'</sub>,  $J_{1',2'e}$  1.2), 5.22–5.30 (m, 1H, H<sub>3'</sub>), 5.35 (br. s, 1H, H<sub>4'</sub>), 5.57 (s, 1H, H<sub>12</sub>).

For **5c**: C<sub>43</sub>H<sub>66</sub>O<sub>10</sub>, mp 200–202 °C;  $[\alpha]_{\text{D}}^{20} + 79 \pm 3^\circ$  (c 0.05, CHCl<sub>3</sub>);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 21.8 (C<sub>2</sub>), 82.9 (C<sub>3</sub>), 23.5 (C<sub>11</sub>), 122.5 (C<sub>12</sub>), 144.4 (C<sub>13</sub>), 177.7 (C<sub>30</sub>), 51.6 (C<sub>31</sub>), 93.2 (C<sub>1'</sub>), 30.8 (C<sub>2'</sub>), 66.5 (C<sub>3'</sub>), 66.9 (C<sub>4'</sub>), 67.0 (C<sub>5'</sub>), 62.5 (C<sub>6'</sub>), 169.8, 170.2, 170.8 (OCOCH<sub>3</sub>);  $^1\text{H}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm, J/Hz): 0.77, 0.81, 0.89, 0.95, 0.96, 1.00, 1.12 (s, 7CH<sub>3</sub>), 1.15–2.00 (m, CH<sub>2</sub>, CH of aglycone), 1.60–2.00 (m, 2H, H<sub>2'</sub>), 1.99, 2.05, 2.17 (s, 3Ac), 3.20 (dd, 1H, H<sub>3</sub>,  $J_{3,2e}$  4.0 Hz,  $J_{3,2a}$  11.0), 3.68 (s, 3H, OCH<sub>3</sub>), 4.02–4.15 (m, 2H, H<sub>6'</sub>), 4.28 (t, 1H, H<sub>5'</sub>,  $J_{4',5'} = J_{5',6'}$  6.3), 5.18 (br. s, 1H, H<sub>1'</sub>), 5.21–5.30 (m, 1H, H<sub>3'</sub>), 5.27 (br. s, 1H, H<sub>12</sub>), 5.35 (br. s, 1H, H<sub>4'</sub>).

- 2 L. N. Atopkina, N. F. Samoshina and N. I. Uvarova, *Khim. Prir. Soedin.*, 1989, **6**, 813 [*Chem. Nat. Compd. (Engl. Transl.)*, 1989, **6**, 690].
- 3 S. Saito, K. Kuroda, Y. Hayashi, Y. Sasaki, Y. Nagamera, K. Nishida and I. Ishiguro, *Chem. Pharm. Bull.*, 1991, **39**, 2333.
- 4 S. Saito, S. Sumita, Y. Kanda and Y. Sasaki, *Chem. Pharm. Bull.*, 1994, **42**, 1016.
- 5 L. A. Baltina, O. B. Flekhter, E. V. Vasil'eva and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1061 (*Russ. Chem. Bull.*, 1995, **44**, 1979).
- 6 L. A. Baltina, O. B. Flekhter and E. V. Vasil'jeva, *Mendelev Comm.*, 1996, 63.
- 7 S. Sabesan and S. Neira, *J. Org. Chem.*, 1991, **56**, 5468.
- 8 G. A. Tolstikov, L. M. Khalilov, L. A. Baltina, R. M. Kondratenko, A. A. Panasenko and E. V. Vasil'jeva, *Khim. Prir. Soedin.*, 1985, **5**, 645 [*Chem. Nat. Compd. (Engl. Transl.)*, 1985, **5**, 605].
- 9 H. Duddeck, M. H. A. Elgamal, G. S. Ricca, B. Danieli and G. Palmisano, *Org. Magn. Reson.*, 1978, **11**, 130.
- 10 G. S. Ricca, B. Danieli and G. Palmisano, *Org. Magn. Reson.*, 1978, **11**, 163.
- 11 R. W. Friesen and S. J. Danishefsky, *J. Am. Chem. Soc.*, 1989, **111**, 6656.
- 12 J. Tiem, S. Kopper and J. Schwenher, *Liebigs Ann. Chem.*, 1985, 2135.
- 13 S. Saito, Sh. Sumita, Y. Kanda and Y. Sasaki, *Chem. Pharm. Bull.*, 1994, **42**, 1016.
- 14 K. Tori, S. Seo, Y. Yoshimura, H. Arita and Y. Tomita, *Tetrahedron Lett.*, 1977, **2**, 179.

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<sup>†</sup>For **6a**: 3-O-2-deoxy- $\alpha$ -D-arabinohexopyranoside of 18 $\beta$ -glycyrrhetic acid methyl ester, decomp. 211 °C;  $[\alpha]_{\text{D}}^{20} + 97 \pm 3^\circ$  (c 0.08, CHCl<sub>3</sub>); lit.<sup>5,6</sup>: decomp. 210–212 °C;  $[\alpha]_{\text{D}}^{20} + 95^\circ$  (c 0.02, CHCl<sub>3</sub>).

For **6b**: 3-O-2-deoxy- $\alpha$ -D-arabinohexopyranoside of 18 $\alpha$ -glycyrrhetic acid methyl ester, C<sub>37</sub>H<sub>58</sub>O<sub>8</sub>, decomp. 140–142 °C;  $[\alpha]_{\text{D}}^{20} + 113 \pm 4^\circ$  (c 0.09, CHCl<sub>3</sub>); UV (MeOH),  $\lambda_{\text{max}}/\text{nm}$ : 245.8 (lg  $\epsilon$  4.27);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 21.8 (C<sub>2</sub>), 81.9 (C<sub>3</sub>), 199.9 (C<sub>11</sub>), 124.3 (C<sub>12</sub>), 165.9 (C<sub>13</sub>), 178.9 (C<sub>30</sub>), 52.0 (C<sub>31</sub>), 93.5 (C<sub>1'</sub>), 38.9 (C<sub>2'</sub>), 72.0 (C<sub>3'</sub>), 69.5 (C<sub>4'</sub>), 73.3 (C<sub>5'</sub>), 62.8 (C<sub>6'</sub>).

For **6c**: 3-O-2-deoxy- $\alpha$ -D-arabinohexopyranoside of 11-deoxy-18 $\beta$ -glycyrrhetic acid methyl ester, decomp. 213–215 °C;  $[\alpha]_{\text{D}}^{20} + 84 \pm 3^\circ$  (c 0.07, CHCl<sub>3</sub>); lit.<sup>5,6</sup>: decomp. 214–216 °C;  $[\alpha]_{\text{D}}^{20} + 83^\circ$  (c 0.05, CHCl<sub>3</sub>).

For **7a**: 3-O-2-deoxy- $\alpha$ -D-lyxohexopyranoside of 18 $\beta$ -glycyrrhetic acid methyl ester C<sub>37</sub>H<sub>58</sub>O<sub>8</sub>, decomp. 226–228 °C;  $[\alpha]_{\text{D}}^{20} + 88 \pm 3^\circ$  (c 0.05, CHCl<sub>3</sub>); UV (MeOH),  $\lambda_{\text{max}}/\text{nm}$ : 248.2 (lg  $\epsilon$  3.89);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 21.7 (C<sub>2</sub>), 81.8 (C<sub>3</sub>), 200.4 (C<sub>11</sub>), 128.6 (C<sub>12</sub>), 169.4 (C<sub>13</sub>), 177.0 (C<sub>30</sub>), 51.8 (C<sub>31</sub>), 93.6 (C<sub>1'</sub>), 33.3 (C<sub>2'</sub>), 65.9 (C<sub>3'</sub>), 69.6 (C<sub>4'</sub>), 70.2 (C<sub>5'</sub>), 64.3 (C<sub>6'</sub>).

For **7b**: 3-O-2-deoxy- $\alpha$ -D-lyxohexopyranoside of 18 $\alpha$ -glycyrrhetic acid methyl ester, C<sub>37</sub>H<sub>58</sub>O<sub>8</sub>, decomp. 163–166 °C;  $[\alpha]_{\text{D}}^{20} + 108 \pm 4^\circ$  (c 0.06, CHCl<sub>3</sub>); UV (MeOH),  $\lambda_{\text{max}}/\text{nm}$ : 246.2 (lg  $\epsilon$  4.20);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 21.7 (C<sub>2</sub>), 81.8 (C<sub>3</sub>), 199.3 (C<sub>11</sub>), 124.1 (C<sub>12</sub>), 165.9 (C<sub>13</sub>), 178.9 (C<sub>30</sub>), 51.9 (C<sub>31</sub>), 93.5 (C<sub>1'</sub>), 33.5 (C<sub>2'</sub>), 65.8 (C<sub>3'</sub>), 69.7 (C<sub>4'</sub>), 70.0 (C<sub>5'</sub>), 64.0 (C<sub>6'</sub>).

For **7c**: 3-O-2-deoxy- $\alpha$ -D-lyxohexopyranoside of 11-deoxy-18 $\beta$ -glycyrrhetic acid methyl ester, C<sub>37</sub>H<sub>60</sub>O<sub>7</sub>, mp 189–191 °C;  $[\alpha]_{\text{D}}^{20} + 82 \pm 3^\circ$  (c 0.06, CHCl<sub>3</sub>);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 21.8 (C<sub>2</sub>), 81.9 (C<sub>3</sub>), 23.6 (C<sub>11</sub>), 122.6 (C<sub>12</sub>), 144.5 (C<sub>13</sub>), 177.8 (C<sub>30</sub>), 51.7 (C<sub>31</sub>), 93.5 (C<sub>1'</sub>), 33.6 (C<sub>2'</sub>), 66.7 (C<sub>3'</sub>), 69.5 (C<sub>4'</sub>), 70.2 (C<sub>5'</sub>), 64.9 (C<sub>6'</sub>).