

## Transformation of 9 $\alpha$ ,14 $\alpha$ -epoxy-14-deoxy-20-hydroxyecdysone diacetone into 25-hydroxydachryhainansterone

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### Experimental

IR spectra were recorded on a Vertex 70V spectrometer. UV spectra were measured on a UV/VIS Spectrometer Lambda 750.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance-400 spectrometer (400.13 MHz for  $^1\text{H}$  and 100.62 MHz for  $^{13}\text{C}$ ). Chemical shifts are given in ppm from TMS as internal standard. Mass spectra were measured on a MALDI TOF/TOF. Specific rotations were measured on a Perkin-Elmer-341 polarimeter. Melting points were determined on a Boetius hot stage. Column chromatography and TLC were carried out using silica gel (< 0.06 mm) and precoated silica gel 60 F<sub>254</sub> plates, respectively.

### Characteristics of compounds 2–4

For **2**: mp 126–128 °C,  $[\alpha]_{\text{D}}^{18}$  21.97 (*c* 0.72,  $\text{CHCl}_3$ ). IR ( $\text{v}/\text{cm}^{-1}$ ): 3019, 2984, 1383, 1216, 777. UV ( $\text{CHCl}_3$ ,  $\lambda_{\text{max}}/\text{nm}$ ): 284.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.68 (s, 3H,  $\text{H}_3\text{C}^{18}$ ), 0.99 (s, 3H,  $\text{H}_3\text{C}^{19}$ ), 1.12 (s, 3H,  $\text{H}_3\text{C}^{21}$ ), 1.20 (s, 6H,  $\text{H}_3\text{C}^{26}$ ,  $\text{H}_3\text{C}^{27}$ ), 1.29, 1.38 and 1.48 (3s, 12H, 2Me<sub>2</sub>C), 1.44 and 2.15 (2m, 2H,  $\text{H}_2\text{C}^1$ ), 1.51 and 1.70 (2m, 2H,  $\text{H}_2\text{C}^{24}$ ), 1.52 (m, 2H,  $\text{H}_2\text{C}^{23}$ ), 1.75 and 1.91 (2m, 2H,  $\text{H}_2\text{C}^{15}$ ), 1.86 and 1.91 (2m, 2H,  $\text{H}_2\text{C}^{16}$ ), 1.96 (m, 1H,  $\text{HC}^5$ ), 1.40 and 2.13 (2m, 2H,  $\text{H}_2\text{C}^4$ ), 2.21 (m, 1H,  $\text{HC}^{17}$ ), 2.19 and 2.48 (2m, 2H,  $\text{H}_2\text{C}^{12}$ ), 3.65 (m, 1H,  $\text{HC}^{22}$ ,  $w_{1/2}$  8.0 Hz), 4.12 (m, 1H,  $\text{HC}^2$ ,  $w_{1/2}$  22.5 Hz), 4.18 (br. s, 1H,  $\text{HC}^3$ ,  $w_{1/2}$  14.8 Hz), 4.69 (d, 1H,  $\text{HC}^6$ ,  $J_{6,5}$  3.5 Hz,  $J_{6,7} < 1$  Hz), 5.49 (s, 1H,  $\text{HC}^7$ ,  $J_{7,6} < 1$  Hz), 5.62 (br. s, 1H,  $\text{HC}^{11}$ ,  $w_{1/2}$  7.6 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 17.4 ( $\text{C}^{18}$ ), 21.6 ( $\text{C}^{21}$ ), 21.8 ( $\text{C}^{16}$ ), 22.9 ( $\text{C}^4$ ), 23.5 ( $\text{C}^{23}$ ), 26.6, 26.8, 28.6 and 29.0 (2Me<sub>2</sub>CO<sub>2</sub>), 29.2 ( $\text{C}^{26}$ ), 29.4 ( $\text{C}^{27}$ ), 30.2 ( $\text{C}^{19}$ ), 30.9 ( $\text{C}^{15}$ ), 37.0 ( $\text{C}^{12}$ ), 38.3 ( $\text{C}^{10}$ ), 39.6 ( $\text{C}^1$ ), 41.1 ( $\text{C}^5$ ), 41.3 ( $\text{C}^{24}$ ), 46.2 ( $\text{C}^{13}$ ), 49.3 ( $\text{C}^{17}$ ), 66.6 ( $\text{C}^6$ ), 70.4 ( $\text{C}^{25}$ ), 71.7 ( $\text{C}^2$ ), 73.2 ( $\text{C}^3$ ), 81.9 ( $\text{C}^{22}$ ), 84.1 ( $\text{C}^{20}$ ), 84.3 ( $\text{C}^{14}$ ), 106.8 (20,22-Me<sub>2</sub>CO<sub>2</sub>), 108.0 (2,3-Me<sub>2</sub>CO<sub>2</sub>), 122.6 ( $\text{C}^{11}$ ), 123.3 ( $\text{C}^7$ ), 133.5 ( $\text{C}^9$ ), 138.0 ( $\text{C}^8$ ).

For **3**: mp 116–118 °C,  $[\alpha]_{\text{D}}^{18}$  –65.30 (*c* 1.01,  $\text{CHCl}_3$ ). IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3019, 1651, 1521, 1383, 1220, 755, 669.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.95 (s, 3H,  $\text{H}_3\text{C}^{19}$ ), 1.00 (s, 3H,  $\text{H}_3\text{C}^{18}$ ), 1.19 (s, 3H,  $\text{H}_3\text{C}^{21}$ ), 1.94 and 2.15 (2m, 2H,  $\text{H}_2\text{C}^1$ ), 1.23 (s, 6H,  $\text{H}_3\text{C}^{26}$ ,  $\text{H}_3\text{C}^{27}$ ), 1.30, 1.33, 1.42 and 1.50 (4s, 12H, 2Me<sub>2</sub>C), 1.68 and 1.71 (2m, 2H,  $\text{H}_2\text{C}^{11}$ ), 1.57 and 1.68 (2m, 2H,  $\text{H}_2\text{C}^{24}$ ), 1.64 and 2.04 (2m, 2H,  $\text{H}_2\text{C}^{12}$ ), 1.54 and 1.57 (2m, 2H,  $\text{H}_2\text{C}^4$ ), 1.94 (m, 1H,  $\text{HC}^{17}$ ), 1.45 and 1.60 (2m, 2H,  $\text{H}_2\text{C}^{23}$ ), 2.26 and 2.53 (2m, 2H,  $\text{H}_2\text{C}^{16}$ ), 2.11 (m, 1H,  $\text{HC}^5$ ), 3.72 (m, 1H,  $\text{HC}^{22}$ ,  $w_{1/2}$  8.8 Hz), 4.31 (br. s, 1H,  $\text{HC}^3$ ,  $w_{1/2}$  15.2 Hz), 4.49 (m, 1H,  $\text{HC}^2$ ,  $w_{1/2}$  23.2 Hz), 4.66 (d, 1H,  $\text{HC}^6$ ,  $J_{6,5}$  5 Hz,  $J_{6,7} < 1$  Hz), 5.65 (s, 1H,  $\text{HC}^7$ ), 5.74 (br. s, 1H,  $\text{H}_2\text{C}^{15}$ ,  $w_{1/2}$  11.6 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 18.1 ( $\text{C}^{18}$ ), 21.2 ( $\text{C}^{21}$ ), 23.7 ( $\text{C}^{23}$ ), 24.2 ( $\text{C}^4$ ), 28.8 ( $\text{C}^{11}$ ), 26.6, 26.8, 28.7 and 28.9 (2Me<sub>2</sub>CO<sub>2</sub>), 27.2 ( $\text{C}^{19}$ ), 29.1 and 29.6 ( $\text{C}^{26}$ ,  $\text{C}^{27}$ ), 31.4 ( $\text{C}^{16}$ ), 36.0 ( $\text{C}^{12}$ ), 39.6 ( $\text{C}^1$ ), 40.6 ( $\text{C}^5$ ), 40.9 ( $\text{C}^{10}$ ), 41.3 ( $\text{C}^{24}$ ), 47.4 ( $\text{C}^{13}$ ), 57.8 ( $\text{C}^{17}$ ), 66.5 ( $\text{C}^6$ ), 70.4 ( $\text{C}^{25}$ ), 72.9 ( $\text{C}^9$ ), 73.6 ( $\text{C}^2$ ), 73.8 ( $\text{C}^3$ ), 81.8 ( $\text{C}^{22}$ ), 83.5 ( $\text{C}^{20}$ ), 106.9 (20,22-Me<sub>2</sub>CO<sub>2</sub>), 107.2 (2,3-Me<sub>2</sub>CO<sub>2</sub>), 124.1 ( $\text{C}^7$ ), 124.3 ( $\text{C}^{15}$ ), 135.9 ( $\text{C}^{14}$ ), 148.3 ( $\text{C}^8$ ).

For **4**: mp 98–100 °C,  $[\alpha]_{\text{D}}^{20}$  –94.50 (*c* 0.42,  $\text{CHCl}_3$ ). IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3000, 2900, 1410, 1250, 810. UV (EtOH,  $\lambda_{\text{max}}/\text{nm}$ ): 235.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.01 (s, 3H,  $\text{H}_3\text{C}^{18}$ ), 1.08 (s, 3H,  $\text{H}_3\text{C}^{19}$ ), 1.19 (s, 3H,  $\text{H}_3\text{C}^{21}$ ), 1.22 (s, 6H,  $\text{H}_3\text{C}^{26}$ ,  $\text{H}_3\text{C}^{27}$ ), 1.31, 1.37, 1.45 and 1.51 (4s, 12H, 2Me<sub>2</sub>C), 1.37 and 2.12 (2m, 2H,  $\text{H}_2\text{C}^1$ ), 1.42 and 1.49 (2m, 2H,  $\text{H}_2\text{C}^{11}$ ), 1.57 and 1.71 (2m, 2H,  $\text{H}_2\text{C}^{24}$ ), 1.62 and 1.95 (2m, 2H,  $\text{H}_2\text{C}^{12}$ ), 1.71 and 1.84 (2m, 2H,  $\text{H}_2\text{C}^4$ ), 1.45 and 1.67 (2m, 2H,  $\text{H}_2\text{C}^{23}$ ), 1.95 (m, 1H,  $\text{HC}^{17}$ ), 2.02 (m, 1H,  $\text{HC}^5$ ), 2.23 and 2.53 (2m, 2H,  $\text{H}_2\text{C}^{16}$ ), 3.71 (m, 1H,  $\text{HC}^{22}$ ,  $w_{1/2}$  9.2 Hz), 3.97 (d, 1H,  $\text{HC}^6$ ,  $J_{6,7}$  4 Hz,  $J_{6,5} < 1$  Hz), 4.23 (br. s, 1H,  $\text{HC}^3$ ,  $w_{1/2}$  4.4 Hz), 4.47 (m, 1H,  $\text{HC}^2$ ,  $w_{1/2}$  20.8 Hz), 5.73 (br. s, 1H,  $\text{HC}^{15}$ ,  $w_{1/2}$  7.2 Hz), 5.86 (d, 1H,  $\text{HC}^7$ ,  $J_{7,6} < 1$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 18.2 ( $\text{C}^{18}$ ), 21.2 ( $\text{C}^{21}$ ), 23.7 ( $\text{C}^{23}$ ), 26.5 ( $\text{C}^{11}$ ), 26.8, 28.6 and 28.9 (2Me<sub>2</sub>CO<sub>2</sub>), 29.1 ( $\text{C}^{19}$ ), 29.2 and 29.5 ( $\text{C}^{26}$  and  $\text{C}^{27}$ ), 29.7 ( $\text{C}^4$ ), 31.3 ( $\text{C}^{16}$ ), 35.9 ( $\text{C}^{12}$ ), 38.5 ( $\text{C}^1$ ), 39.4 ( $\text{C}^{10}$ ), 41.3 ( $\text{C}^{24}$ ), 43.3 ( $\text{C}^5$ ), 47.4 ( $\text{C}^{13}$ ), 57.9 ( $\text{C}^{17}$ ), 70.37 ( $\text{C}^6$ ), 70.42 ( $\text{C}^{25}$ ), 73.5 ( $\text{C}^2$ ), 73.6 ( $\text{C}^3$ ), 73.6 ( $\text{C}^9$ ), 81.8 ( $\text{C}^{22}$ ), 83.4 ( $\text{C}^{20}$ ), 106.9 (20,22-Me<sub>2</sub>CO<sub>2</sub>), 107.3 (2,3-Me<sub>2</sub>CO<sub>2</sub>), 122.2 ( $\text{C}^7$ ), 124.7 ( $\text{C}^{15}$ ), 136.6 ( $\text{C}^{14}$ ), 148.7 ( $\text{C}^8$ ).