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Corrigendum

Corrigendum to “Enantioselective synthesis of 1(*R*)-hydroxypolygodial”

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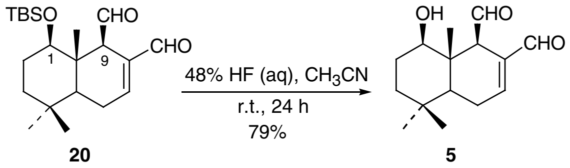
Recently, we published in this journal a letter describing the enantioselective preparation of 1(*R*)-hydroxypolygodial (**5**). In the last step of the synthesis the hydroxy group was deprotected using TBAF. However, during synthetic efforts aimed to the preparation of related analogs, we realized that the reported procedure does not afford the desired compound **5**. In fact, although spectroscopic analysis was in good accordance with the structure of the expected compound, we discovered that TBAF caused epimerization at C-9, due to the basicity of F^-. We found that the correct condition to yield the desired compound, avoiding epimerization, consisted in using HF in the deprotection step.



^{1}H NMR NOE experiments allowed inferring the correct stereochemistry of the obtained compound **5**. In fact, irradiation of H-1 (δ 3.62 ppm) led to the enhancement of the signal due to H-9 (δ 3.20 ppm). Furthermore, irradiation of H-5 (δ 1.25 ppm) caused enhancements of both signals at δ 3.20 ppm (H-9) and at δ 3.62 ppm (H-1). Therefore, H-1, H-9, and H-5 are all in cis-relationship confirming that these deprotection conditions (48% HF (aq), CH_3CN, rt) do not cause epimerization at C-9.

Analytical data given in note 15 on page 4063 are incorrect and correct data are given below:

Physical data of 1(*R*)-hydroxypolygodial (**5**): $[\alpha]_D^{25}$ −8.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (3H, s, CH_3), 0.91 (3H, s, CH_3), 0.94 (3H, s, CH_3), 1.25 (1H, dd, $J = 4.9$, 11.4 Hz, H-5), 1.36 (1H, m, H-3), 1.51 (1H, ddd, $J = 3.2$, 3.2, 13.5 Hz, H′-3), 1.56–1.66 (2H, m, H-2 and H′-2), 2.37 (1H, dddd, $J = 2.4$, 3.8, 11.4, 20.0 Hz, H-6), 2.45 (1H, *m*, H′-6), 3.20 (1H, br s, H-9), 3.62 (1H, dd, $J = 7.6$, 8.2 Hz, H-1), 7.09 (1H, m, H-7), 9.37 (1H, s, OHCC-8), 9.82 (1H, d, $J = 3.2$ Hz, OHCC-9). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 9.3 (q), 22.0 (q), 24.8 (t), 27.8 (t), 32.7 (q), 32.8 (s), 39.6 (t), 43.5 (s), 48.5 (d), 59.8 (d), 79.8 (d), 139.5 (s), 153.1 (d), 192.9 (d), 203.9 (d). ESIMS: *m*/*z* 273 $[M+Na]^+$.

A full account, with experimental details, will be published elsewhere.

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