SUPPLEMENTAL DATA

Mechanism of 17*a*,20-Lyase and New Hydroxylation Reactions of Human Cytochrome P450 17A1
^{18}O-LABELING AND OXYGEN SURROGATE EVIDENCE FOR A ROLE OF A PERFERRYL OXYGEN

Francis K. Yoshimoto, Eric Gonzalez, Richard J. Auchus, and F. Peter Guengerich
J. Biol. Chem. **291**, xxx-xx (2016)

CONTENTS

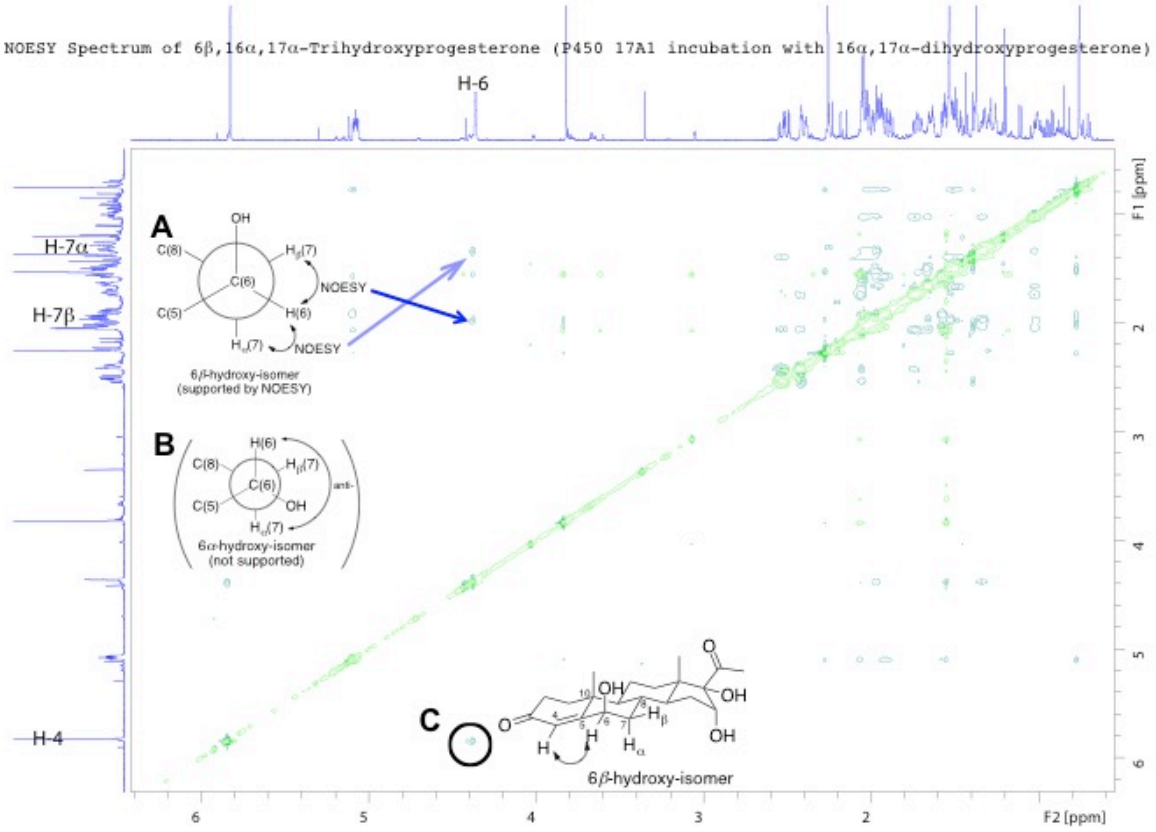

FIGURE S1. **NOESY NMR spectrum of 6β,16α,17α-trihydroxyprogesterone derived from 16α,17α-dihydroxyprogesterone (600 MHz, $CDCl_3$).** (A) Newman projection along C6-C7 bond axis to show the proximity between H-6α (δ 4.38 ppm) with H-7α (δ 1.34 ppm) and H-7β (δ 1.98 ppm) protons that is supported by the NOESY data, and for comparison: (B) a Newman projection along the C6-C7 bond axis of a hypothetical 6α-hydroxy epimer (6α,16α,17α-trihydroxyprogesterone) to show anti-configuration of H-6β with H-7α. (C) NOESY interaction between H-6 (δ 4.38 ppm) and H-4 (δ 5.84 ppm) protons.

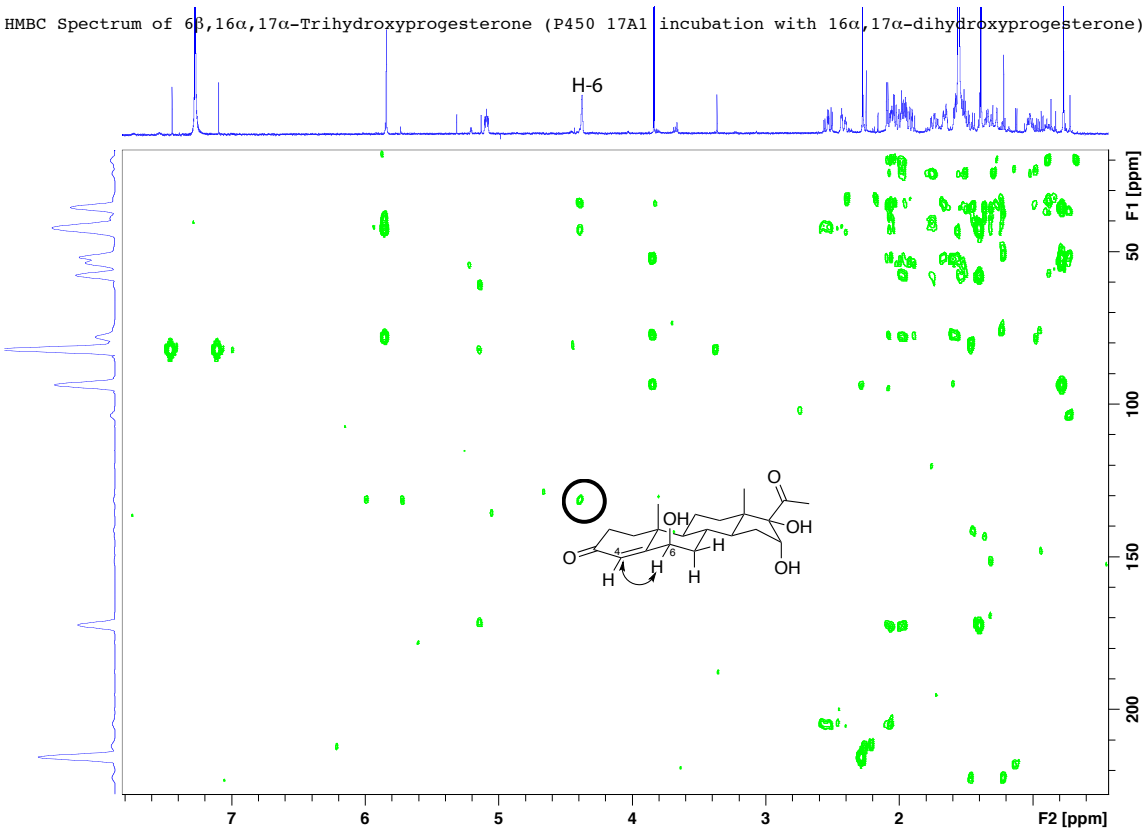

FIGURE S2. **HMBC NMR spectrum of 6β,16α,17α-trihydroxyprogesterone derived from 16α,17α-dihydroxyprogesterone (600 MHz, $CDCl_3$).** The H-6 hydroxymethine proton (δ 4.38 ppm) is shown to have a 3-bond coupling to the C4-carbon (δ 128 ppm).

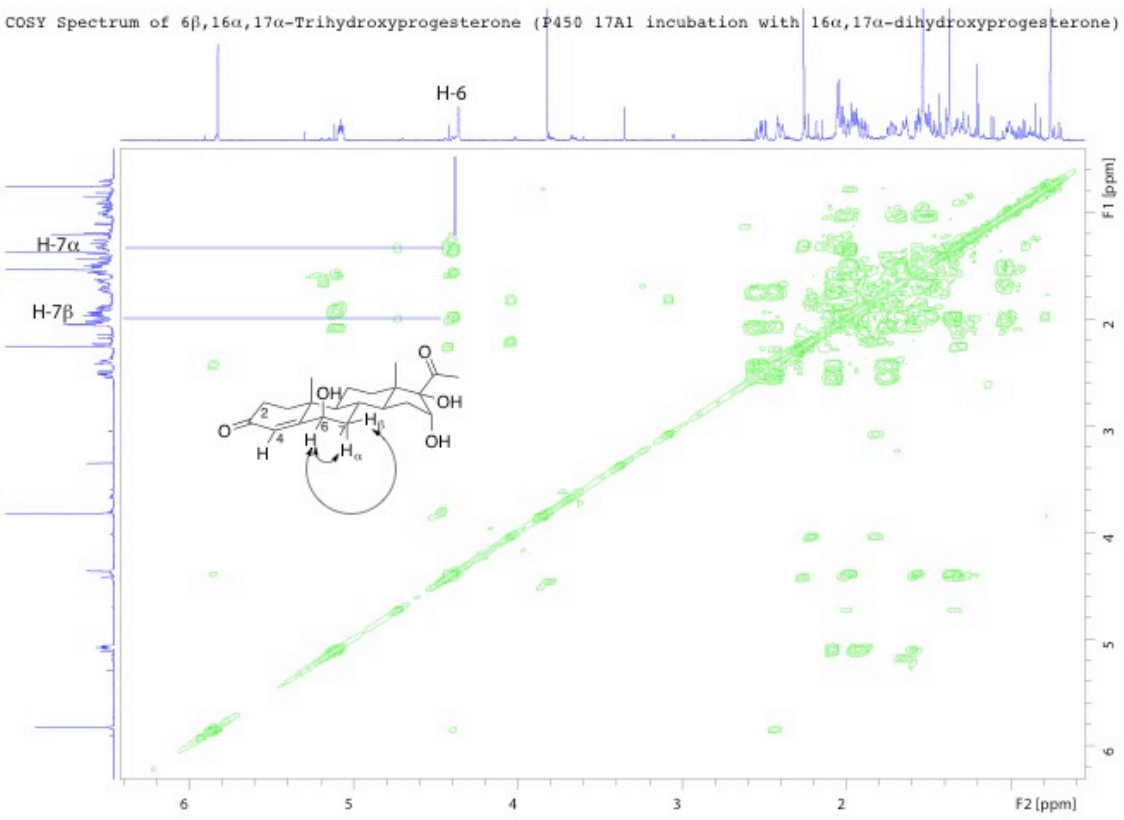

FIGURE S3. **COSY NMR spectrum of 6β,16α,17α-trihydroxyprogesterone derived from 16α,17α-dihydroxyprogesterone (600 MHz, $CDCl_3$).** Shown with the lines are the 3-bond coupling interaction between the H-6 proton (δ 4.38 ppm) with the H-7 protons (δ 1.34 and 1.98 ppm).

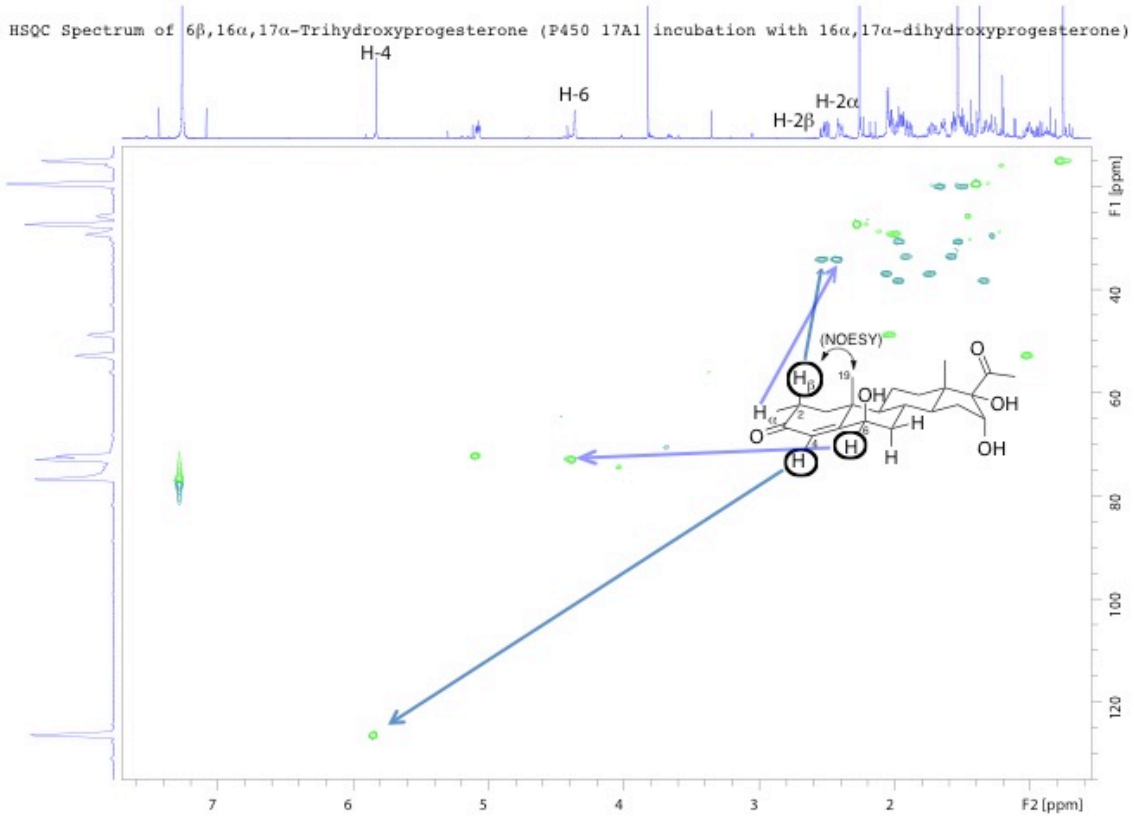

FIGURE S4. **HSQC NMR spectrum of 6β,16α,17α-trihydroxyprogesterone derived from 16α,17α-dihydroxyprogesterone (600 MHz, $CDCl_3$).** The arrows show the assignment of C2, C4, and C7 carbons (δ 34.2, 127.7, and 38.5 ppm) with their respective one-bond heteronuclear correlations to assign their attached protons.