

Supporting Information to “Clarification of the Crystalline Forms of Androsterone”

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Variable Temperature X-ray Powder Diffraction

X-Ray Powder Diffraction patterns were collected on a Bruker AXS C2 GADDS diffractometer using Cu K α radiation (40kV, 40mA), automated XYZ stage, laser video microscope for auto-sample positioning and a HiStar 2-dimensional area detector. X-ray optics consists of a single Göbel multilayer mirror coupled with a pinhole collimator of 0.3mm.

The beam divergence was approximately 4 mm. A θ - θ continuous scan mode was employed with a sample - detector distance of 20 cm, which gives an effective 2θ range of 3.2° – 29.7°. Typically the sample would be exposed to the X-ray beam for 120 seconds.

Samples were run under ambient conditions prepared as flat plate specimens using powder as received without grinding. Approximately 1-2mg of the sample was lightly pressed on a glass slide to obtain a flat surface. Samples run under non-ambient conditions were mounted on a glass slide with heat conducting compound. The sample was then heated to the appropriate temperature at *ca.* 20°C/minute and subsequently held isothermally for *ca.* 1 minute before data collection was initiated.

The first data set in Fig. S1 (25 °C) corresponds to androsterone hemihydrate (see Fig. S2) and the final data set (170 °C) corresponds to anhydrous androsterone (see Fig. S3). The second data set (65 °C) exhibits peaks attributable to both the anhydrous and hemihydrate forms, hence is only partially dehydrated. The dehydration can be seen to be complete by the third data set (130°C), which contains peaks only attributable to the anhydrous androsterone structure.

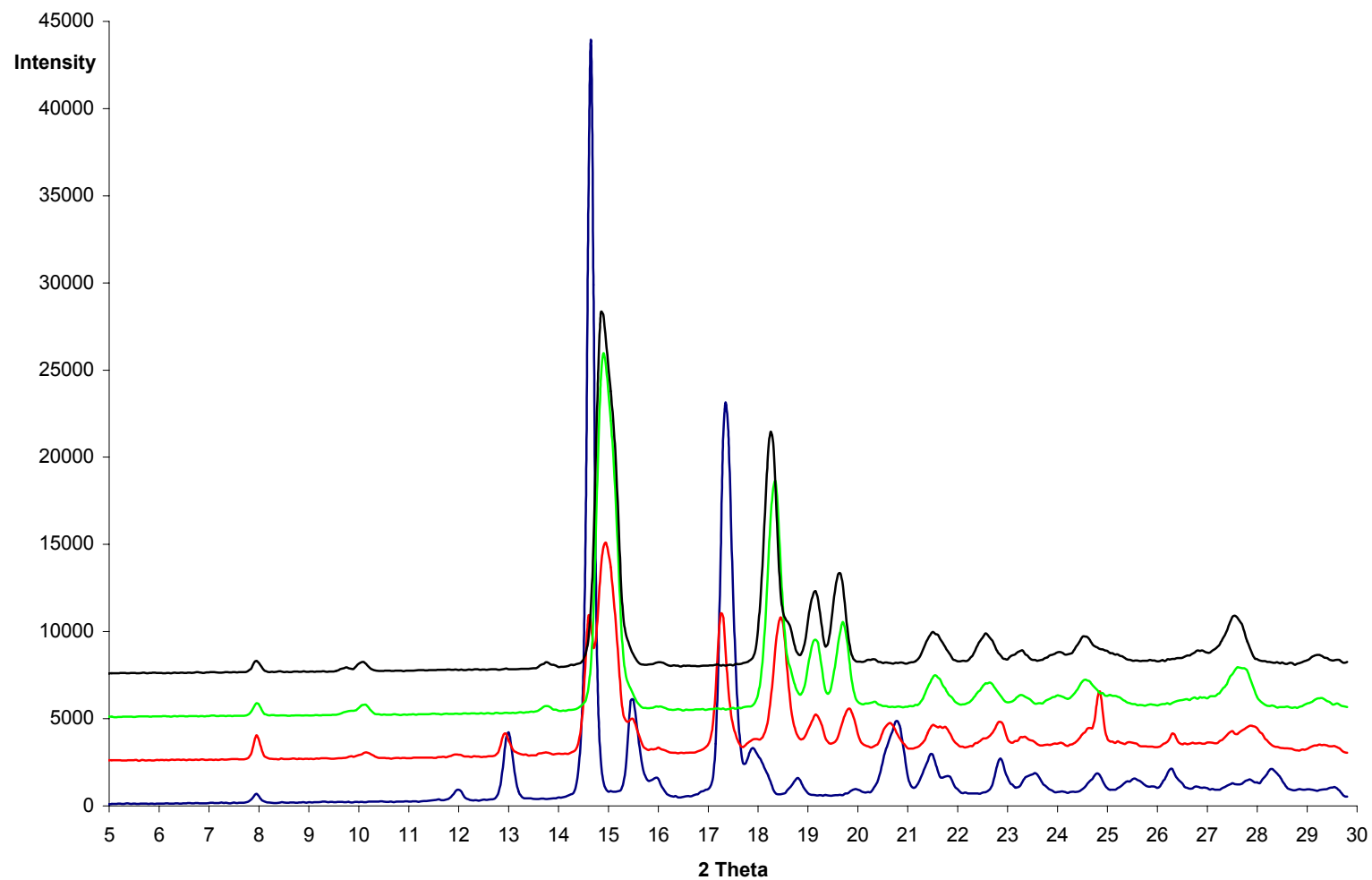


Figure S1: Variable temperature X-ray powder diffraction. (1) 25 °C = blue; (2) 65 °C = red; (3) 130 °C = green; (4) 170 °C = black

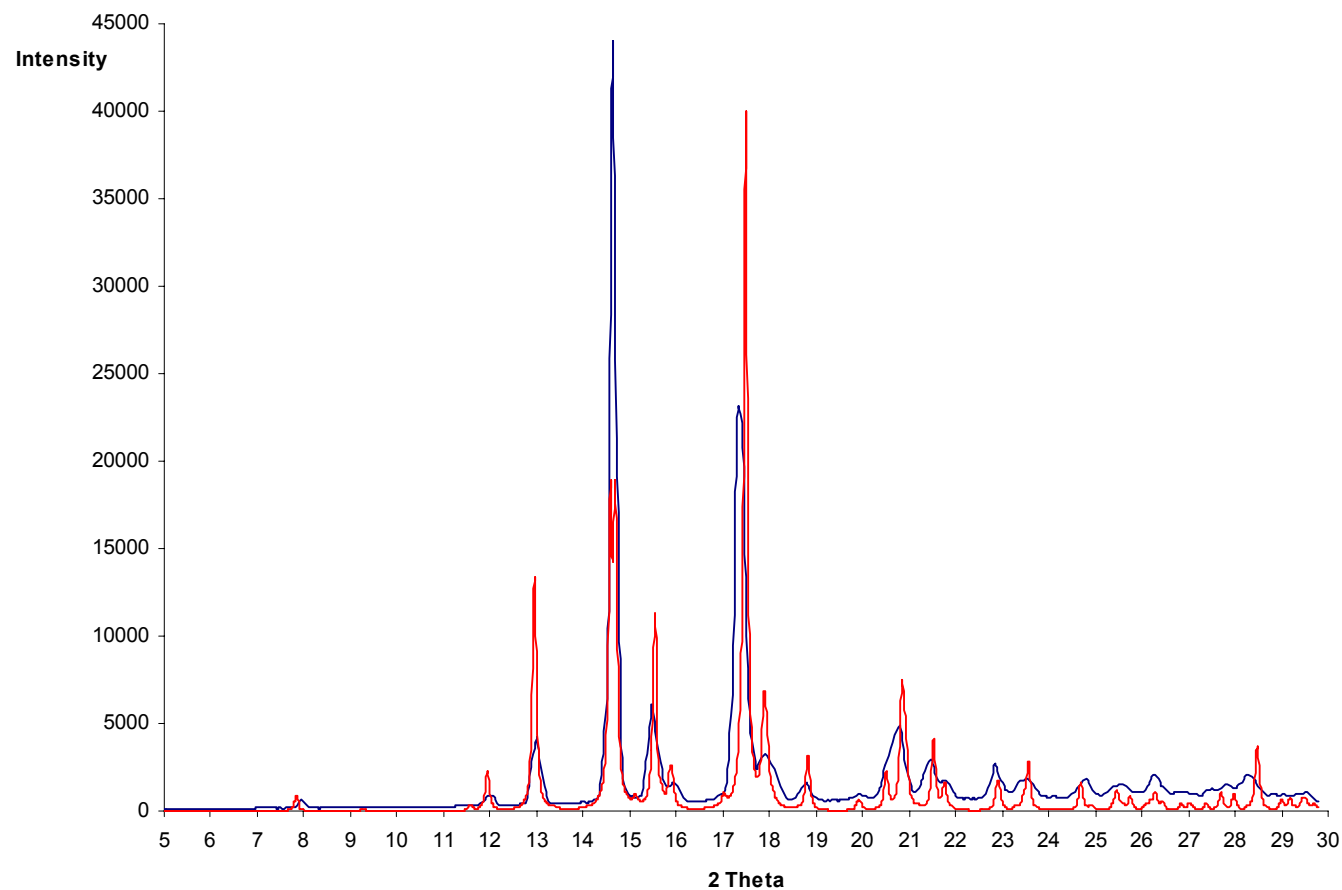


Figure S2: simulated powder pattern from androsterone hemihydrate (red) and from variable temperature powder X-ray diffraction experiment data set collected at 25 °C (blue). Peaks positions correspond closely. Simulated powder patterns produced using Mercury 1.4.1 (Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J.; Taylor, R., *Acta Crystallogr.* **2002**, B58, 389–397).

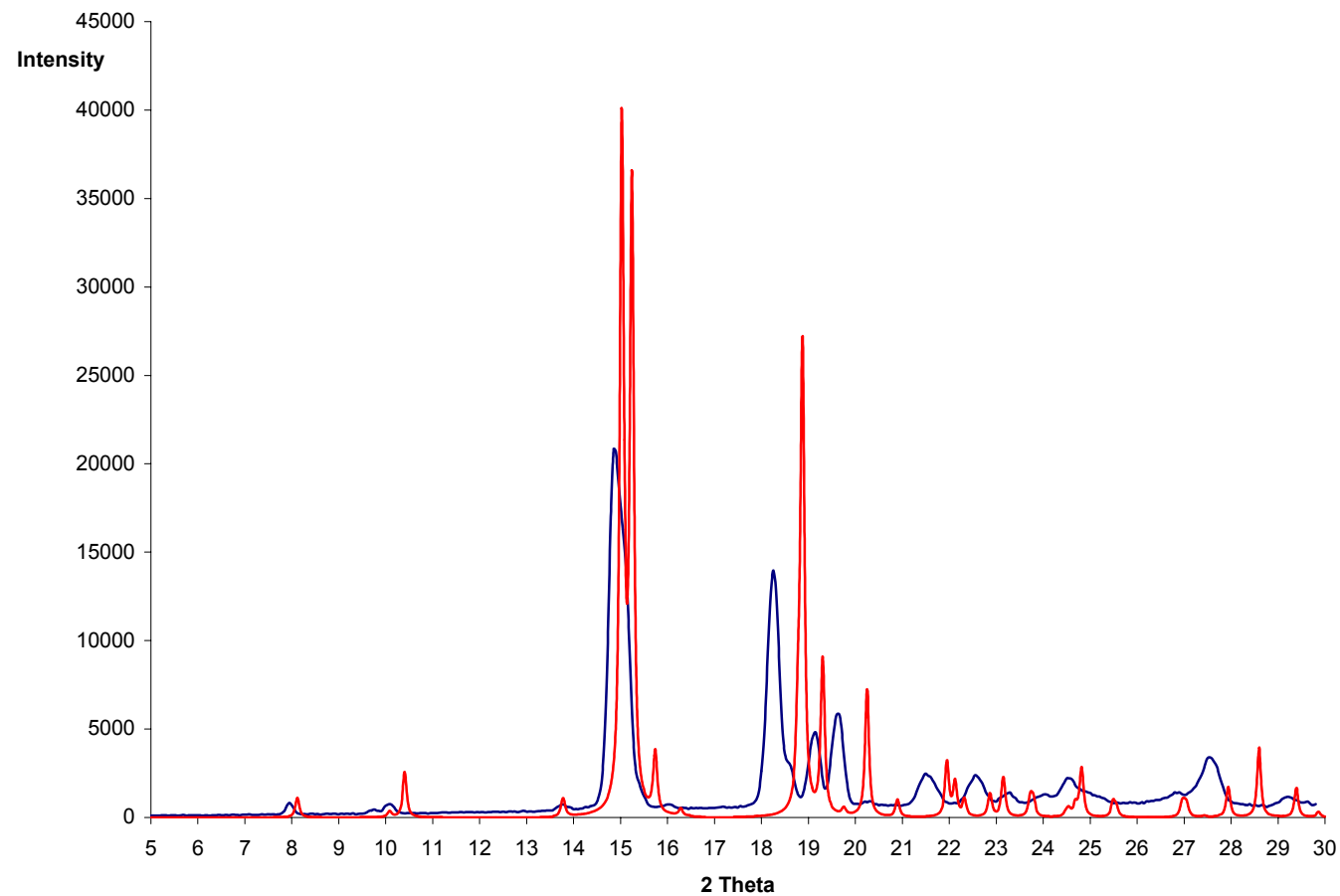


Figure S3: simulated powder pattern from androsterone (red) and from variable temperature powder X-ray diffraction experiment data set collected at 170 °C. The simulated pattern was generated from the single crystal structure, determined at -123 °C. The two patterns correspond but some peak shift is evident due to the 193 °C temperature difference.