Supporting Information:

Experimental and theoretical studies of a naturally occurring non-oligomeric steroidal supramolecular zipper

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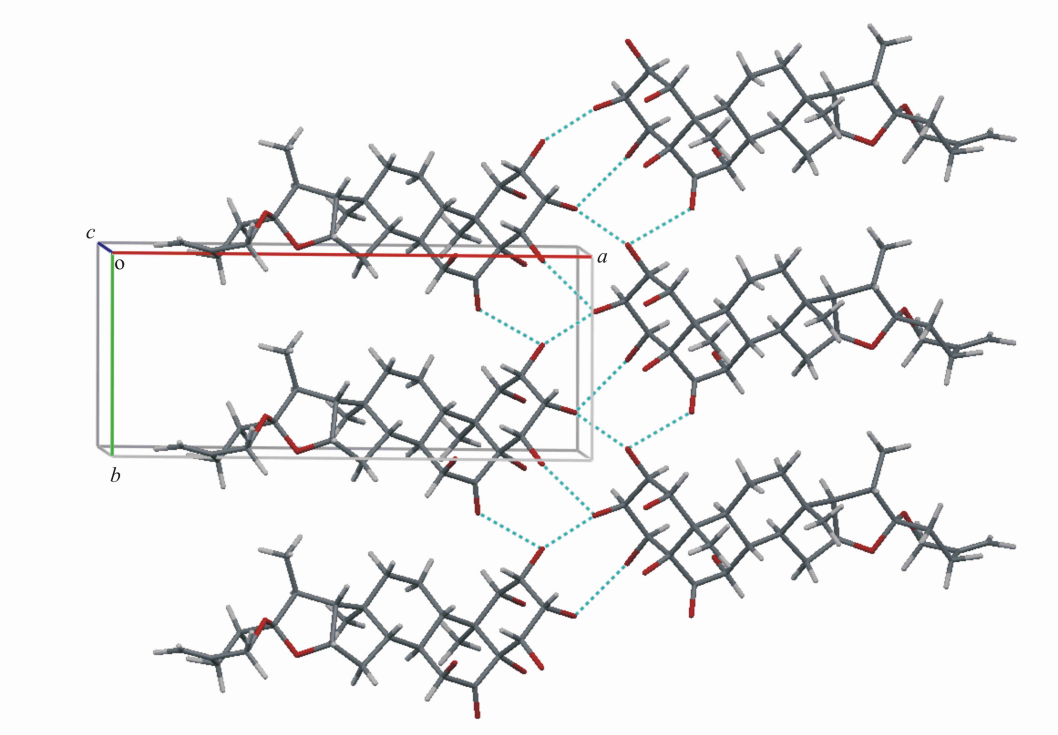

Fig. S1 View approximately down the *c*-axis of the unit cell of β,2β,3β,4β,5β,7α-hexahydroxy-spirost-25(27)-en-6-one (K. Miyahara, F. Kumamoto, and T. Kawasaki, *Tetrahedron Lett.* 1980, **21**, 83; CSD code: HXSPEO) illustrating the hydrogen-bonded supramolecular structure. The axis of the one-dimensional hydrogen-bonded supramolecular zipper runs co-linear with the *b*-axis of the unit cell.

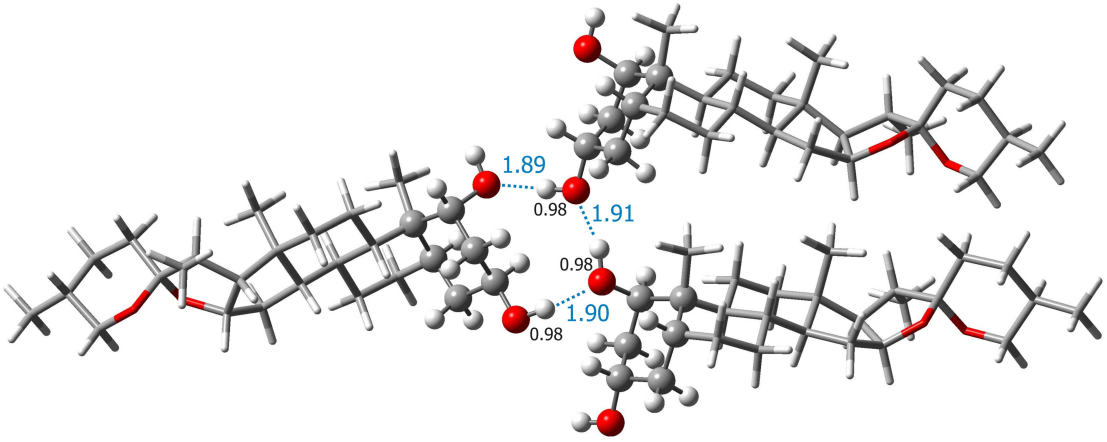

Fig. S2 DFT/AM1-calculated structure of the trimer geometry of 25R,5β-spirostane-1β,3α-diol (compound **1**). Selected distances are given in Å. The portion of the structure rendered as a ball-and-stick model was calculated at the B3LYP/6-31+G** level of theory; the remainder of the structure was calculated at the AM1 level of theory (semi-empirical).

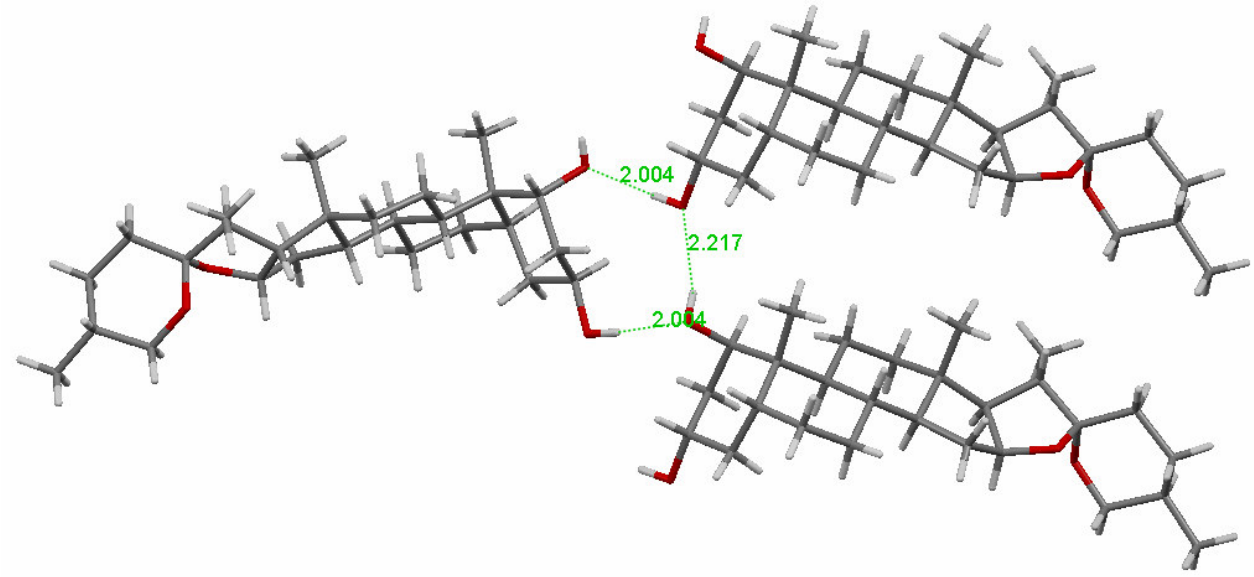

Fig. S3 Experimental (X-ray diffraction, 295 K) hydrogen bond distances (in Å) for compound **1**. The distances shown above, correct to three significant numbers and consistent with the accuracy of the experimental measurement, are 2.22(6) Å and 2.00(3) Å. Although the theoretical distances (Fig. S2) are in good agreement with the experimental values, they do not fully distinguish between lateral and vertical hydrogen bonds in the structure.