As part of our continuing interest on the structural characterization of active pharmaceutical ingredients and the formation of possible new structural forms, we have tried to recrystallize, under different conditions, thiocolchicoside, a popular API prescribed as a muscle relaxant. It also has anti-inflammatory and analgesic effects. Related to this compound, only one report was found in the Cambridge Structural Database. It is for its ethanol solvate hydrate (Refcode: THCLCS). The ICDD PDF-4/Organics database contains its calculated powder diffraction pattern (entry: 02-073-3591). The powder diffraction pattern recorded for the raw material obtained from a pharmaceutical company does not match the pattern calculated using the single crystal data. The indexing of this pattern carried out with DICVOL06 lead to an orthorhombic unit cell with \( a = 28.018(7) \, \text{Å} \), \( b = 12.519(2) \, \text{Å} \), \( c = 8.519(1) \, \text{Å} \), \( V = 2988.01 \, \text{Å}^3 \), \( M_{20} = 56.5 \), \( F_{20} = 137.6 \) (0.0035, 42). In the search of possible polymorphs of this API, recrystallization studies under different conditions were carried out. Crystals in the form of irregular blocks were obtained from an aqueous solution in an oven at 37 °C, after 48 hours. The powder pattern recorded for this phase indicated a different structure. The X-ray single crystal study concluded that these crystals correspond to a dihydrate phase which crystallizes in an orthorhombic unit cell with space group \( P2_12_12_1 \), and \( a = 8.564(2) \, \text{Å} \), \( b = 13.537(3) \, \text{Å} \), \( c = 25.303(5) \, \text{Å} \) and \( V = 2933.0(2) \, \text{Å}^3 \). The powder diffraction pattern, indexed with good figure-of-merits (\( M_{20} = 47.3 \), \( F_{20} = 131.2 \) (0.0040, 38) in the same unit cell, also led to the crystal structure after a study carried out with the program TALP. The powder diffraction pattern obtained for these crystals, after heating them in an oven at 80 °C for 4 hours, was totally different from those previously recorded. In this contribution, the results of these studies will be presented.