Supplementary Information: Unheralded forms of the natural osmolyte floridoside

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Supplementary Figure 1: 1H NMR (400 MHz) of filtered UCM (a and b) and UCM-T (c and d) (Referenced with respect to HOD at 4.75 ppm).
Supplementary Figure 2: Blank TGA run (100:20 mL min⁻¹, Air:N₂, 5 K min⁻¹) based on a 50 mg sample mass.

Supplementary Figure 3: Unit cells of (from 1st to 3rd column F₁, F₂ and F₃) viewed along the (from top to bottom) a-, b- or c axes (red, green or blue cuboid edges). Hydrogen atoms, except those belonging to H₂O (coloured blue) in F₃ are omitted for clarity.
Supplementary Figure 4: Structural overlays of thermal ellipsoid representations for (from left to right) F_{I} & F_{II}, F_{I} & F_{h}, and F_{II} and F_{h} at the 50 % probability level wherein hydrogens are drawn with arbitrary radii.

Supplementary Figure 5: Simulated pXRD traces (full width at half-maximum is 0.20) for F_{I}, F_{II} and F_{h} with experimental UCM, UCM-T, KCl and NaCl spectra added for comparison.
Supplementary Figure 6: ATR-FTIR spectra (650 – 3750 cm$^{-1}$) of pure crystalline $F_h$, $F_{II}$ and $F_i$. 
Supplementary Fig. 7: Hot-stage micrographs of crystalline F₁ recorded upon heating from 45 to 139 °C.
Supplementary Figure 8: DSC thermogram showing the; 1st heating (to 100 °C), 1st cooling (to -80 °C, 2nd heating (to 150 °C) and isothermal cycles for crystalline F₈₅ (mg) at 5 K min⁻¹.
Supplementary Figure 9: Hot-stage micrographs of a single F<sub>h</sub> crystal heated from 35 to 135 °C at a rate of 5 K min<sup>-1</sup>.
**Supplementary Figure 10**: Graphical and tabulated representation of hydrogen bonds found for the water (ball and stick) with the surrounding floridoside molecules (wireframe) in Fh as defined by the following criteria: < 3.00 Å (H···A) and > 90° (O-H···A), OH donor only, and > 1 bond separation between intramolecular donor/acceptor. The navy or cyan dashed lines indicate whether a H···A length is ≤ 2.20 or 2.21 – 3.00 Å respectively and the bracketed numbers in the table denote the identity of the floridoside oxygen atom involved (w = water).
**Supplementary Table 1**: Tabulated crystal and structural refinement data for F₁ (this work, CCDC 2004260), F₁ (this work, CCDC 2004259) and F₁ (Vonthron-Senecheau *et al.*, CCDC 680442).

| Polymorph Code | Empirical formula | Formula weight | Temperature/K | Crystal system | Space group | a/Å | b/Å | c/Å | α/° | β/° | γ/° | Volume/Å³ | Z | ρcalc/g/cm³ | μ/μm⁻¹ | F(000) | Θ range for data collection/° | Index ranges | Reflections collected | Independent reflections | Data/restraints/parameters | Goodness-of-fit on F² | Final R indexes [I>=2σ (I)] | Final R indexes [all data] | Largest diff. peak/hole/e Å³ | Flack parameter |
|----------------|------------------|---------------|---------------|---------------|-------------|-----|-----|-----|-----|-----|-----|------------|---|-------------|---------|--------|-----------------------------|---------------|-----------------------------|------------------------|-----------------------------|------------------------|-----------------------------|------------------------|-----------------|
| F₁             | C₉H₂₀O₉          | 272.25        | 110.00(10)    | orthorhombic  | P₂₁2₁2₁     | 8.22038(16) | 11.2533(3) | 12.9852(2) | 90  | 90  | 90  | 1201.22(4) | 4  | 1.505       | 1.185   | 584.0  | 10.402 to 134.146           | -9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -15 ≤ l ≤ 8 | 8062                        | 2155 [Rint = 0.0225, Rsigma = 0.0199] | 2155/0/196 | 1.044        | R₁ = 0.0221, wR₁ = 0.0545   | R₁ = 0.0221, wR₁ = 0.0545 | 0.18/-0.14         | -0.02(8)       |
| F₉₁           | C₉H₁₈O₈          | 254.23        | 110.00(10)    | orthorhombic  | P₂₁,2₁2₁    | 8.54811(10) | 9.19251(10) | 14.34851(17) | 90  | 90  | 90  | 1127.49(2) | 4  | 1.498       | 1.154   | 544.0  | 11.432 to 133.962           | -10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -17 ≤ l ≤ 16 | 10041                       | 2012 [Rint = 0.0222, Rsigma = 0.0151] | 2012/0/179 | 1.036        | R₁ = 0.0215, wR₁ = 0.0550   | R₁ = 0.0223, wR₁ = 0.0556 | 0.23/-0.16         | -0.02(6)       |
| F₁            | C₉H₁₈O₈          | 254.23        | 150           | orthorhombic  | P₂₁₂₁       | 4.88440(10) | 9.7259(3)   | 23.8754(6)  | 90  | 90  | 90  | 1134.21(5) | 4  | 1.489       | 0.132   | 544.0  | 2.70 to 38.67               | -8 ≤ h ≤ 8, -16 ≤ k ≤ 16, -41 ≤ l ≤ 41 | 63701                       | 6386 [Rint = 0.0264] | 6386/0/226 | 1.095        | R₁ = 0.0326, wR₁ = 0.0852   | R₁ = 0.0392, wR₁ = 0.0894 | 0.362/-0.21        | 0.1(4)         |

**Supplementary References**

1. Vonthron-Senecheau, C., Santos, J., Mussio, I. & Rusig, A. X-ray structure of floridoside isolated from the marine red algae Dilsea carnosa. *Carbohydrate Research* **343**, 2697-2698, doi:10.1016/j.carres.2008.06.017 (2008), CCDC 680442.