SUPPORTING INFORMATION

Fatty acid epoxidation by *Collariella virescens* peroxygenase and heme-channel variants

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This supporting information includes Sephadex 75 chromatography (**Fig. S1**), GC-MS of the reactions with unsaturated and saturated fatty acids (**Fig. S2**), molecular model of *C. virescens* UPO (**Fig. S3**), GC-MS of the reactions of *C. virescens* UPO and variants with oleic (**Fig. S4**), linoleic (**Fig. S5**) and α-linolenic (**Fig. S6**) acids, and formulae of fatty acid derivatives (**Fig. S7**).

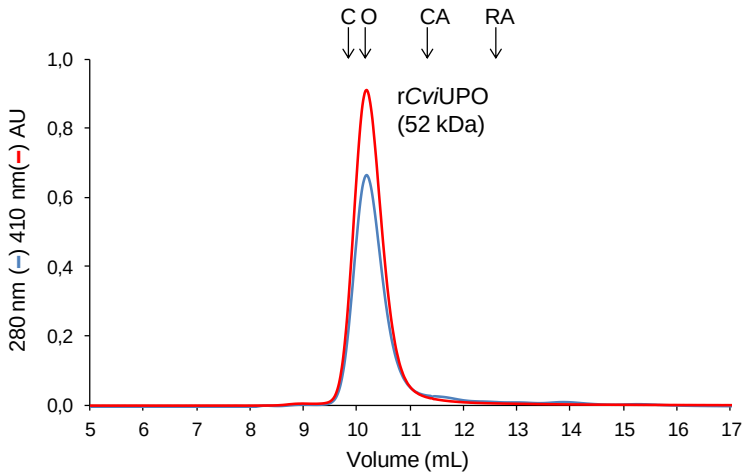

Fig. S1. Sephadex 75 chromatography of purified *C. virescens* UPO showing elution profiles at 280 nm (cyan) and 410 (red) nm. Elution volumes of the conalbumin (75 kDa, C), ovoalbumin (44 kDa, O), carbonic anhydrase (29.3 kDa, CA) and ribonuclease-A (13.7 kDa, RA) standards, used for estimation of the UPO molecular mass, are indicated.

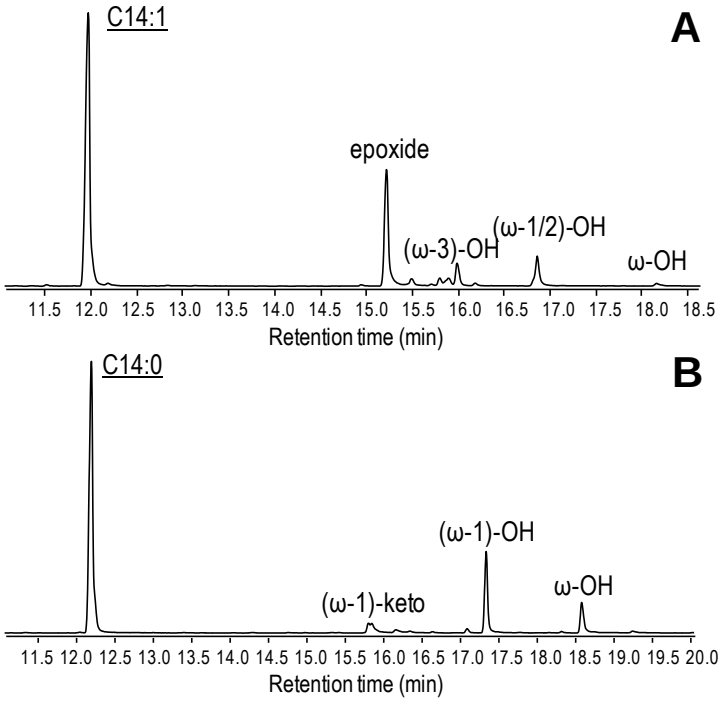

Fig. S2. GC-MS comparison of reactions of *C. virescens* UPO with unsaturated myristoleic acid (**A**) and its saturated counterpart myristic acid (**B**). The reaction conditions are the same of **Fig. 2**. Peaks of hydroxy and epoxy derivatives are shown, together with the remaining substrate (underlined).

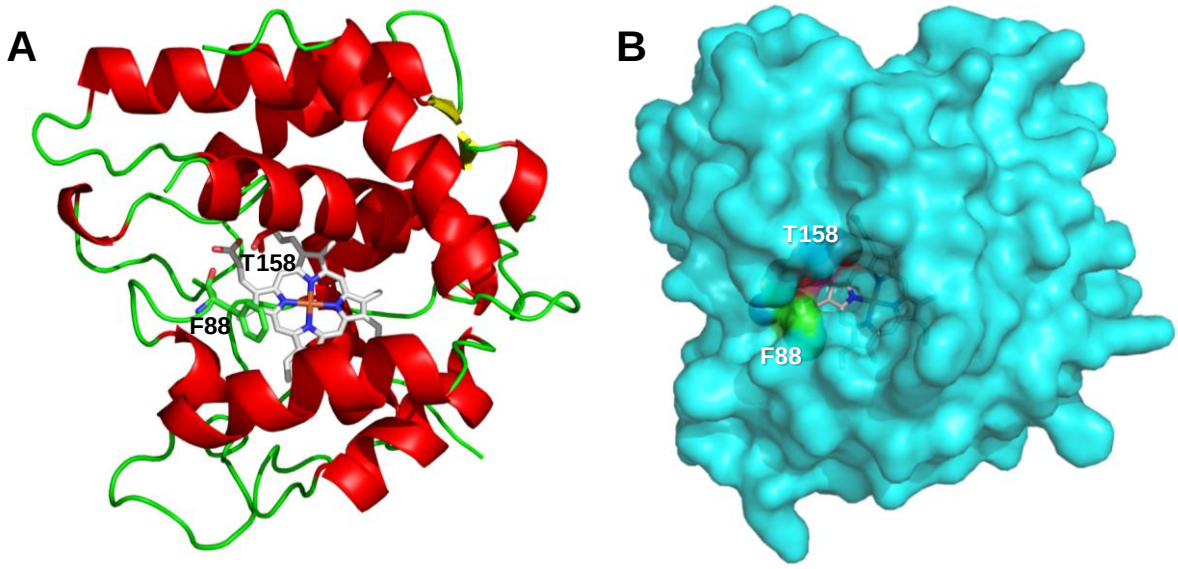

Fig. S3. Molecular model of the *C. virescens* UPO monomer. **A**) Ribbon representation with predominant helices in red and heme cofactor and selected Phe88 and Thr158 residues as sticks. **B)** Solvent access surface with colored areas corresponding to the above Phe88 and Thr158 residues, and access channel to the buried heme (cofactor as sticks).

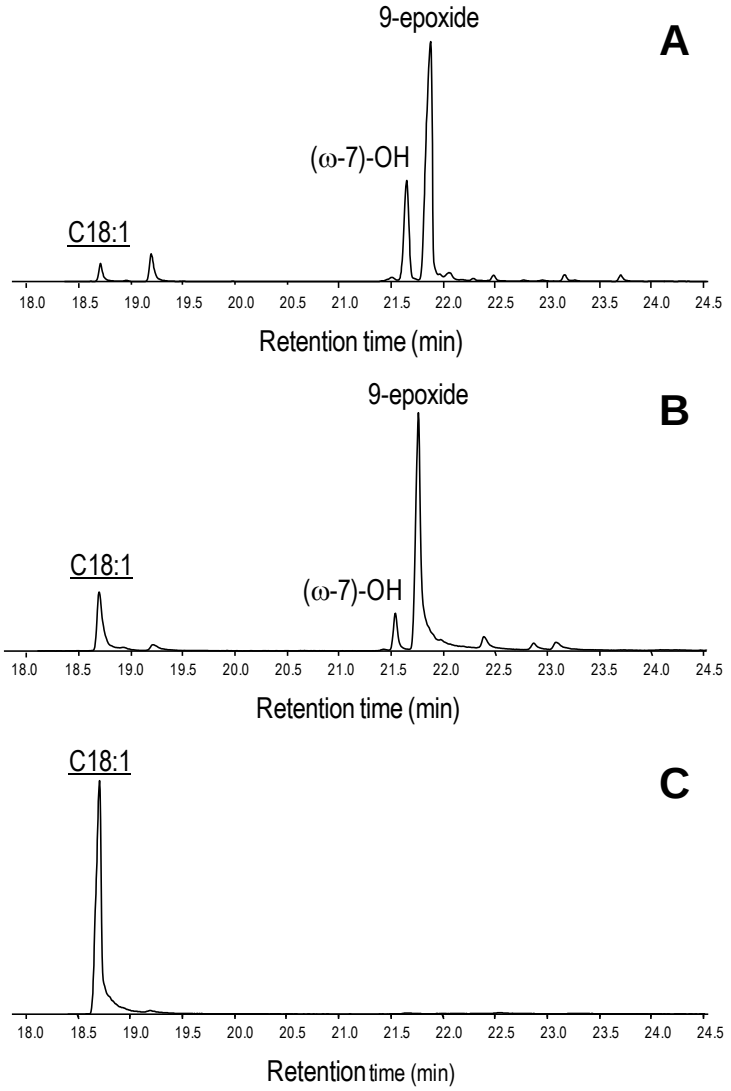

Fig. S4. GC-MS analysis of the reactions of oleic acid with *C. virescens* UPO (**A**) and its F88L (**B**) and T158F (**C**) variants. Peaks of epoxy and hydroxy derivatives are shown, together with the remaining substrate (underlined). See **Fig. 2** for reaction conditions and **Table 2** for peak quantification.

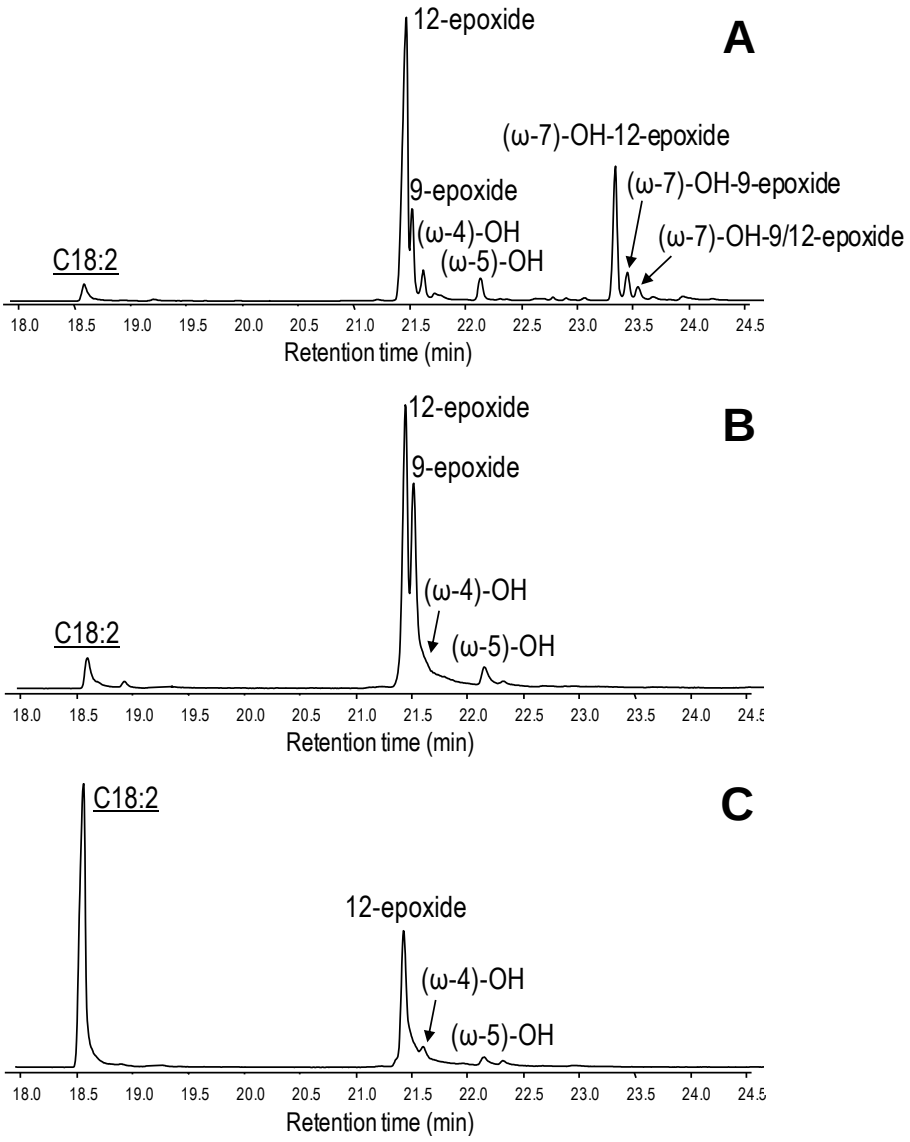

Fig. S5. GC-MS analysis of the reactions of linoleic acid with *C. virescens* UPO (**A**) and its F88L (**B**) and T158F (**C**) variants. Peaks of epoxy, hydroxy and hydroxy-epoxy derivatives are shown, together with the remaining substrate (underlined). See **Fig. 2** for reaction conditions and **Table 2** for peak quantification.

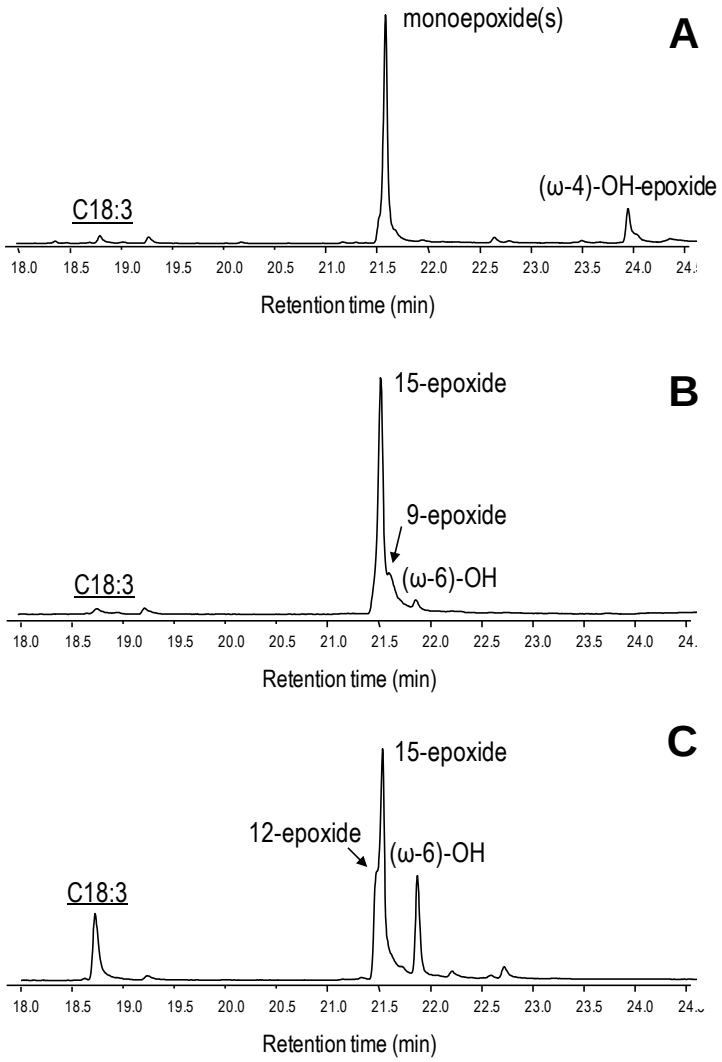

Fig. S6. GC-MS analysis of the reactions of α-linolenic acid with *C. virescens* UPO (**A**) and its F88L (**B**) and T158F (**C**) variants. Peaks of epoxy, hydroxy and hydroxy-epoxy derivatives are shown, together with the remaining substrate (underlined). See **Fig. 2** for reaction conditions and **Table 2** for peak quantification.

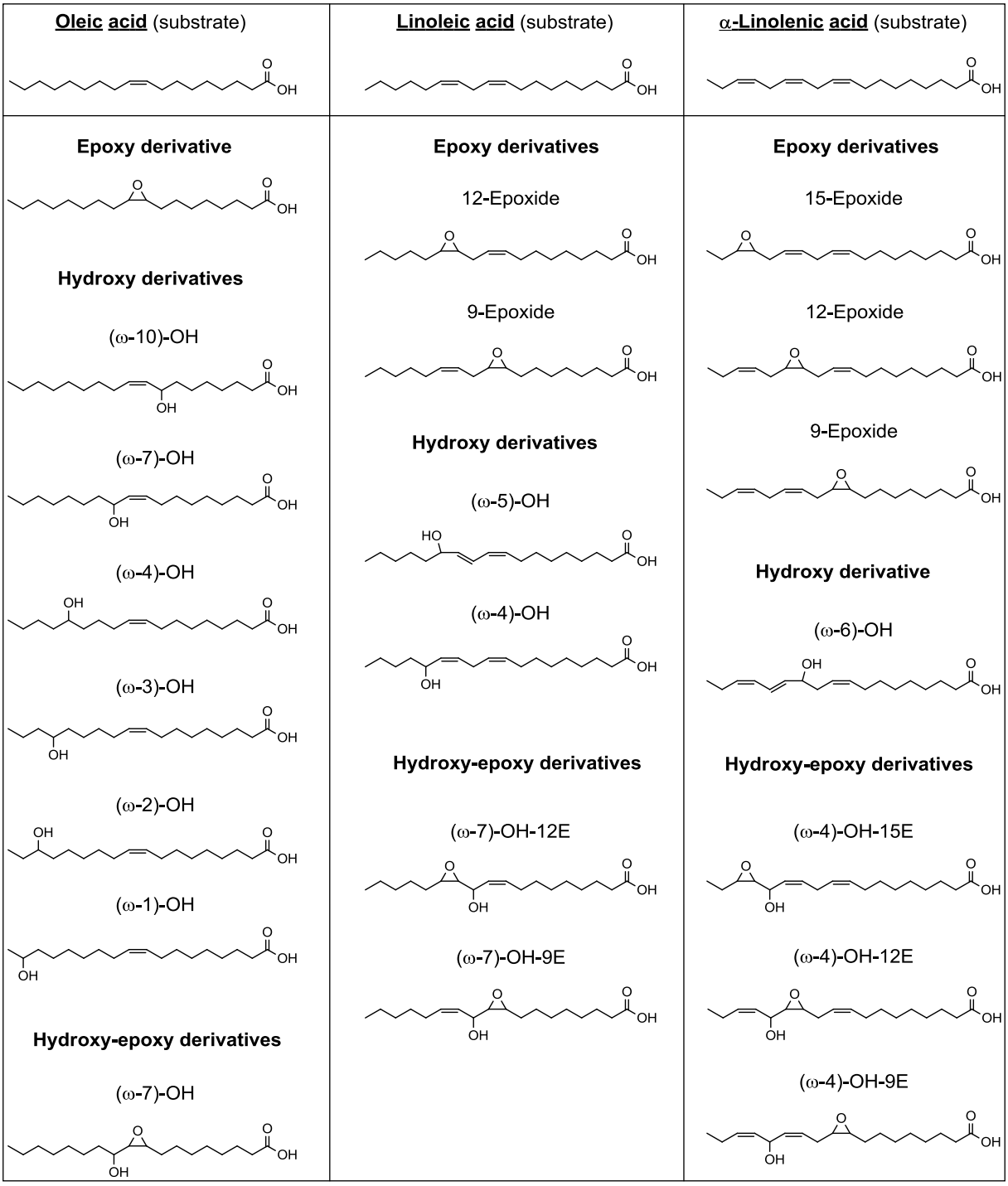

Fig. S7. Formulae of the epoxy, hydroxy (two of them including double-bond displacement) and hydroxy-epoxy derivatives identified in the different UPO reactions with oleic, linoleic and α-linolenic acids (see **Figs. S4-S6** for the GC-MS analyses, and **Table 2** for their relative abundances).