**Supplemental material**

**Table and figure captions:**

**Table S1.** Summary of the sample names and their obtainment.

**Figure S1.** GC profiles of the TMS derivatives of glycosides generated after acid hydrolysis of TB-EPS total sample (A) and both polysaccharidic sub-samples, water-soluble (TB-PS-aq) (B) and low water-soluble (TB-PS-inter) (C). Erythritol was used as internal reference.

**Figure S2.** Elution HPGPC profiles, monitored by RI detector, of LB-PS–aq and -inter in comparison to TB-PS-aq and -inter.

**Figure S3.** Percentage (w/w) of each ion exchange chromatography fraction eluted from TB-PS-inter (A) and TB-PS-aq (B) by increasing sequentially the NaCl concentration.

**Figure S4.** 1H–NMR spectra of TB-PS-inter 0 M (PS I) (A) and TB-PS-aq 0.4 M (mainly PS II) (B).

**Figure S5.** 1H–NMR spectra of TB-PS-inter 0.8 M (PGG).

**Figure S6.** Comparative OD evolution at 600 nm, related to bacteria growth in MB medium, for 3 strains, in absence and in presence of polysaccharide enriched-fractions: TB-PS-inter 0 M (PS I) (A), TB-PS-aq 0.4 M (mainly PS II) (B).

**Figure S7.** Elution HPGPC profiles, monitored by RI detector, of Sol-PS-aq,TB-PS-aq and TB-PS-inter isolated or extracted from planktonic cultures of *P. ulvae* TC14.

Table S1. Summary of the sample names and their obtainment.

|  |  |  |
| --- | --- | --- |
| Sample abbreviation | Corresponding sample | Obtainment |
| **TB-EPS** | **Tightly bound exopolymers**  | Extraction from biofilms |
| * TB-EPS-**inter**
 | Low water-soluble exopolymers recovered in the **inter**phase | CHCl3/MeOH/H2O partition of TB-EPS |
| * + TB-**PS**-inter
 | Low water-soluble **polysaccharide**-enriched fraction | Removing of lipids and proteins from low water-soluble exopolymers |
| * TB-PS-inter **0 M** (PSI)\*
 | Neutral low water-soluble polysaccharide-enriched fractioncontaining PSI as main component | Ion exchange chromatography. Fraction eluted with **0 M** NaCl from TB-PS-inter |
| * TB-PS-inter **0.8 M** (PGG)\*
 | Acidic low water-soluble polysaccharide-enriched fractioncontaining PGG as main component | Ion exchange chromatography. Fraction eluted with **0.8 M** NaCl from TB-PS-inter |
| * TB-EPS-**aq**
 | Water-soluble polymers recovered in the **aq**ueous phase | CHCl3/MeOH/H2O partition of TB-EPS |
| * TB-**PS**-aq
 | Water-soluble **polysaccharide**-enriched fraction | Removing of lipids and proteins from water-soluble exopolymers |
| * TB-PS-aq **0.4 M** (PSII)\*
 | Acidic low water-soluble polysaccharide-enriched fraction containing PSII as main component | Ion exchange chromatography. Fraction eluted by **0.4 M** NaCl from TB-PS-aq |

Note: TB: tightly bound; PS: polysaccharide; inter: interphase; aq: aqueous phase; PGG: poly(glutamyl glutamate). \*PSI, PSII and PGG were the main components of each fraction



Figure S1.GC profiles of the TMS derivatives of glycosides generated after acid hydrolysis of TB-EPS total sample (A) and both polysaccharidic sub-samples, water-soluble (TB-PS-aq) (B) and low water-soluble (TB-PS-inter) (C). Erythritol was used as internal reference.



Figure S2. Elution HPGPC profiles, monitored by RI detector, of LB-PS–aq and -inter in comparison to TB-PS-aq and -inter.



Figure S3.Percentage (w/w) of each ion exchange chromatography fraction eluted from TB-PS-inter (A) and TB-PS-aq (B) by increasing sequentially the NaCl concentration.



Figure S4.1H–NMR spectra of TB-PS-inter 0 M (PS I) (A) and TB-PS-aq 0.4 M (mainly PS II) (B).



Figure S5.1H–NMR spectra of TB-PS-inter 0.8 M (PGG).



Figure S6.Comparative OD evolution at 600 nm, related to bacteria growth in MB medium, for 3 strains, in absence and in presence of polysaccharide enriched-fractions: TB-PS-inter 0 M (PS I) (A), TB-PS-aq 0.4 M (mainly PS II) (B). Bars represent means ± standard errors for six replicates.



Figure S7. Elution HPGPC profiles, monitored by RI detector, of Sol-PS-aq, TB-PS-aq and TB-PS-inter isolated or extracted from planktonic cultures of *P. ulvae* TC14.