- 2 FIG S1 SDS- PAGE (8% acrylamide) of EPS stained with Coomassie Brilliant Blue R-250 (left) and silver-
- 3 stained SDS-PAGE (8% acrylamide) of EPS (right).
- 4 FIG S2 GC/MS chromatogram performed on EPS sample isolated from *Psa* NZ V-13.
- 5 FIG S3 <sup>1</sup>H-NMR spectrum of the EPS dissolved in  $D_2O$  recorded at 60°C (500MHz). Insert shows expanded
- 6 plot of anomeric region. Letters refer to sugar residues shown in Fig. 5.
- 7 FIG S4 <sup>13</sup>C -NMR spectrum of the EPS dissolved in D<sub>2</sub>O recorded at 60°C (500MHz). Inserts show expanded
- 8 plot of anomeric region (left) and CH3 of C-6 of deoxysugars (right). Letters refer to sugar residues shown in

9 Fig. 5.

- 10 FIG S5 HSQC spectrum of the *Psa* NZ V-13 EPS dissolved in D<sub>2</sub>O recorded at 60°C (500MHz).
- 11 FIG S6 <sup>1</sup>H-<sup>13</sup>C-HSQC spectrum of the ring sugar (A) and anomeric (B) regions of the *Psa* NZ V-13- EPS
- 12 dissolved in  $D_2O$  recorded at 60°C (500MHz). Letters refer to sugar residues shown in Fig. 5 and numbers to

13 carbons in sugar rings.

- **FIG S7** <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of the *Psa* NZ V-13 -EPS dissolved in  $D_2O$  recorded at 60°C (500MHz).
- 15 **FIG S8** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of the *Psa* NZ V-13 -EPS dissolved in D<sub>2</sub>O recorded at 60°C (500MHz). Letters
- 16 refer to sugar residues shown in Fig. 5 and numbers to proton cross-peaks in the sugar rings.
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## Continued

## GCMS Peak Report TIC

			GCMS Peak Report IIC	
Peak#	R.Time	Area	Name	Area%
1	7.034	32442842	Ethane, 1,1,2-trimethoxy-	1.29
2	7.640	3209375	Ethane, 1,1,2-trimethoxy-	0.13
3	8,900	5181291	2-Furancarboxaldehyde	0.21
4	10,384	5449126	Ethylbenzene	0.22
5	10.525	40505528	Sulfuric acid, dimethyl ester	1.61
6	10.861	21779483	Benzene, 1,2-dimethyl-	0.86
7	12.285	7919916	Benzene, 1,2-dimethyl-	0.31
8	16.249	7503712		0.30
9	16,529	30717337	2-Furancarboxaldehyde, 5-methyl-	1.22
10	17.016	72795021	Furancarboxylic acid, methyl ester	2.89
11	17.277	9684831		0.38
12	17.419	113833982	Pentanoic acid, 4-oxo-, methyl ester	4,52
13	18.418	5780403	2-Propyl-1-pentanol	0.23
14	18,560	10574206		0.42
15	18.676	26796056		1.06
16	19.470	3981213		0.16
17	19.711	461618225	Octade cane, 5-methyl-	18.32
18	20.341	4166092	2-Hexanone, 3-methoxy-5-methyl-	0.17
19	20.981	4755279		0.19
20	21.344	3637879		0.14
21	21.442	8387363		0.33
22	21,705	11584631	methyl 3-hydroxydecanoate	0.46
23	21,762	10272315		0.41
24	21,938	9611419		0.38
25	22.041	3787038		0.15
26	22,397	8675618	Decanoic acid, methyl ester	0.34
27	22,469	8277321	L-Glucose, 6-deoxy-3-O-methyl-	0.33
28	22.871	6593497	2-Decenoic acid, methyl ester	0.26
29	23,000	3699611		0.15
30	23,194	19839738	Dimethyl 2,5-thiophene dicarboxy late	0.79
31	23,574	8286898		0.33
32	23.749	229704737	methyl 3-hydroxydecanoate	9.11
33	24.025	4507784		0.18
34	24,180	30517822		1.21
35	24,268	239095717	C12: FAME - Lauric	9.49
36	24.676	44699399	Cholestan-15-one, 3-(acetyloxy)-14-butyl-, (3.beta, 5.alpha.)-	1.77
37	25.012	4587064		0.18
38	25.142	3548025		0.14
39	25,238	289978755	Hexadecanoic acid, 2-hydroxy-, methyl ester	11.51
40	25.481	390188035	Methyl 3-hydroxytetrade canoate ?	15,48
41	25,732	14477950		0.57
42	25,824	6331957	Ethane, 1,1,2,2-tetramethoxy-	0.25
43	25,884	8178309	Tetradecanoic acid, methyl ester	0.32
44	26.096	5207149		0.21
45	26.992	2876159	methyl 3-hydroxyhexade canoate ?	0.11
46	27.228	124276484	Methyl palmitolenate, C16:1 (cis-9) Me ester	4.93
47	27,354	95075856	Hexadecanoic acid, methyl ester	3.77
48	28,161	4230986	Methyl 2-ethylhexyl phthalate	0.17
49	28.282	15418871	Octadecanoic acid, 10-hydroxy-, methyl ester	0.61
50	28,581	32785234	methyl elaidate, C18.1 (trans-9) Me ester	1.30
51	28.692	3379566	Octadecanoic acid, methyl ester	0.13

56 Fig. S2



- 58 Fig. S3







Sugar residue	Nucleus Chemical shift of proton and carbon (ppm)							
		1	2	3	4	5	6	
$\rightarrow$ 4)- $\alpha$ -D-Glc <i>p</i> -(1 $\rightarrow$	$^{1}$ H	5.36	3.60	3.91 <sup>b</sup>	3.63 <sup>b</sup>	3.72	3.87/3.81	
	<sup>13</sup> C	100.4	72.1	77.9 <sup>b</sup>	77.7 <sup>b</sup>	73.2	61.1	
$\alpha$ -D-Fuc <i>f</i> -(1 $\rightarrow$	$^{1}$ H	5.27	4.02	3.95 <sup>d</sup>	3.51	3.86	1.20	
	<sup>13</sup> C	102.0	77.3	75.6 <sup>d</sup>	84.8	69.9	18.1	
$\rightarrow$ 2)- $\alpha$ -D-Rhap-(1 $\rightarrow$	$^{1}$ H	5.20	4.07	3.94 <sup>b</sup>	3.52 <sup>b</sup>	3.79	1.31 <sup>°</sup>	
	<sup>13</sup> C	101.2	78.5	70.3 <sup>b</sup>	72.7 <sup>b</sup>	69.5	17.1 <sup>°</sup>	
$\rightarrow$ 3)- $\alpha$ -D-Rhap-(1 $\rightarrow$	$^{1}$ H	4.99	4.06	3.95 <sup>d</sup>	3.64 <sup>b</sup>	3.92	1.30 <sup>°</sup>	
	<sup>13</sup> C	102.9	70.6	73.7 <sup>d</sup>	72.0 <sup>b</sup>	69.8	17.0 <sup>°</sup>	
$\rightarrow$ 3,4)- $\alpha$ -D-Rhap-(1 $\rightarrow$	$^{1}$ H	4.96	4.16	3.99	3.69	3.83	1.34	
· - · ·	<sup>13</sup> C	102.2	70.4	80.9	77.9	68.5	17.6	

**TABLE S1** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of the EPS composition

<sup>b</sup> assignments are only tentative <sup>c, d</sup> assignments are interchangeable

140