Supplementary information

Role of the hydrophobic phase for the unique rheological properties of saponin adsorption layers

By Konstantin Golemanov, Slavka Tcholakova, Nikolai Denkov, Eddie Pelan, Simeon D. Stoyanov

Table S1.
Studied saponins. The molecular structures (A) – (E) are shown in Figure S1.The critical micellization concentrations (CMC) were determined by measuring the surface tension isotherms and are presented as weight concentration of saponin in the solution

Table S2
Rheological parameters describing the behavior of adsorption layers of tea saponin or escin on air-water and hexadecane-water interfaces. Results from a creep and recovery experiments were fitted with an appropriate rheological model: escin on Hex-W interface - with the Burgers model, the rest of the systems - with the compound Voigt model.

Table S3
Parameters from the best fit of the experimental data shown in Figure S3 with eq. (8).

Figure S1. Structure of the saponins in the studied extracts. R1–R2 and X1-X3, designate sugar chains with different length and/or composition; X1-X3 can also designate H atom. (A) Monodesmosidic and (B) bidesmosidic triterpenoids with oleanane type of aglycone. (C) Mono- or bidesmosidic triterpenoids with dammarane type of aglycone. Steroid saponins of (D) spirostanol and (E) furastanol type.

Figure S2. Creep and relaxation of different saponin adsorption layers from group LV. The experimental conditions are: t_A = 30 min; t_{CR} = 100 s; torque M = 1 μN.m.

Figure S3. Surface storage modulus as a function of aging time for (A) QD adsorption layers and (B) Escin and TS adsorption layers, formed on different interfaces as indicated in the figure. Experiments are performed at constant frequency of 1 Hz and constant strain amplitude of 0.1 %.

Table S1. Studied saponins. The molecular structures (A) – (E) are shown in Figure S1.The critical micellization concentrations (CMC) were determined by measuring the surface tension isotherms and are presented as weight concentration of saponin in the solution

Type of aglycone	Molecular structure	Trade Name	Abbreviation used in text	Plant species	Extracted from	Supplier	Concentration of saponin, wt%	CMC, wt % saponin
Triterpenoid	A	Horse chestnut extract	HC	*Aesculus hippocastanum*	Seeds	Xi'an Biof Bio-technology Co.,Ltd	20	0.146
	A	Escin	ES	*Aesculus hippocastanum*	Seeds	Sigma	≥95	0.008
	A	Glycyrrhizic acid ammonium salt	LIC	*Glycyrrhiza glabra*	Roots	Sigma	≥95	Not measured
	A+B	Tea Saponin	TS	*Camelia Oleifera Abel*	Seeds	Zhejiang Yuhong Import&Export Co., Ltd	96.2	0.017
	A+B	Berry Saponin Concentrate	BSC	*Sapindus Mukurossi*	Fruits	Ecological Surfactants, LLC	53	≈ 0.1
	A+B	Sapindin	SAP	*Sapindus Triofilatus*	Fruits	Sabinsa Corporation	50	≈ 0.03
	B	Quillaja Dry 100, Non-preserved	QD	*Quillaja Saponaria Molina*	Bark	Desert King, Chilie	25.6	0.025
	C	Ginsenosides	GS	*Panax Ginseng*	Roots	Xianyang Hua Yue Biol. Engin. Co., Ltd.	80	0.019
	-	Ayurvedic Saponin Concentrate	ASC	*Acacia concinna*	Pods	Ecological Surfactants, LLC	30	≈ 0.3
Steroid	D+E	Tribulus terrestris extract	TT	*Tribulus Terrestris*	Herb	Sabinsa Corporation	45	0.048
	D+E	Foamation Dry 50	FD	*Yucca Schidigera*	-	Desert King, Chilie	9	≈ 0.03
	E	Fenusterols®	FS	*Trigonella foenum graecum*	Seeds	Sabinsa Corporation	50	0.089

Table S2. Rheological parameters describing the behavior of adsorption layers of tea saponin or escin on air-water and hexadecane-water interfaces. Results from a creep and recovery experiments were fitted with an appropriate rheological model: escin on Hex-W interface - with the Burgers model, the rest of the systems - with the compound Voigt model.

Parameter	**Tea Saponin**		**Escin**	
	A-W	C16-W	A-W	C16-W
G_0, mN/m	460 ± 40	95 ± 3	660 ± 20	210 ± 10
G_1, mN/m	460 ± 50	43 ± 1	2430 ± 300	111 ± 6
G_2, mN/m	190 ± 60	8.1 ± 0.6	800 ± 300	-
η_0, Pa.m.s	13.2 ± 1.2	1.9 ± 0.2	120 ± 30	1.6 ± 1
η_1, Pa.m.s	5.3 ± 0.6	0.5 ± 0.1	31 ± 9	2.9 ± 0.2
η_2, Pa.m.s	28.4 ± 2.2	2.1 ± 0.1	135 ± 20	-
λ_0, s	27 ± 2	20 ± 1	183 ± 36	7.6 ± 0.3
λ_1, s	12 ± 2	13 ± 1	14 ± 4	26 ± 3
λ_2, s	180 ± 60	255 ± 12	190 ± 80	-

Table S3. Parameters from the best fit of the experimental data shown in Figure S3 with eq. (8).

Parameters	QD			Escin		TS	
	Air-water	Hexadecane-water	Tricaprylin-water	Air-water	Hexadecane-water	Air-water	Hexadecane-water
$G_0^{'}$, mN/m	49.8	34.5	16.5	522	164	0	0
$G_1^{'}$, mN/m	34.6	20.3	6.8	288	216	728	400
$G_2^{'}$, mN/m	31.5	21.6	6.6	318	363	368	165
t_{R1}, min	17.9	17.5	19.3	18	33	17	75
t_{R2}, min	211	225	227	260	267	192	429
$G'(t \rightarrow \infty)$, mN/m	115.9	76.4	29.9	1128	743	1096	565

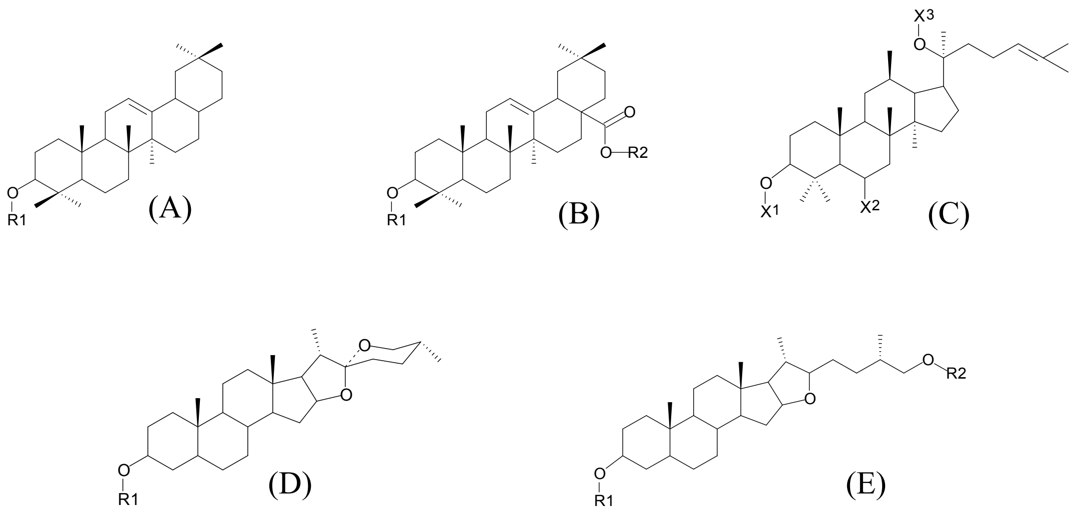


Figure S1. Structure of the saponins in the studied extracts. R1−R2 and X1-X3, designate sugar chains with different length and/or composition; X1-X3 can also designate H atom. (A) Monodesmosidic and (B) bidesmosidic triterpenoids with oleanane type of aglycone. (C) Mono- or bidesmosidic triterpenoids with dammarane type of aglycone. Steroid saponins of (D) spirostanol and (E) furastanol type.

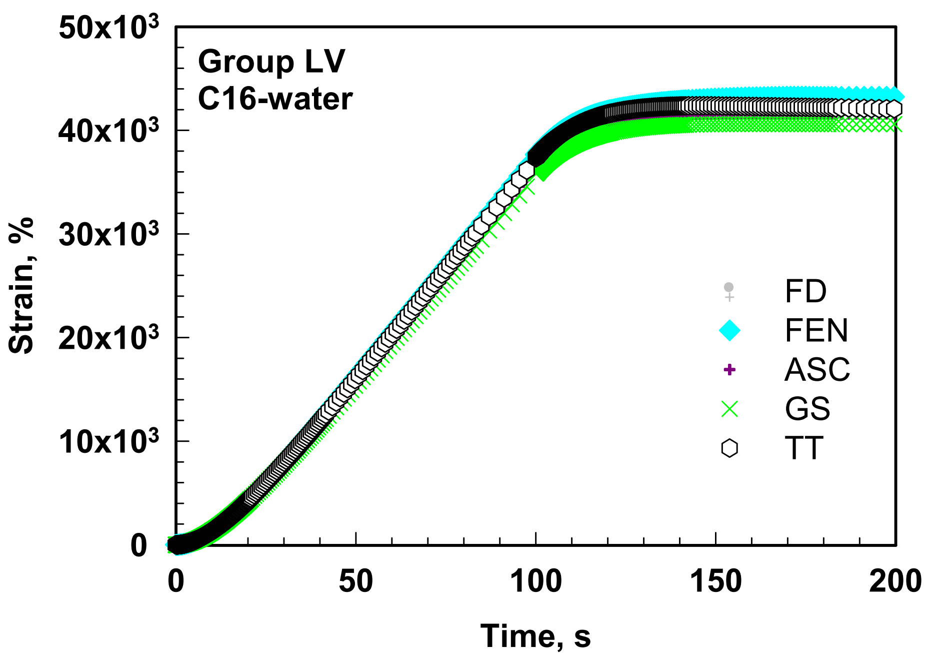
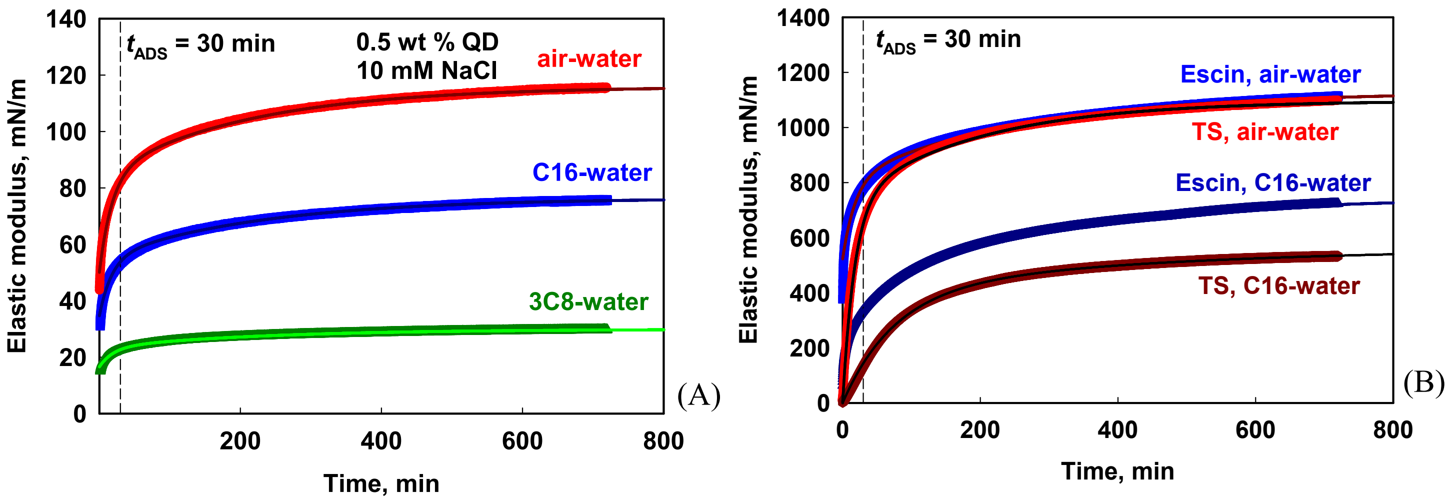


Figure S2. Creep and relaxation of different saponin adsorption layers from group LV. The experimental conditions are: t_A = 30 min; t_{CR} = 100 s; torque M = 1 μN.m.



<u>Figure S3.</u> Surface storage modulus as a function of aging time for (A) QD adsorption layers and (B) Escin and TS adsorption layers, formed on different interfaces as indicated in the figure. Experiments are performed at constant frequency of 1 Hz and constant strain amplitude of 0.1 %.