

Supplementary Materials: The Riddle of Cetuximab Related Skin Toxicity: ^1H -NMR Sebum Analysis Revealed in Metastatic Colorectal Cancer Patients Dynamic Lipids Alterations Associated with Skin Toxicity Development

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Table S1. NMR Selected sebum signal assignment.

Peak name	chemical shift (ppm)		multiplicity	type of protons	assignment
A	5.22	5.45	m	$-\underline{\text{CH}}=\underline{\text{CH}}-$, $\underline{\text{CH}}(\text{OR}')-\text{CH}_2\text{R}''$	unsaturated acyl groups and FA (e.g. TG(9,10,32,33,52,53), CE/COH(6), CE(39,38,40,41)), glyceryl group TG(21)
B	5.065	5.22	m	$-\underline{\text{CH}}=\text{C}$	SQ (3,7,11,14,18,22)
C	4.57	4.61	m	$\text{RCOO}\underline{\text{CH}}$	CE (3)
D	4.26	4.32	dd,dd*	$\text{RO}\underline{\text{CH}}_2-\text{CH}(\text{OR}')-\underline{\text{CH}}_2\text{OR}''$	TG (20,22)
E	4.175	4.115			
F	4.14	4.2	t	$-\underline{\text{CH}}_2\text{COOR}$	WE (15)
G	2.24	2.4	m	$\text{RCOO}\underline{\text{CH}}_2-$, $-\underline{\text{CH}}_2\text{COOR}$	FA(2),DG(17,24), TG(17,25,44), WE(19),CE(30), COH/CE(4)
H	2.097	1.952	m	$\underline{\text{CH}}_2-\text{CH}=\text{CH}$	SQ(4,5,8,9,12,13,16,17,20,21), CE/COH(7,12) and unsaturated acyl chain and FA
I	1.67	1.68	s	$-\text{CH}_3$	SQ (25,24)
L	1.61	1.58	s	$-\text{CH}_3$	SQ (1,26,27,28,29,30)
M	1.24	1.26	s	$-(\text{CH}_2)_n-$	overlapping of methylene hydrogens in acyl groups
N	0.86	0.85	t	$-\text{CH}_3$	
O	0.668	0.682	s	$-\text{CH}_3$	CE,COH (18)

*other lower signals in this interval of ppm can be attributed to glycerol group of 1,3 and 1,2 DG.

Peaks B,D,F,O were selected as diagnostic ones and used for the quantification of squalene, pool of triglycerides, pool of wax esters and cholesterol/cholesterol esters, respectively. In the case of free fatty acids and diglycerides there are no selective peaks.

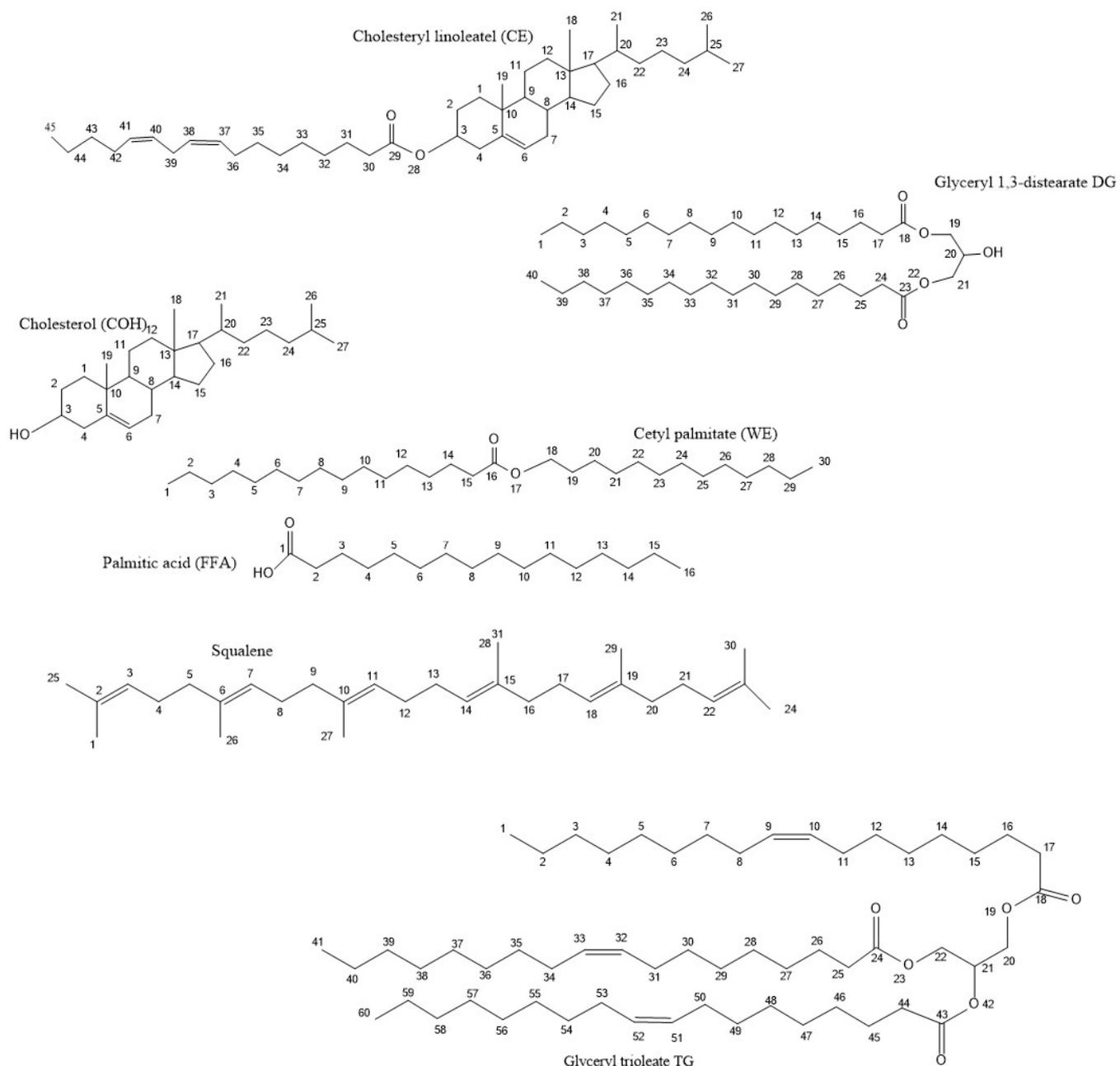


Figure S1 standard lipids molecules with numbering referring to proton assignment.

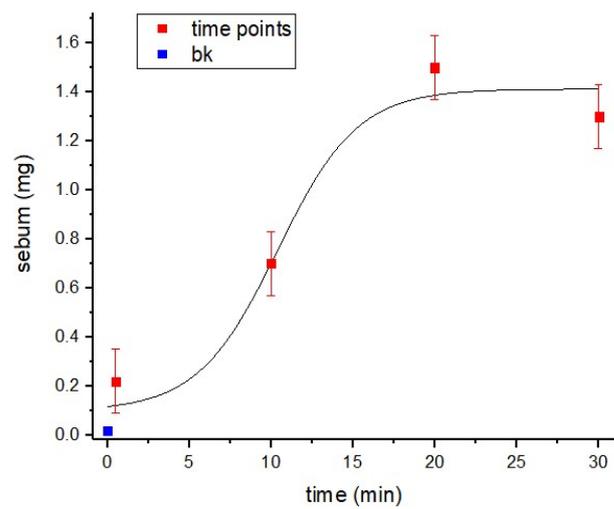


Figure S2. $^1\text{H-NMR}$ determined weight of sebum obtained at different Sebutape® application time collected from healthy volunteer. In blue average value obtained from clean tapes (blank).