SUPPORTING INFORMATION

Table S1. Theoretical and observed *b*- and *y*-ions from MS/MS analysis of native and labeled L32-K42 in apoMb labeled with pLeu in lyophilized solids.

Table S2. Theoretical and observed *b*- and *y*-ions from MS/MS analysis of GCG (1-8)* dimer in formulation containing peptide lyophilized with L-Leu.

Fig S1. FTIR (A) and far UV-CD spectra (B) of labeled and unlabeled apoMb.

Fig S2. Digest map of native apoMb digested with a combination of trypsin and chymotrypsin.

Table S1. Theoretical and observed *b*- and *y*-ions from MS/MS analysis of native and labeled L32-K42 in apoMb labeled with pLeu in lyophilized solids.

I. Product ions with *z*=+1 produced by fragmenting native L32-K42 (*m/z* = 424.5609; *z*=+3)

	b-ions	**Theoretical m/z**[a]	**Observed m/z**[b]	**y-ions**	**Theoretical m/z**[a]	**Observed m/z**[b]
L	b_1	114.0919		y_{11}	1271.6636	
F	b_2	261.1604	261.1586	y_{10}	1158.5796	
T	b_3	362.2080	362.2050	y_9	1011.5111	1011.5070
G	b_4	419.2295	419.2223	y_8	910.4635	910.4603
H	b_5	556.2884	556.2834	y_7	853.442	853.4381
P	b_6	653.3412		y_6	716.3831	716.3800
E	b_7	782.3838	782.3758	y_5	619.3303	619.3267
T	b_8	883.4314	883.4253	y_4	490.2877	490.2852
L	b_9	996.5155		y_3	389.2401	389.2385
E	b_{10}	1125.5581		y_2	276.1560	276.1544
K	b_{11}	1253.6531		y_1	147.1134	147.1119

II. Product ions with *z*=+2 produced by fragmenting native L32-K42 (*m/z* = 424.5609; *z*=+3)

	***y*-ions**[c]	**Theoretical m/z**[a]	**Observed m/z**[b]
L	y_{11}	636.3357	636.3344
F	y_{10}	579.7937	579.7910
T	y_{9}	506.2595	506.2572
G	y_{8}	455.7357	455.7332
H	y_{7}	427.2249	427.2230
P	y_{6}	358.6955	358.6935
E	y_{5}	310.1691	
T	y_{4}	245.6478	
L	y_{3}	195.1240	
E	y_{2}	138.5819	
K	y_{1}	74.0606	

III. Product ions with *z*=+2 produced by fragmenting labeled L32-K42 (*m/z* = 462.9133; *z*=+3)

	y-ions	(A) Theoretical *m/z* (labeled)	(B) Observed *m/z* (labeled)	(C) Observed *m/z* (unlabeled)	Mass difference (u)[d] $M = M_{labeled} - M_{unlabeled}$
L	y_{11}	693.8674	693.8649		
F	y_{10}	637.3254	637.3184	579.789	115.0588
T	y_9	563.7912	563.7873	506.2524	115.0698
G	y_8	513.2673	513.2592	455.7365	115.0454
H	y_7	484.7566	484.7525	427.2245	115.0560
P	y_6	416.2271	416.2189	358.6996	115.0386
E	y_5	367.7008			
T	y_4	303.1795			
L	y_3	252.6556			
E	y_2	196.1136			
K	y_1	131.5923			

[a] Calculated *m/z* values.

[b] *m/z* values obtained experimentally using mass spectrometry.

[c] No *b*-ions were detected by MS for *z* = +2.

[d] Mass difference M was calculated from *m/z* values in columns (B) and (C), using the formula M =(m/z)*n – nH+, where n is the number of charges on the *y*-ion and H is the mass of a proton (H=1.01 u).

IV. Product ions with *z*=+1 produced by fragmenting labeled L32-K42 (*m/z* = 462.9133; *z*=+3)

	y-ions[c]	(A) Theoretical *m/z* (labeled)	(B) Observed *m/z* (labeled)	(C) Observed *m/z* (unlabeled)	Mass difference $M = M_{labeled} - M_{unlabeled}$
L	y_{11}	1386.7269			
F	y_{10}	1273.6429			
T	y_9	1126.5744			
G	y_8	1025.5268			
H	y_7	968.5053			
P	y_6	831.4464	831.4462	716.3819	115.0643
E	y_5	734.3936	734.3989	619.3205	115.0784
T	y_4	605.3510	605.3535	490.289	115.0645
L	y_3	504.3034		389.2466	
E	y_2	391.2193		276.1541	
K	y_1	262.1767		147.1118	

[a] Calculated *m/z* values.

[b] *m/z* values obtained experimentally using mass spectrometry.

[c] No *b*-ions were detected by MS for *z* = +2.

[d] Mass difference M was calculated from *m/z* values in columns (B) and (C), using the formula M =(m/z)*n – nH+, where n is the number of charges on the *y*-ion and H is the mass of a proton (H=1.01 u).

Table S2. Theoretical and observed *b*- and *y*-ions from MS/MS analysis of GCG (1-8)* dimer from formulation containing peptide lyophilized with L-Leu. F* denotes p-benzoyl-L-phenylalanine (pBpA). Calculated m/z values are denoted as 'Theoretical m/z' while m/z values obtained experimentally using mass spectrometry are denoted as 'Observed m/z'.

I. Internal fragment (non-cross-linked) product ions with z=+1 produced by fragmenting GCG (1-8)* dimer (m/z = 646.2783; z=+3)

	***b*-ions**	**Theoretical *m/z*[b]**	**Observed *m/z*[c]**	***y*-ions**	**Theoretical *m/z*[b]**	**Observed *m/z*[c]**
H	b_1	138.0668	138.0656	y_8	968.4110	
S	b_2	225.0988	225.0973	y_7	831.3521	
Q	b_3	353.1574	353.1502	y_6	744.3201	
G	b_4	410.1789		y_5	616.2615	
T	b_5	511.2265	511.2234	y_4	559.2400	559.2367
F*[a]	b_6	762.3207		y_3	458.1923	458.1916
T	b_7	863.3684		y_2	207.0981	207.0963
S	b_8	950.4004		y_1	106.0505	106.0497

II. Cross-linked product ions with *z*=+2 produced by fragmenting GCG (1-8)* dimer (*m/z* = 646.2783; *z*=+3)

	***b*~α-ions**[d]	**Theoretical *m/z*[b]**	**Observed *m/z*[c]**	**α~*y*-ions**	**Theoretical *m/z*[b]**	**Observed *m/z*[c]**
H	b_1	553.2400		y_8	968.9173	968.9178
S	b_2	596.7560		y_7	890.8773	
Q	b_3	660.7853		y_6	847.3613	847.3526
G	b_4	689.2960	689.2939	y_5	783.3320	783.3290
T	b_5	739.8198	739.8130	y_4	754.8213	
F*	b_6	865.3669	865.3627	y_3	704.2975	
T	b_7	915.8908	915.8929	y_2	578.7504	
S	b_8	959.4068		y_1	528.2265	

[a] F* = p-benzoyl-L-phenylalanine (pBpA).

[b] Calculated *m/z* values.

[c] *m/z* values obtained experimentally using mass spectrometry.

[d] α = GCG (1-8)* monomer.

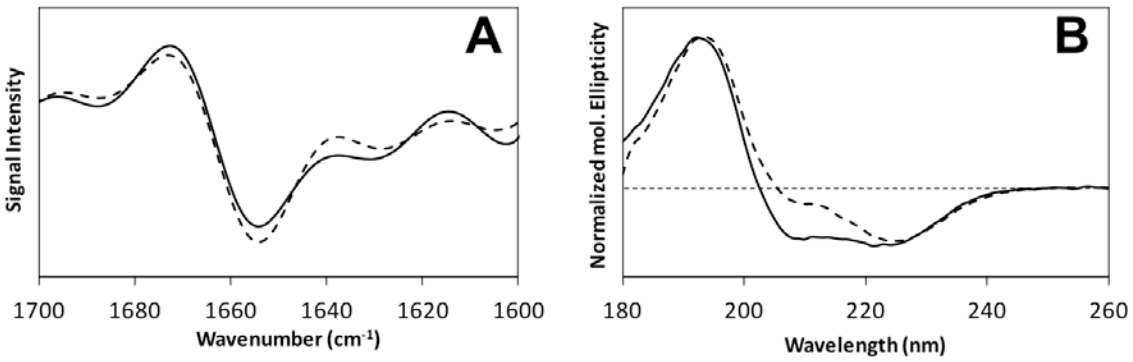

Fig S1. FTIR (A) and far UV-CD spectra (B) of labeled and unlabeled apoMb in lyophilized solids. ApoMb was co-lyophilized with sucrose and 100x molar excess of pLeu. The lyophilized formulation was irradiated at 365 nm for 40 min (dotted line), while the control was not irradiated (solid line).

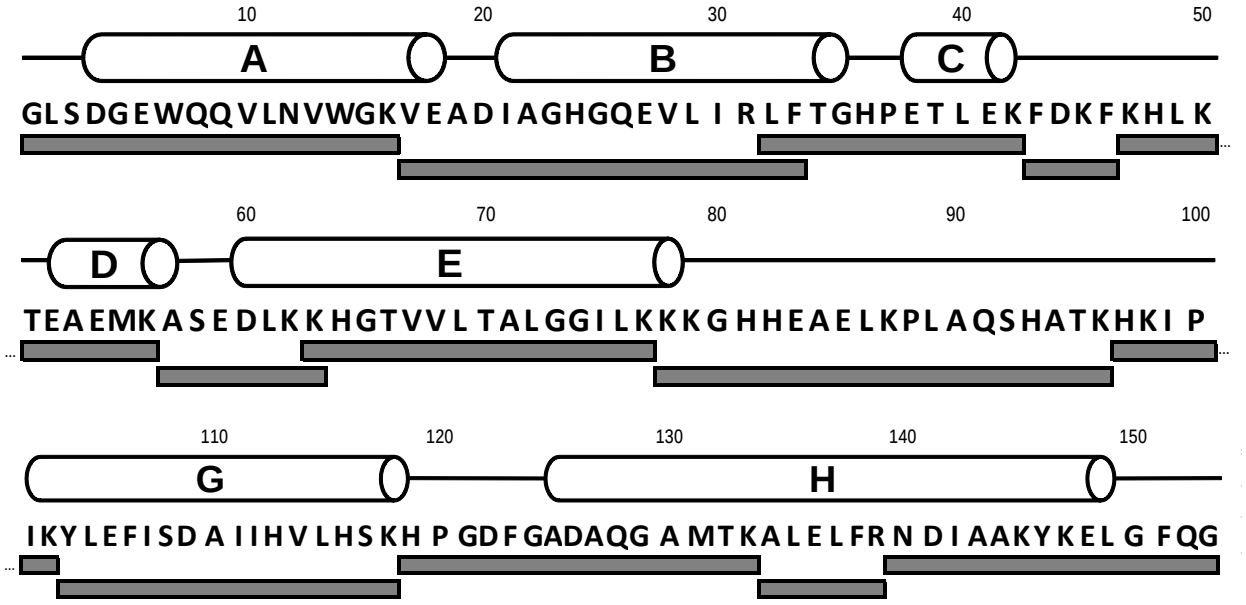

Fig S2. Digest map of native apoMb digested with a combination of trypsin and chymotrypsin. A total of 36 peptides were produced, of which the 13 shown by the shaded bars were selected to provide 100% sequence coverage.