	Web collection																																	
Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
Araneus cavaticus																																		
Penultimate instar																																		
Female																																		
Starving		8	8	8	8	8	8	8	8	8	8	7	5	1	1	1	1	1	1															
Resumed Feeding	5	4	4	4	4	3	1	1																										
Feeding		8	8	8	8	7	5	3	3	2	2	1	1	1	1	1	1																	
Male																																		
Starving		11	11	11	10	9	9	9	8	7	6	6	5	4	3	3	3	3	2	1	1	1	1	1	1	1								
Resumed feeding	4	4	3	2	2																													
Feeding		11	11	10	9	9	8	5	1	1																								
Adult female																																		
Starving		10	10	9	9	8	7	6	5	5	5	3	2	2	1	1	1																	
Resumed feeding	6	6	6	5	5	4	3	2	2	1	1	1																						
Feeding		6	8	8	7	6	5	5	5	5	5	5	5	4	3	3	1	1	1															
Argiope aurantia																																		
Adult Female																																		
Starving		11	11	11	11	11	10	10	9	8	8	7	7	7	7	6	4	4																
Resumed feeding	7	7	7	7	7	7	6	6	6	6	6	6	5	5	5	4	4	4	4	2	2	1												
Feeding		10	11	10	10	10	10	10	10	10	9	9	8	8	7	7	7	6	3	3	3	2	1	1	1	1	1	1	1					
Post-egg-sac 1	12	12	12	12	12	12	12	11	11	8	7	6	5	2	1	1	1	Ũ	U	U	U	-	•	-	-	-		<u> </u>						
Post-egg-sac 2	5	6	6	6	6	6	6	6	5	5	3	3	1	-	-	-	<u> </u>																	
Post-egg-sac 3	2	1	1	1	1	1	1	1	1	U	2	U	•																					
Argiope trifasciata	-	-					1		1																									
Adult Female																																		
Starving		8	8	8	8	8	8	8	8	8	7	7	7	7	7	6	6	5	4															
Resumed feeding	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	5	<del></del> 4	4	4	4	4	4	3	2	2	2	1					
Feeding	0	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	7	7	7	7	6	5	5	4	4	4	4	4	3	3	2	2
Post-egg-sac 1	4	4	4	4	4	4	4	4	4	4	4	4	4	4	1	1	0	0	,	,	,	,	0	5	5	т	т	т	Ŧ	Ŧ	5	5	4	2
Post-egg-sac 1 Post-egg-sac 2	4	4	4	4	4	4	4	4	4	4	4	4	4	+ 1	1	<u>+</u> 1																		
	2	2	2	2	2	2	2	2	2	2	2	1	5 1	1	1	<u> </u>																		
Post-egg-sac 3	2	2	2	2	2	2	2	2	2	2	2	1	1	1	1																			

Table S1. Number of webs in each of the analyzed non-radioactive web collections

In general, the number of webs per web collection decreased over the series for a given group because different individuals built different numbers of webs before their inclusion in the group ended. In two instances a web of one group was mistakenly added to webs of a different group, resulting in a total of five webs having to be discarded. This is the explanation for the anomalous number of webs in the web two collections of the *A. aurantia* feeding adult and *A. cavaticus* feeding adult groups and in the web one collection of the *A. aurantia* PES2 group.

Underlining is used to show those web collections that were 'horizontally pooled' prior to NMR analysis (see 'Gravimetric measurements of orb webs' in Materials and methods).

In all starving and feeding groups, spiders were allowed to recycle their web 1; thus, there is no web collection 1 from these groups.

Table S2. Effect of different pulse repetition and/or acquisition times on LMM quantitation by <sup>1</sup>H-NMR, as determined by analyzing a standard solution containing the 11 organic LMM in equimolar concentration

Time	(s)	Percentage error in measured molar %						
Pulse repetition	Acquisition	Assumption A	Assumption B					
3.28 <sup>a</sup>	3.28	7.3±2.55	6.5±1.80					
8.28	3.28	6.1±1.61	3.0±0.73					
8.28 <sup>b</sup>	6.55	4.0±1.25	3.8±0.77					
16.55	6.55	4.3±0.90	2.9±0.77					
33.11	6.55	5.4±1.26	_					

Values are means  $\pm$  s.e.m. (N=11).

<sup>1</sup>H-NMR analysis of the equimolar solution was performed four times with each of the five different sets of acquisition parameters. Thus, the measured molar percentage of each of the 11 LMM, used to calculate % error, is the average of four analyses.

In Assumption A, the actual molar percentage of each LMM is assumed to be 9.09 mole % (100 mole % / 11 LMM). This approach assumes an exactly equimolar standard solution was prepared. In Assumption B, the molar percentages obtained using the longest repetition time (33.11 s) are assumed to be closest to the true molar percentages.

<sup>a</sup>These acquisition parameters were used in the analysis of all *Araneus cavaticus* web extracts.

<sup>b</sup>These acquisition parameters were used in the analysis of all *Argiope aurantia* and *Argiope trifasciata* web extracts.

over the series of web collections									
Group	Slope	Ν							
A. cavaticus									
Feeding juvenile males	-1.598***	7							
Starving juvenile males	-0.497***	13							
Resumed feeding juvenile males	3.136	4							
Feeding juvenile females	-0.095	10							
Starving juvenile females	-0.648**	12							
Resumed feeding juvenile females	-0.461	6							
Feeding adult females	-0.591***	16							
Starving adult females	-0.442	10							
Resumed feeding adult females	0.119	9							
A. aurantia									
Feeding adult females	-0.224*	27							
Starving adult females	-0.811***	17							
Resumed feeding adult females	-0.328***	22							
Post-egg-sac 1 adult females	-1.367**	17							
Post-egg-sac 2 adult females	-0.612***	13							
Post-egg-sac 3 adult females	1.092	9							
A. trifasciata									
Feeding adult females	-0.162	33							
Starving adult females	-0.504**	17							
Resumed feeding adult females	-0.479**	29							
Post-egg-sac 1 adult females	-0.976***	15							
Post-egg-sac 2 adult females	-1.363**	15							
Post-egg-sac 3 adult females	-1.646***	14							

Table S3. *Linear regression slopes describing the change in the water-soluble percentage of the web over the series of web collections* 

Slope differs significantly from zero, \*P<0.05, \*\*P<0.01, \*\*\*P<0.001.

N, number of web collections water-extracted separately.