Table S1. ^{13}C chemical shifts of sugars[a] in artificial mixture (**bold**) and in honey (*italics*). The numbering system is shown in **Fig. 1**.

Sugar	C1	C2	C3	C4	C5	C6	C1´	C2´	C3´	C4´	C5´	C6´	C1´´	C2´´	C3´´	C4´´	C5´´	C6´´
Monosaccharides																		
α-D-glycopyranose (1*α*-GP)	92.66	72.05	73.34	70.22	71.99	61.17												
β-D-glycopyranose (1*β*-GP)	96.47	74.70	76.32	70.17	76.30	61.33												
α-D-fructopyranose (2*α*-FP)	65.74			71.03	71.03	61.70												
β-D-fructopyranose (2*β*-FP)	64.46	98.63	68.13	70.25	69.77	63.92												
α-D-fructofuranose (2*α*-FF)	63.48	104.99	82.54	76.61	81.86	61.66												
β-D-fructofuranose (2*β*-FF)	63.24	102.06	75.95	74,98	81.23	62.94												
Disaccharides																		
α-D-maltose (3*α*-GP)	100,18	72,30	73,40	69,89	73,21	61,05	92,42	71,84	73,77	77,49	70,49	61,15						
β-D-maltose (3*β*-GP)	100,13	72,22	73,40	69,89	73,21	61,06	96,31	74,54	76,74	77,28	75,09	61,31						
α-D-isomaltose (4*α*-GP)	98.55	72.09	73.60	70.08	72.38	61.07	92.76	72.00	73,57	70.13	70.61	66.33						
β-D-isomaltose (4*β*-GP)	98.51	72.05	73.63	70.08	72.35	61.04	96.66	74.63	76.54	69,94	74.87	66.25						
α-D-nigerose (5*α*-GP)	99.63	72.26[b]	73.46	70.00	72.32[b]	60.94	92.80	70.67	80.17	70.59	71.76	60.77						

β-D-nigerose (5*β*-GP)	99.53	72.20[b]	73.44	69.86	72.29[b]	60.94	96.53	73.40	82.69	70.61	76.21	61.10
Sucrose (6*β*-FF)	92.72	71.61	73.11	69.76	72.94	60.66	61.88	104.23	76.94	74.53	81.91	62.91
turanose (7*α*-FF)	97.41	71.76	73.44	69.88	72.80	60.84	63.28	104.81	85.33	75.06	82.07	61.57
Turanose (7*β*-FF)	99.03	71.98	73.23	69.88	72.88	60.84	63.40	102.25	81.07	74.90	81.40	62.84
turanose (7*β*-FP)	101.49	72.58	73.44	69.88	73.30	61.02	64.60	98.28	77.22	70.85	69.64	63.92
maltulose (8*α*-FF)	98.27	71.74	73.31	69.97	72.97	60.97	63.20	105.81	80.63	82.72	81.69	61.90
maltulose (8*β*-FF)	98.86	71.77	73.27	69.97	72.94	60.94	62.91	102.49	75.77	81.75	80.54	63.27
maltulose (8*β*-FP)	101.08	72.36	73.41	70.16	72.87	61.10	64.32	98.86	67.45	78.59	69.74	64.01

Trisaccharides

Erlose (9*β*-FF)	100.32	72.30	73.53	69.86	73.23	61.02	92.50	71.35	73.44	77,32	71,53	60.69	61.87	104.16	77.01	74.57	81.93	62.89
α-D-maltotriose (10*α*-GP)	100.07	72.26	73.40	69.84	73.21	61.02	100.28	72.10	73,87	77.32[b]	71.69	61.02	92.42	71.81	73.73	77.32[b]	70.45	61.06
β-D-maltotriose (10*β*-GP)	100.07	72.26	73.40	69.84	73.21	61.02	99.98	72.00	73.86	77.27[b]	71.69	61.02	96.30	74.52	76.68	77.27[b]	75.04	61.21
α-D-isomaltotriose (11*α*-GP)	98.33[b]	72,03	73.92	70,04	70,75	66,01	98.50	71,97	73.65	70,04	72,37	61,01	92.78	72,03	73.92	70,13	70,49	66,34
β-D-isomaltotriose (11*β*-GP)	98.31[b]	72,03	73.92	70,04	70,75	66,01	98.47	71,97	73.65	70,04	72,37	61,01	96.67	74.63	76.57	69,99	74.79	66,69
α-D-panose (12*α*-GP)	98.57	71.98	73.58	70.03	72.31	60.98	100.27	72.21	73.58	69.91	71.81	66.39	92.41	71.78	73.70	77.81	70.45	61.30[b]
β-D-panose (12*β*-GP)	98.57	71.98	73.58	70.03	72,35	60.98	100.17	72.12	73.58	69.91	71.81	66.39	96.28	74.48	76.69	77.69	75.08	61.17[b]

Melizitose (13*α*-GP)	100.82	71.97	73.32	70.14	72.82	60.83	92.25	104.19	83.79	73.75	81.68	62.52	92.25	71.50	73.75	70.01	72.71	61.10
1-kestose (14*β*-FF)	93.03	71.66	73.11	69.75	72.96	61.43	60.63	103.77	77.17	75.00	81.66	62.70	60.94	104,25	77,17	74.38	81.75	62.86

[a]the tautomeric form of the reducing sugar is denoted in parentheses.

[b]Chemical shifts may be interchanged

Table S2. Assignment of the carbon resonances in the five ^{13}C NMR subspectra of Fig. S3a to S3e.

Signal	Tautomer[a,b]	Signal	Tautomer	Signal	Tautomer	Signal	Tautomer
1	2αFF^{2}, 2αFP^{2}	15	5βGP^{1},5αGP^{1}	29	7αFF$^{3'}$	43	12βGP$^{4''}$,10βGP$^{4'}$
2	7αFF$^{2'}$,	16	7βFF$^{1'}$	30	13αGP$^{3''}$	44	10βGP$^{4''}$,10αGP$^{4'}$,9βFF$^{4'}$,3βGP$^{4'}$,3αGP$^{4'}$
3	9βFF$^{2''}$,6βFF$^{2'}$	17	12βGP^{1},12αGP^{1},8βFP^{2},8βFF^{1},2βFP^{2},11βFP^{2}	31	8αFF$^{3'}$,5βGP$^{3'}$	45	14βFF$^{3''}$,14βFF$^{3'}$,7βFP$^{3'}$
4	13αGP$^{2''}$,12βGP$^{2''}$,13αGP$^{2''}$,14βFF$^{2'}$	18	11αGP^{1},4αGP^{1}	32	2αFF^{3},2αGP^{1}	46	6βFF$^{3'}$
5	13αGP$^{2'}$,14βFF$^{2'}$	19	11βGP$^{1'}$,11αGP$^{1'}$,8αFF^{1}, 7βFP$^{2'}$,4βGP^{1}	33	7αFF$^{5'}$,6βFF$^{5'}$	47	12βGP$^{3''}$
6	8βFF$^{2''}$	20	7αFF^{1}	34	9βFF$^{5''}$	48	3βGP$^{3'}$
7	7βFF^{2}	21	11βGP$^{1''}$,4βGP$^{1'}$,1αGP^{1}	35	14βFF$^{5''}$,2αFF^{5}	49	4βGP$^{3'}$,2αFP^{4},2αFF^{4}
8	2βFF^{2}	22	5βGP$^{1'}$,1βGP^{1}	36	13αGP$^{5''}$,14βFF$^{5'}$,8βFF$^{4'}$,8αFF$^{5'}$	50	10αGP$^{4''}$,1βGP^{5},1βGP^{3}
9	7βFP^{1}	23	12βGP$^{1'}$,10βGP$^{1''}$,3βGP$^{1'}$	37	7βFF^{5}	51	10βGP$^{3''}$
10	8βFP^{1}	24	11αGP$^{1''}$	38	2βFF^{5},2αFP^{5}	52	5βGP$^{5'}$
11	13αGP^{1}	25	14βFF^{1}	39	7βFF^{3}	53	2βFF^{3}
12	12αGP$^{1'}$,10βGP^{1},9βFF^{1},10αGP$^{1'}$	26	10αGP$^{1''}$,6βFF^{1},5αGP$^{1'}$,4αGP$^{1'}$,3αGP$^{1'}$	40	8βFF$^{5'}$,8αFF$^{4'}$	54	8βFF$^{3'}$
13	12βGP$^{1''}$	27	12αGP$^{1''}$,9βFF$^{1'}$	41	8βFP$^{4'}$,5αGP$^{3'}$	55	12αGP$^{5''}$
14	10βGP^{2},10αGP$^{1'}$,3βGP^{1},3αGP^{1}	28	13αGP$^{1'}$	42	12αGP$^{4''}$	56	10βGP$^{5''}$,7αFF^{5},3βGP$^{5'}$

Signal	Tautomer	Signal	Tautomer	Signal	Tautomer	Signal	Tautomer
57	14βFF$^{4'}$,2βFF^{5}	69	13αGP^{5},12βGP^{5},12αGP^{5},11βGP$^{5'}$,11αGP$^{5'}$,10βGP^{2},10αGP^{2},8βFP^{2},5βGP^{5},5βGP^{3},4αGP^{5},4βGP^{5},3αGP^{2}, 5αGP^{5},5αGP^{3},5αGP^{2}	81	12βGP^{4},12αGP^{4},11βGP^{4},11αGP^{4},1αGP^{4}	93	8βFP$^{6'}$,8αFF$^{1'}$,2βFP^{6}
58	11βGP$^{5''}$,4βGP$^{5'}$	70	12βGP$^{2'}$,12αGP$^{2'}$,10αGP$^{2''}$,5βGP^{2},3βGP^{2}	82	13αGP$^{4'}$,13αGP^{4},11βGP$^{4''}$,11αGP$^{4''}$,11αGP$^{4'}$,8βFP^{5},4αGP$^{4'}$,4βGP^{4},4αGP^{4},1βGP^{5}	94	7βFP$^{6'}$,7βFF^{6},2αFF^{1}
59	12αGP$^{2''}$,11βGP$^{2''}$,11αGP$^{3''}$,4βGP$^{2'}$,1βGP^{2}	71	13αGP^{2},12αGP^{2},12αGP^{2},11βGP^{2},11αGP$^{2''}$,11αGP^{2},10αGP$^{2'}$,6βFF^{5},1αGP^{1},1αGP^{5},4αGP^{2}, 4βGP^{2}	83	12αGP$^{4'}$,12αGP$^{4'}$,11βGP$^{4''}$,10βGP^{4},10αGP^{4},9βFF^{4},8αFF^{4},8βFF^{4},7αFF^{4},7βFP^{4},5βGP^{4},4βGP$^{4'}$,3βGP^{4} ,3αGP^{4}	95	8βFF$^{6'}$,7αFF$^{6'}$,2βFF^{1}
60	14βFF$^{4''}$,12βGP$^{2''}$,11βGP$^{3''}$,10βGP$^{2''}$,9βFF$^{4''}$,6βFF$^{4'}$,3βGP$^{2'}$	72	11βGP$^{2'}$,11αGP$^{2'}$,7βFP^{2},4αGP$^{2'}$	84	14βFF^{4},8βFP$^{5'}$,7βFP$^{5'}$,7βFF$^{4'}$,6βFF^{4},2βFP^{5}	96	14βFF$^{6''}$,9βFF$^{6''}$,7βFF^{1},6βFF$^{6'}$,2βFF^{6}
61	13αGP$^{3'}$,12αGP$^{5''}$,11αGP$^{3'}$,10βGP$^{3'}$,10αGP$^{3''}$,10αGP$^{3'}$,3αGP$^{2'}$	73	12βGP$^{5'}$,12αGP$^{5'}$,3αGP$^{2'}$	85	2βFP^{3}	97	13αGP$^{1''}$,14βFF$^{6'}$,7βFF$^{5'}$

62	13αGP$^{4''}$,12βGP$^{3'}$,12αGP$^{3'}$,12βGP^{3},12αGP^{3},11βGP$^{3''}$,11βGP^{3},11αGP^{3},10βGP^{3},10αGP^{3},9βFF^{3},4αGP$^{3'}$,4αGP^{3},4αGP^{3}	74	14βFF^{2},8αFF^{2},8βFF^{2},7αFF^{2},5αGP$^{5'}$	86	8βFP$^{4'}$	98	13αGP$^{6''}$
63	13αGP^{3},14βFF^{3},9βFF$^{3'}$,8βFP^{3},7αFF^{3},7βFP^{3},3βGP^{3},3αGP^{3}	75	9βFF$^{5'}$,6βFF^{2}	87	11βGP$^{6''}$	99	9βFF$^{1''}$,8αFF$^{6'}$,8βFF$^{1'}$,6βFF$^{1'}$,2αFP^{6}
64	8βFF^{3},8αFF^{3},7βFP^{5},5βGP$^{2'}$,1αGP^{3}	76	13αGP$^{2'}$	88	12βGP$^{6'}$, 12αGP$^{6'}$	100	7αFF$^{1'}$,7αFF^{6},2αFP^{1},2αFF^{6}
65	10βGP^{5},9βFF^{5},10αGP^{5},7βFF$^{3'}$,3βGP^{5},3αGP^{5}	77	9βFF$^{2'}$	89	11αGP$^{6''}$,4αGP$^{6'}$	101	14βFF$^{1''}$,12βGP$^{6''}$,3βGP$^{6'}$,1βGP^{6}
66	6βFF^{3}	78	10βGP$^{5'}$,10βGP$^{2'}$,10αGP$^{4'}$,9βFF$^{3''}$,7βFP$^{4'}$	90	4βGP$^{6'}$	102	13αGP$^{6'}$,12αGP$^{6''}$,10βGP$^{6''}$,5βGP$^{6'}$,3αGP$^{6'}$
67	14βFF^{5},9βFF^{2},8αFF^{5},8βFF^{5},7βFF^{4}	79	11βGP^{5},11αGP$^{5''}$,11αGP^{5},10αGP$^{5''}$,5βGP$^{4'}$,5αGP$^{3'}$,5αGP^{4},4αGP$^{5'}$,3αGP$^{5'}$	91	2βFP^{1}	103	13αGP^{6},14βFF$^{1'}$,12αGP^{6},12αGP^{6},11βGP$^{6'}$,11αGP$^{6'}$,10βGP$^{6'}$,10βGP^{6},10αGP$^{6''}$,10αGP$^{6'}$,10αGP^{6},9βFF^{6},8βFP^{6},8αFF^{6},8βFF^{6},7βFP^{6},7βFF$^{6'}$,5βGP^{6},5αGP$^{6'}$,5αGP^{6},4βGP^{6},4αGP^{6},3βGP^{6},3αGP^{6},1αGP^{6}
68	13αGP$^{5'}$,8βFP^{5},7αFF$^{4'}$	80	2βFP^{4}	92	8βFP$^{1'}$,7βFP$^{1'}$,2βFP^{1}	104	14βFF^{6},9βFF$^{6'}$,6βFF^{6}

[a]the tautomeric form of the reducing sugar is denoted for the tautomers (see Fig. 1)

[b]The superscript in each tautomer denotes carbon number (see Fig. 1)

Table S3. Comparison of the measured amount (%w/w) of each tautomer of D-fructose and D-glucose in the isoglucose mixture from integration of the ^{13}C NMR signals to that of the actual concentration (weighted amount).

Tautomers	**Actual concentration**	**Concentration determined by ^{13}C NMR**
α-D- fructofuranose	118.5	118.2
β-D-fructofuranose	1659.1	1654.1
α-D-fructopyranose	47.4	44.5
β-D- fructopyranose	545.1	537.2
Total D-fructose	2370.1	2354.0
α-D-glucopyranose	723.3	708.6
β-D-glucopyranose	1205.5	1183.3
Total D-glucose	1928.9	1891.9

Table S4. Comparison of the measured amount (%w/w) of each sugar tautomer in the artificial mixture from integration of the ^{13}C NMR signals to that of the actual concentration (weighted amount).

Tautomer	Actual concentration	Concentration determined by ^{13}C NMR
α-D-fructofuranose (2*α*-FF)	118.5	117.6
turanose (7*β*-FF)Τυρανόζη	19.6	19.2
1-kestose (14*β*-FF)	9.9	9.6
maltulose (*8*β-FF)	20.2	20.4
turanose (7*β*-FP)	38.2	38.0
maltulose (*8*β-FP)	40.4	39.8
melisitose (13*α*-GP)	4.5	4.4
α-D-nigerose (5*α*-GP)	10.7	10.7
β-D-nigerose (5*β*-GP)	17.1	17.1
turanose (7α-FF)	39.2	38.5
β-D-glycopyranose (1*β*-GP)	1205.5	1188.0
β-D-fructofuranose (2*β*-FF)	545.1	543.9
erlose (9*β*-FF)	49.6	49.4
β-D-fructopyranose (2*β*-FP)	1659.1	1650.3

Table S2. Continued