THE RELATION OF PHYSICOCHEMICAL CHARACTERISTICS OF HONEY AND THE CRYSTALLIZATION SENSITIVE PARAMETERS

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Introduction

Honey is a highly concentrated solution of simple sugars that contains more dissolved material than can remain in solution. All honeys do not precipitate their sugars and granulate at the same rate. Their tendency to granulate is directly related to some sensitive parameters (crystallisation indices) such as glucose, the ratio glucose/water (D/W), glucose-water/fructose (D-W/L), fructose/glucose (L/D) and melezitose.

Specifically, honey generally is crystallising fast when has more than 28-30% glucose, (PHILLIPS, 1929, KODOUNIS, 1962; BOGDANOV, 1993), D/W ratio of 2.1 and higher (AUSTIN, 1953; JAMIESON, 1954; WHITE 1962, 1975; KODOUNIS, 1962), high ratio D-W/L (JACKSON and SILSBEE, 1924), L/D ratio <1.14 (JAMIESON, 1954, KOUDOUNIS, 1962, WHITE, 1975) and melesitose content more than 10% (BOGDANOV, 1993).

In this study, we fit the so far proposed crystallisation indices to data from the international literature and from Greek honeys as well, to find their predictability on the phenomenon and consequently search practicable ways to predict and control granulation.

Materials and methods

Data concerning international monofloral honeys were retrieved mainly from CRANE et al., (1984). Data concerning Greek monofloral honeys were obtained through gas chromatographic analysis of 20 samples each of pine, fir, thymus and hellianthus honey.

Sugars converted to volatile trimethylsilyl ethers are resolved and determined by gas chromatograph equipped with splitless injection system and FID detector. Capillary column SE-52 or equivalent (i.e. DB-5, length 30 M, ID 0.32 mm, film thickness 0.25 μ).

Results and Discussion

Table I shows the granulation indices and the tendency of granulation of international monofloral honeys and tables II-V the relative data for Greek honeys. The bold figures indicate values with correct prediction.

Table I

Granulation indices of monofloral honeys

Type of honey	D	$\frac{D.}{W}$	$\frac{D-W}{L}$	$\frac{L.}{D}$	Crystallization*
016 Actinodaphne angustifolia	35.5	1.89	0.44	1.07	medium
023 Aloe davyana	39.1	2.30	0.61	0.92	rapid
031 Anchusa officinalis	37.5	2.2	0.43	1.26	slow
034 Antigonon leptopus	28.6	1.75	0.31	1.35	rare
035 Asclepias syriaca	33.4	1.96	0.34	1.44	rare
054 Brassica campestris	26.4	1.45	0.22	1.40	rapid
060 Brassica napus	35.2	2.10	0.47	1.05	rapid
072 Calluna vulgaris	33.7	1.70	0.36	1.12	slow
077 Calvia callosa	28.2	1.50	0.25	1.35	rare
080 Castanea sativa	32.4	1.80	0.34	1.31	slow
081 Catunaregam spinosa	35.6	2.06	0.44	1.77	medium
097 Citrus sinensis	28.2	1.83	0.36	1.17	slow
140 Echium vulgaris	31.2	1.90	0.93	1.19	slow
144 Epilobium angustifolium	28.8	1.73	0.30	1.38	medium
152 Eucalyptus albens	29.6	1.66	0.32	1.22	rapid

156 Eucalyptus camaldulensis	32.7	1.92	0.41	1.16	rapid
158 Eucalyptus cladocalyx	25.2	1.72	0.25	1.66	none
172 Eucalyptus leucoxylon	29.1	1.81	0.28	1.57	rapid
176 Eucalyptus melliodora	30.4	2.17	0.38	1.41	slow
198 Euphoria longa	29.9	1.66	0.35	1.29	rare
199 Fagopyrum esculentum	33.4	1.61	0.38	0.99	slow
210 Gossypium hirsutum	33.4	2.14	0.44	1.18	medium
220 Hedysarum coronarium	44.5	2.90	0.62	1.04	rapid
221 Helianthus annuus	34.7	2.30	0.57	1.00	rapid
223 Hevea brasiliensis	40.7	1.60	0.57	0.66	rapid
230 Ilex glabra	27.4	1.77	0.30	1.44	slow
265 Lippia nodiflora	31.6	1.41	0.25	1.14	rapid
272 Lotus corniculatus	42.9	2.52	0.49	1.21	rapid
286 Marrubium vulgare	26.6	1.56	0.18	1.98	rare
290 Medicago sativa	32.6	1.90	0.43	1.11	rapid
296 Melilotus alba	33.7	1.79	0.40	1.08	rapid
311 Nyssa ogeche	23.8	1.36	0.15	1.77	never
314 Onobrychis viciaefolia	41.8	2.45	0.49	1.20	rapid
316 Oxydendron arboreum	25.5	1.53	0.21	1.59	slow
324 Phacelia tanacetifolia	35.0	2.15	0.36	1.42	rapid
342 Prunus yetoensis	40.4	2.12	0.40	1.25	rapid
347 Rabdosia rugosa	38.4	2.19	0.52	1.4	rapid
354 Robinia pseudacacia	29.0	1.90	0.33	1.42	slow
358 Rubus idaeus	32.9	2.15	0.50	1.06	medium
370 Salvia officinalis	34.4	2.02	0.49	1.17	slow
382 Serenoa repens	30.8	2.13	0.42	1.21	rapid
395 Sysygium cuminii	32.6	1.77	0.32	1.32	slow
401 Terminalia chebula	35.6	2.06	0.45	1.12	medium
403 Thelepaepale ixiocephala	38.3	2.09	0.50	1.02	rapid
407 Thymus vulgaris	24.3	1.42	0.19	1.50	slow
428 Trifolium hybridum	31.0	1.86	0.37	1.23	rapid
430 Trifolium pratense	49.0	2.8	0.63	1.02	rapid
431 Trifolium repens	30.1	1.50	0.23	1.33	rapid
440 Vicia villosa	29.5	1.71	0.26	1.43	rapid (+mel)
448 Ziziphus mauritania	31.5	1.36	0.24	1.12	slow

** rapid crystallization: complete within 1 month, medium: 1-12 months, slow: >1 year, rare >4-5 yrs.*
Data were retrieved from CRANE et al. (1984). D=glucose, W=water, L=fructose

Glucose

Data on international honeys fit well with the general belief that the greater the glucose content the higher the tendency of crystallisation. All types of honeys that have glucose lower than 30%, are slow or non-granulating honeys. *Brassica campestris* honey (field cabbage or rape) is an exception.

This honey although has low glucose content (26.4%) shows an unexpected rapid granulation. The given low value of glucose for this honey is surprising since rape honey is known for its high glucose content (MAURIZIO, 1964, POURTALLIER and TALIERCIO, 1970).

Out of the 16 honeys that have more than 34% glucose, two show slow crystallisation tendency and the rest are as expected fast or medium crystallised honeys.

Glucose content of honey from Greek pine trees (a non-crystallised honey) and of sunflower (a fast crystallised honey) is good indication of crystallisation tendency. The maximum glucose content of pine honey is 29.3 (table II) and the minimum content of sunflower honey is 35.2% (table III). The conclusion with international honeys, that glucose is not very useful index in samples that have medium crystallisation tendency, is also applied with the Greek thymus honey.

Table II

Granulation indices of Greek honeydew honey from pine trees (non-granulating honey)

Sample number	Glucose (D)	D/W	$\frac{D-W}{L}$	L/D
1	**26.5**	**1.6**	0.32	1.16
2	**27.0**	**1.6**	0.32	1.19
3	**25.2**	**1.5**	0.29	1.24
4	**26.6**	**1.5**	0.31	1.16
5	**27.0**	**1.5**	0.30	1.16
6	29.3	**1.7**	0.35	1.16
7	**27.1**	**1.7**	0.37	**1.80**
8	**27.3**	**1.6**	0.34	1.13
9	**28.4**	**1.5**	0.27	1.26
10	**28.8**	**1.7**	0.39	1.08

11	**27.5**	**1.6**	0.35	1.11
12	**25.2**	**1.4**	0.25	1.30
13	**27.0**	**1.5**	0.28	1.29
14	**27.5**	**1.6**	0.28	1.36
15	**28.4**	**1.5**	0.28	1.29
16	**25.2**	**1.5**	0.31	1.10
17	**25.2**	**1.6**	0.32	1.19
18	**25.2**	**1.4**	**0.20**	1.42
19	**28.8**	**1.8**	0.36	1.11
20	**25.7**	**1.4**	**0.19**	1.40

Glucose/water (D/W) ratio

The best index of granulation tendency is the ratio D/W that predicted correctly 34 cases out of 50 (68%) international data. Eleven out of 16 honeys that have misleading D/W values have low D/W index (1.41-1.92) and rapid tendency of cristallisation. Possibly the relative inaccurancy of the different methods of analysis may obscure the relationship.

Table III

Granulation indices of Greek sunflower honey (rapid-granulating honey)

Sample number	Glucose (D)	D/W	$\frac{D-W}{L}$	L/D
1	**36.8**	1.99	0.45	1.09
2	**37.8**	**2.22**	**0.50**	1.11
3	**36.3**	**2.26**	0.49	1.13
4	**38.2**	2.00	0.48	1.04
5	**35.2**	**2.07**	0.45	1.14
6	**36.9**	**2.10**	0.48	1.08
7	**37.4**	1.92	0.44	1.07
8	**37.2**	1.95	0.43	1.12
9	**38.3**	**2.19**	**0.51**	1.05
10	**36.9**	**2.17**	0.49	1.08
11	**38.9**	**2.22**	0.53	1.02
12	**39.4**	**2.18**	**0.53**	1.03
13	**39.3**	**2.38**	**0.55**	1.05
14	**39.2**	**2.45**	**0.56**	1.05
15	**41.3**	**2.23**	**0.54**	1.02
16	**38.3**	2.01	0.49	1.02
17	**39.2**	**2.24**	**0.52**	1.06
18	**37.8**	**2.16**	**0.53**	1.01
19	**36.8**	**2.23**	**0.50**	1.09
20	**37.2**	**2.25**	**0.52**	1.06

In all samples of Greek honey granulating or not D/W ratio gave good prediction. Even in the case of thymus honey with the medium granulation tendency the prediction is accurate.

The ratio D-W/L

D-W/L ratio predicts 14 cases out of 50 (28%). Only extreme values of this ratio can give good prediction of granulation tendency. Honeys that remain liquid over years have a ratio below 0.20, and those that crystallised fast have the ratio over 0.50. Values between these two figures are equal distributed between rapid and slow crystallised honeys.

D-W/L ration of Greek honeys gave very poor prediction for granulating tendency of all samples examined. The result is specially discouraging with pine and thymus honey (tables II and IV).

Fructose/Glucose (L/D) ratio

L/D ratio is the worse index for granulation tendency (predict 7 cases). It can not be used as predictor indicator of crystallisation since only the extreme values (>1.66 or <0.90) indicate good relation to granulation tendency.

Table IV

Granulation indices of Greek thymus honey (medium tendency of granulation)

Sample number	Glucose (D)	D/W	D-W / L	L/D	Crystallization (months)
1	31.0	**1.97**	0.36	1.37	11
2	**29.7**	**1.98**	0.36	1.36	12
3	30.1	**1.66**	0.27	**1.49**	.>17
4	31.2	**1.93**	0.35	1.36	14
5	30.1	**2.01**	0.34	**1.48**	12
6	**28.8**	**1.62**	0.28	1.37	>17
7	31.2	**1.83**	0.32	1.41	15
8	31.1	**1.98**	0.35	1.41	13
9	**27.6**	**1.55**	0.25	**1.43**	>17
10	29.2	**1.94**	0.34	1.40	11
11	30.6	**1.98**	0.39	1.26	12
12	**28.6**	**1.58**	0.26	1.36	>17
13	30.8	**1.91**	0.35	1.35	16
14	31.5	**1.95**	0.35	1.37	14
15	32.6	**1.91**	0.39	1.27	14
16	30.2	**1.66**	0.27	**1.47**	>17
17	**26.3**	**1.45**	**0.18**	**1.41**	>17
18	31.1	**2.00**	0.83	1.31	>17

Table V

Granulation indices of Greek fir honey (non-crystallized)

Sample number	Glucose (D)	D/W	D-W / L	L/D	Melezitose
1	**19.4**	**1.21**	**0.11**	1.54	10.9
2	**20.6**	**1.30**	**0.18**	1.41	**5.3**
3	**17.3**	**1.14**	**0.01**	**1.59**	10.3
4	**15.4**	**1.10**	**0.05**	**1.61**	12.9
5	**16.4**	**1.13**	**0.07**	**1.59**	12.4
6	**17.2**	**1.17**	**0.09**	1.53	12.3
7	**15.6**	**1.08**	**0.05**	1.52	21.1
8	**14.1**	**0.95**	**-0.03**	**1.65**	12.3
9	**16.2**	**1.05**	**0.07**	1.55	13.0
10	**15.0**	**0.92**	**-0.04**	**1.65**	11.2
11	**16.1**	**0.99**	**-0.04**	1.37	9.5
12	**17.1**	**1.14**	**0.09**	1.29	**5.5**
13	**18.7**	**1.28**	**0.14**	1.37	**5.3**
14	**21.3**	**1.41**	**0.21**	1.41	11.2
15	**15.6**	**1.06**	**0.04**	1.46	**7.7**
16	**17.1**	**1.17**	**0.11**	1.56	**6.1**
17	**17.1**	**0.99**	**-0.01**	1.44	9.0
18	**17.6**	**1.15**	**0.09**	1.40	**8.3**
19	**17.2**	**1.13**	**0.07**	1.50	**8.0**
20	**17.0**	**1.06**	**0.04**	**1.61**	**6.0**

L/D ratio gives the poorest results also in all types of Greek honey (tables II-IV). In pine honey it predicted correctly only one sample, in sunflower none and in thymus 5 out of 20.

Table VI

D/W values of honeys with different content of glucose and water

D%	14%	15%	16%	17%	18%	19%	20%	21%
26	1.85	1.75	**1.62**	**1.53**	**1.44**	**1.36**	**1.30**	**1.23**
27	1.92	1.80	**1.68**	**1.58**	**1.50**	**1.42**	**1.35**	**1.28**
28	2.00	1.86	1.75	**1.64**	**1.55**	**1.47**	**1.40**	**1.33**
29	2.07	1.93	1.81	**1.70**	**1.61**	**1.52**	**1.45**	**1.38**
30	**2.14**	2.00	1.87	1.76	**1.66**	**1.57**	**1.50**	**1.42**
31	**2.21**	2.06	1.94	1.82	1.72	**1.63**	**1.55**	**1.47**
32	**2.28**	**2.13**	2.00	1.88	1.77	**1.68**	**1.60**	**1.52**
33	**2.35**	**2.20**	2.06	1.94	1.83	1.73	**1.65**	**1.56**
34	**2.42**	**2.26**	**2.12**	2.00	1.89	1.78	**1.70**	**1.61**
35	**2.50**	**2.30**	**2.18**	2.06	1.94	1.84	1.75	**1.66**
36	**2.57**	**2.40**	**2.25**	**2.11**	2.00	1.89	1.80	**1.71**
37	**2.60**	**2.47**	**2.31**	**2.17**	2.06	1.94	1.85	1.75
38	**2.71**	**2.53**	**2.37**	**2.23**	**2.11**	1.99	1.90	1.80

39	**2.78**	**2.60**	**2.44**	**2.29**	**2.17**	2.05	1.95	1.85
40	**2.85**	**2.66**	**2.50**	**2.35**	**2.22**	**2.10**	2.00	1.90
41	**2.92**	**2.73**	**2.56**	**2.41**	**2.27**	**2.15**	2.05	1.95
42	**3.00**	**2.80**	**2.62**	**2.47**	**2.33**	**2.21**	**2.10**	1.99
43	**3.07**	**2.86**	**2.68**	**2.52**	**2.38**	**2.26**	**2.15**	2.04
44	**3.14**	**2.93**	**2.75**	**2.58**	**2.44**	**2.31**	**2.20**	**2.09**
45	**3.21**	**3.00**	**2.81**	**2.64**	**2.50**	**2.36**	**2.25**	**2.14**

Melezitose

Generally honeydew honeys have high content of melezitose. Honeydew honey from *Abies alba* has 8.1% melezitose, 36.9 glucose, and from *Larix decidua* has 44.5% melezitose and 15.9% glucose. Both honeys crystallised very fast.

Greek fir honey was analysed because is a type of honey that never crystallised and yet is rich in melezitose. As table V indicates half of fir samples have melezitose over 10%. All glucose values are below 21%, D/W and D-W/L indices are very low. Obviously the melezitose concentration and L/D values are not correspond to non-granulating honeys.

Conclusions

From the above examination on the relation of crystallisation indices and the tendency of crystallisation we conclude the following:

- Glucose is useful as indicator for honey granulation only in its lower (<28%) and higher values (>38%). The prediction of granulation in intermediate values is impossible since no consistency can be found.
- The ratio D/W is one of the most useful indices to predict granulation. It gave accurate prediction in 68% cases of international and 93% of Greek honeys.
- The ratio D-W/L gave poor prediction and only extreme values (>0.50 for rapid and <0.20 for slow granulation) can be used.
- The ratio L/D failed to predict crystallisation in both international (prediction=14%) and Greek honeys (prediction=10%).
- Melezitose is not good index since the majority of Greek fir honey have >10% melezitose and still never crystallise.
- Results of this research indicate that D/W ratio can be used either to predict or to control granulation tendency of honey. It requires minimum analytical work to find glucose concentration and then adjust the water content to level that retard the granulation. The adjustment of water content will not be a problem.
- To facilitate the further work, we constructed the table VI where we put on the first left column the glucose values from 26% to 45% and on the first row the water content of honey from 14% to 21%. In that way D/W ratio is distributed as is shown. The area with the bold figures represents conditions that favour fast granulation (D/W ratios equal or exceed 2.10). The area with regular figures represents the non granulated honeys (D/W ration equal or less than 1.70). What remain is to confirm this table with further analytical work and honeys that have different water content but the same value of glucose.

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