A comprehensive analysis of ^{13}C isotope ratios data of authentic honey in China by the EA-IRMS and LC-IRMS methods

Dr. Jinzhong Xu

Jiangsu Sinography Testing CO., LTD.

Email: xujz01@163.com

JSST
中谱检测
SINOGRAPHY TESTING

Honey samples

- **Total number:** 96
- **Honey species:** rape honey, acacia honey,Vitex honey, sunflower honey, cotten honey, Linden honey, Jujube honey, buckwheat honey
- **Geographical origin:** Henan, Sichuan, Hubei, Jiangsu, Jilin, Shanxi, Xinjiang Uygur Autonomous, and Inner Mongolia Autonomous

Authenticity and reliability of samples

- Sampled and sealed by SGS
- Gathered in full-bloom stage
- Stored at -20℃

JSST
中谱检测
SINOGRAPHY TESTING

Test items

- Physical and chemical properties
- Antibiotics
- ^{13}C isotope ratios
- GMO
- Adulteration identification

JSST
中谱检测
SINOGRAPHY TESTING

Meaningful

- Established a ^{13}C isotope ratios database of different honey species in China
- To resolve the international trade dispute
- Aimed to beat the audluteration of honey

JSST
中谱检测
SINOGRAPHY TESTING

^{13}C isotope ratios data of authentic honey in China

- Conventional $\delta^{13}C$-EA-IRMS method proposed by JW White

- $\delta^{13}C$-LC-IRMS method proposed by Intertek laboratory in Europe

JSST
中谱检测
SINOGRAPHY TESTING

Conventional $\delta^{13}C$-EA-IRMS method ($\Delta\delta^{13}C$ (‰) $_{P\text{-}H}$: ≥ -1.0‰)

Rape honey

- $\delta^{13}C_H$ values: ranged from -26.55 to -29.76
- The $\delta 13C_H$ values that greater than -29.0 are found chiefly concentrated in the regions of Sichuan province.
- $\delta^{13}C_P$ values: ranged from -25.15 to -28.64
- About 70% samples have the $\Delta\delta^{13}C_{P\text{-}H}$ values that greater than 1.0

JSST
中谱检测
SINOGRAPHY TESTING

Results from different Lab

NO.	Lab 1		Lab 2		Lab 3	
	C_H	C_P	C_H	C_P	C_H	C_P
A007	-29.42	-27.62	-29.31	-27.48	-29.41	-27.48
A008	-29.68	-27.48	-29.43	-27.15	-29.63	-27.31
B003	-27.72	-27.08	-27.85	-27.20	-27.77	-27.10
B004	-27.59	-27.22	-27.74	-27.09	-27.70	-27.10
C001	-28.08	-26.36	-28.40	-26.46	-28.21	-26.34
C002	-27.00	-25.49	-27.30	-25.53	-27.01	-25.34
C009	-27.94	-26.60	-28.14	-26.38	-27.94	-26.53
D005	-27.94	-26.84	-28.09	-27.17	-27.93	-26.80
D006	-28.12	-26.31	-28.39	-26.62	-28.13	-26.32

Acacia honey

- $\delta^{13}C_H$ values: ranged from -23.82 to -25.20
- $\delta^{13}C_P$ values: ranged from -22.79 to -24.75
- About 5% samples have the $\Delta\delta^{13}C_{P\text{-}H}$ values that greater than 1.0

Linden honey

- Produced from Jilin province
- $\delta^{13}C_H$ values: ranged from -24.20 to -24.52
- $\delta^{13}C_P$ values: ranged from -23.66 to -24.12
- The $\Delta\delta^{13}C_{P\text{-}H}$ values are less than 1.0

JSST
中谱检测
SINOGRAPHY TESTING

Vitex honey

- Produced from Hubei and Henan province
- $\delta^{13}C_H$ values: ranged from -25.38 to -26.56
- $\delta^{13}C_P$ values: ranged from -23.73 to -24.30
- About 27% samples have the $\Delta\delta^{13}C_{P-H}$ values that greater than 1.0

JSST
中谱检测
SINOGRAPHY TESTING

Cotten honey

- Originated from Xinjiang Uygur Autonomous Region
- $\delta^{13}C_H$ values: ranged from -24.28 to -25.14
- $\delta^{13}C_P$ values: ranged from -19.44 to -24.83
- More than 70% samples have the $\Delta\delta^{13}C_{P-H}$ values that greater than 1.0
- The maximum $\Delta\delta^{13}C_{P-H}$ values reached to 4.90

JSST
中谱检测
SINOGRAPHY TESTING

Sunflower honey

- Produced from Inner Mongolia Autonomous region and Xinjiang Uygur Autonomous region
- $\delta^{13}C_H$ values: ranged from -25.02 to -25.39
- $\delta^{13}C_P$ values: ranged from -23.39 to -24.55
- Honey produced from Xinjiang have the $\Delta\delta^{13}C_{P\text{-}H}$ values that greater than 1.0

JSST
中谱检测
SINOGRAPHY TESTING

Conclusion

- The C4 sugar of all honey samples are qualified, that is, fall within the theoretical ranges of JW White.
- Affected by climatic fluctuations, some samples have $\delta^{13}C_H$ values greater than -29.0.
- The $\Delta\delta^{13}C_{P\text{-}H}$ values of cotton honey and vitex honey are relatively larger than other honey samples.

δ^{13}C-LC-IRMS method proposed by Intertek laboratory in Europe

The limits for Δδ13C values of pure honey are as follows:

- $\Delta\delta^{13}C$ (‰) max. (maximum difference between all measured $\delta^{13}C$ values): $\leq \pm$ 2.1‰;
- $\Delta\delta^{13}C$ (‰) fru-glu (differences between fructose and glucose $\delta^{13}C$ values): $\leq \pm$1.0‰.
- $\Delta\delta^{13}C$ (‰) $_{P\text{-}H}$ (differences between protein and honey $\delta^{13}C$ values): $\geq$ –1.0‰

$\delta^{13}C$-LC-IRMS method
Rape honey

- 21 among 33 pure honey samples from **Qinhuangdao CIQ** were failed to pass the test and the qualification yield is 36.4%.The $\Delta\delta^{13}C$ (‰) max. value is 4.12

- 11 among 32 samples from **Jiangsu CIQ** were failed to pass the test and the qualification yield is 65.6%. The $\Delta\delta^{13}C$ (‰) max. value is 4.36

- The difference values between $\delta^{13}C_{ds}$ and $\delta^{13}C_{P}$ of all rape honey samples are much larger.

JSST
中谱检测
SINOGRAPHY TESTING

Results from Qinhuangdao CIQ

Location number	**$\delta^{13}C$ (‰)** protein	**$\delta^{13}C$ (‰)** honey	**$\delta^{13}C$ (‰)** fuu	**$\delta^{13}C$ (‰)** gru	**$\delta^{13}C$ (‰)** ds	**$\delta^{13}C$ (‰)** ts	**fru-gru Δδ13C (‰)**	**$\Delta\delta^{13}C$ (‰) max.**
A009	-27.46	-29.14	-29.30	-29.49	-31.04	n.a.	0.19	3.58
A010	-28.42	-29.62	-29.37	-29.50	-31.48	n.a.	0.13	3.06
B001	-26.82	-27.41	-27.54	-27.66	-29.65	n.a.	0.12	2.83
B002	-27.39	-27.84	-28.00	-28.10	-29.31	n.a.	0.10	1.92
B003	-27.08	-27.72	-27.89	-27.92	-29.26	n.a.	0.03	2.18
C008	-26.64	-27.78	-28.09	-28.22	-27.36	n.a.	0.13	1.58
C009	-26.60	-27.94	-27.98	-28.08	-28.49	n.a.	0.10	1.89
D001	-26.34	-28.44	-28.40	-28.54	-27.22	n.a.	0.14	2.20
D002	-26.04	-28.54	-28.53	-28.67	-27.49	n.a.	0.14	2.63

Acacia honey

- 24 among 29 pure honey samples from **Qinhuangdao CIQ** were failed to pass the test and the qualification yield is 17.2%.The $\Delta\delta^{13}C$ (‰) max. value is 4.39.
- 24 among 28 samples from **Jiangsu CIQ** were failed to pass the test and the qualification yield is 14.3%. The $\Delta\delta^{13}C$ (‰) max. value is 4.20.
- The difference values between $\delta^{13}C_{ds}$ and $\delta^{13}C_{mono}$ of all rape honey samples except for those originated from Henan province are much larger.
- Trisaccharide was detected from all these samples

JSST
中谱检测
SINOGRAPHY TESTING

Results from Qinhuangdao CIQ

Location number	**$\delta^{13}C$ (‰)** protein	**$\delta^{13}C$ (‰)** honey	**$\delta^{13}C$ (‰)** fuu	**$\delta^{13}C$ (‰)** gru	**$\delta^{13}C$ (‰)** ds	**$\delta^{13}C$ (‰)** ts	**fru-gru $\Delta\delta$13C (‰)**	**$\Delta\delta^{13}C$ (‰) max.**
F008	-23.90	-24.44	-25.05	-25.40	-22.12	-23.27	0.35	-3.28
F009	-23.94	-24.31	-24.99	-25.27	-22.13	-23.36	0.28	-3.14
E002	-24.75	-24.13	-24.37	-24.13	-25.65	-23.55	-0.24	-2.10
E003	-24.31	-24.90	-25.34	-25.03	-25.79	-23.48	-0.31	-2.31

Vitex honey

- 11 among 11 pure honey samples from **Qinhuangdao CIQ** were failed to pass the test and the qualification yield is 0%.The $\Delta\delta^{13}C$ (‰) max. value is 4.34.
- 10 among 11 samples from **Jiangsu CIQ** were failed to pass the test and the unqualification yield is 9.1%. The $\Delta\delta^{13}C$ (‰) max. value is 4.16.
- About 63.6% of these samples have large difference values between $\delta^{13}C_{ds}$ and $\delta^{13}C_{mono}$ while the left 36.4% have large difference values between $\delta^{13}C_{H}$ and $\delta^{13}C_{P}$.
- Trisaccharide was detected from 80% of these samples.

JSST
中谱检测
SINOGRAPHY TESTING

Cotten honey

- 3 among 10 pure honey samples from **Qinhuangdao CIQ** were failed to pass the test and the qualification yield is 70%.The $\Delta\delta^{13}C$ (‰) max. value is 5.24.
- 3 among 10 samples from **Jiangsu CIQ** were failed to pass the test and the unqualification yield is 70%. The $\Delta\delta^{13}C$ (‰) max. value is 5.13.
- All samples have large difference values between $\delta^{13}C_H$ and $\delta^{13}C_P$
- No trisaccharide was detected from all samples.

JSST
中谱检测
SINOGRAPHY TESTING

Linden honey

- 4 among 4 pure honey samples from **Qinhuangdao CIQ** were failed to pass the test and the qualification yield is 0%.The $\Delta\delta^{13}C$ (‰) max. value is 2.81.
- 3 among 4 samples from **Jiangsu CIQ** were failed to pass the test and the unqualification yield is 25%. The $\Delta\delta^{13}C$ (‰) max. value is 2.37.
- The difference values between $\delta^{13}C_{mono}$ and $\delta^{13}C_P$ are relatively larger.
- Trisaccharide was detected from Qinhuangdao CIQ

Sunflower honey

- 0 among 4 pure honey samples from **Qinhuangdao CIQ** were failed to pass the test and the qualification yield is 100%.

- 1 among 4 samples from **Jiangsu CIQ** were failed to pass the test and the unqualification yield is 75%. The $\Delta\delta^{13}C$ (‰) max. value is 2.41.

JSST
中谱检测
SINOGRAPHY TESTING

Conclusion

- All samples have $\Delta\delta^{13}C$ (‰) fru-glu values less than or equal to $\pm$1.0‰
- A large number of pure honey samples have $\Delta\delta^{13}C$ (‰) max. values larger than $\pm$ 2.1‰
- According to the method of the LC-IRMS, about 70% pure honey samples in China were considered to be adulterated, although those are 100% natural honeys.