

Unraveling The Distribution and Enantiomer Ratio of Selected Carotenoid-derived Aroma Compounds In Oolong Tea Using MD-GC Coupled with MS*

* MD-GC: Multidimensional-gas chromatography; MS: Mass spectrometry

Yunle HUANG^a, Rui Min Vivian GOH^a, Kim Huey EE^a, Aileen PUA^a, Lionel JUBLOT^a, Shao Quan LIU^b, and Bin YU^a

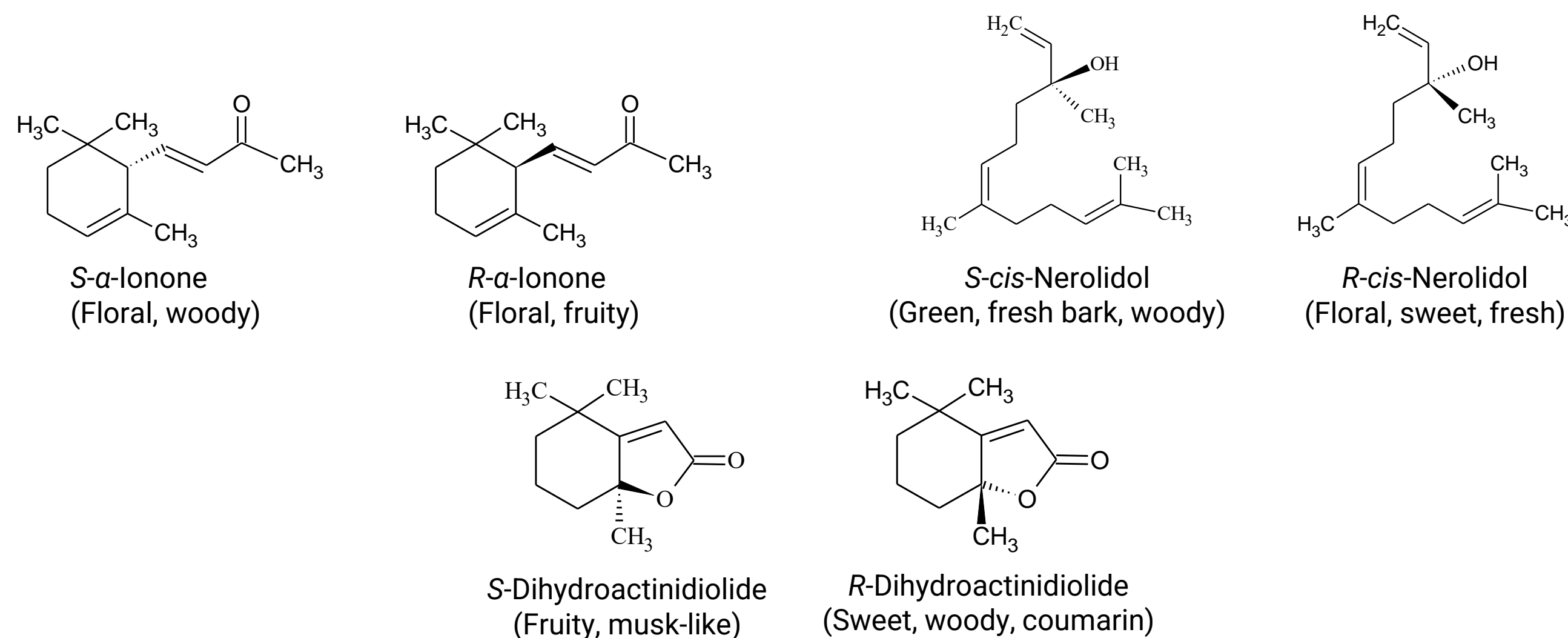
^a Mane SEA PTE LTD, Singapore

^b Food Science and Technology Programme, Department of Chemistry, National University of Singapore

INTRODUCTION



Carotenoid-derived compounds (CDCs) are important contributors to the characteristic flavour of oolong tea. These compounds can exist in different isomeric forms that have similar structural, physical and chemical but different sensory properties, making their differentiation difficult but important.

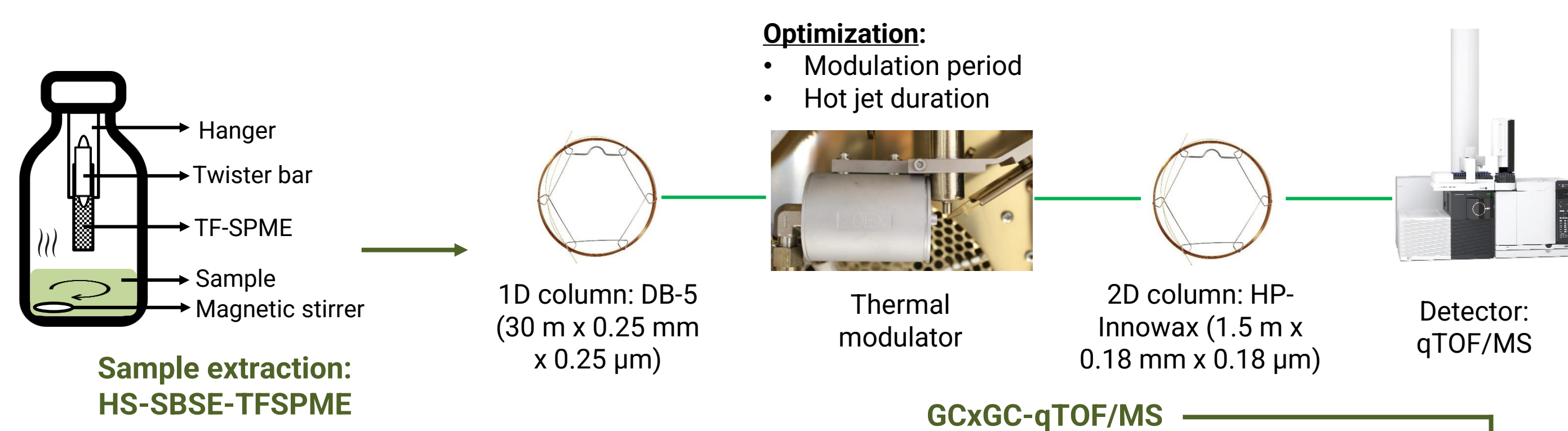


However, the analysis of these carotenoid-derived compounds and determination of their enantiomeric distributions in tea is challenging due to their low concentrations and wide variability. In consideration of their impact on sensory perception, these challenges faced in their detection and quantification need to be addressed.

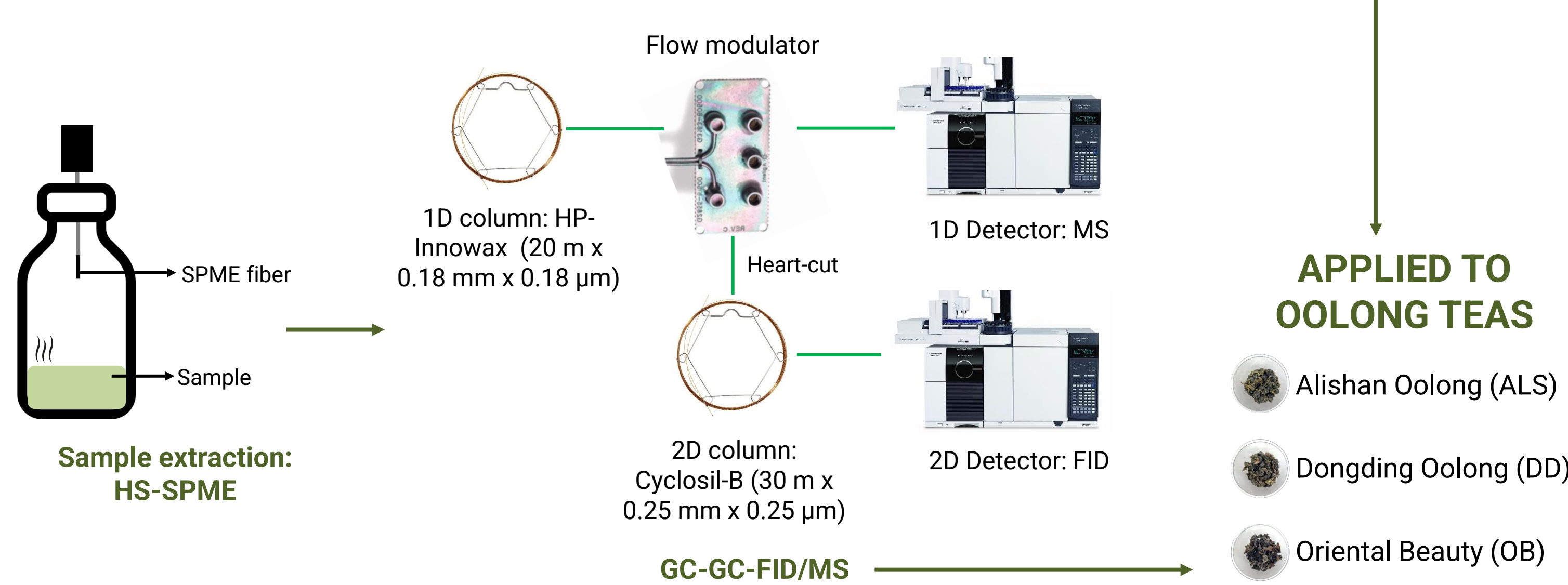
OBJECTIVE: To develop and optimize two-dimensional gas chromatography methods for the detection of CDCs and investigate their enantiomer distribution in different oolong teas.

ANALYTICAL WORKFLOW

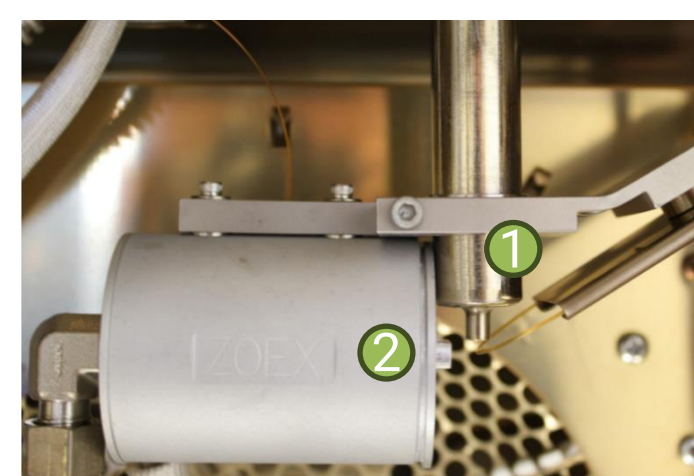
COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY (GCXGC)



HEART-CUTTING TWO-DIMENSIONAL GAS CHROMATOGRAPHY (GC-GC)



GCxGC-qTOF/MS OPTIMISATION



- Continuous cold jet to trap the analytes at the head of the 2D column
- Pulsed hot jet set at a fixed interval to release the trapped analytes

Modulation period: amount of time between hot jet pulses
Hot jet duration: length of time when the hot jet is turned on

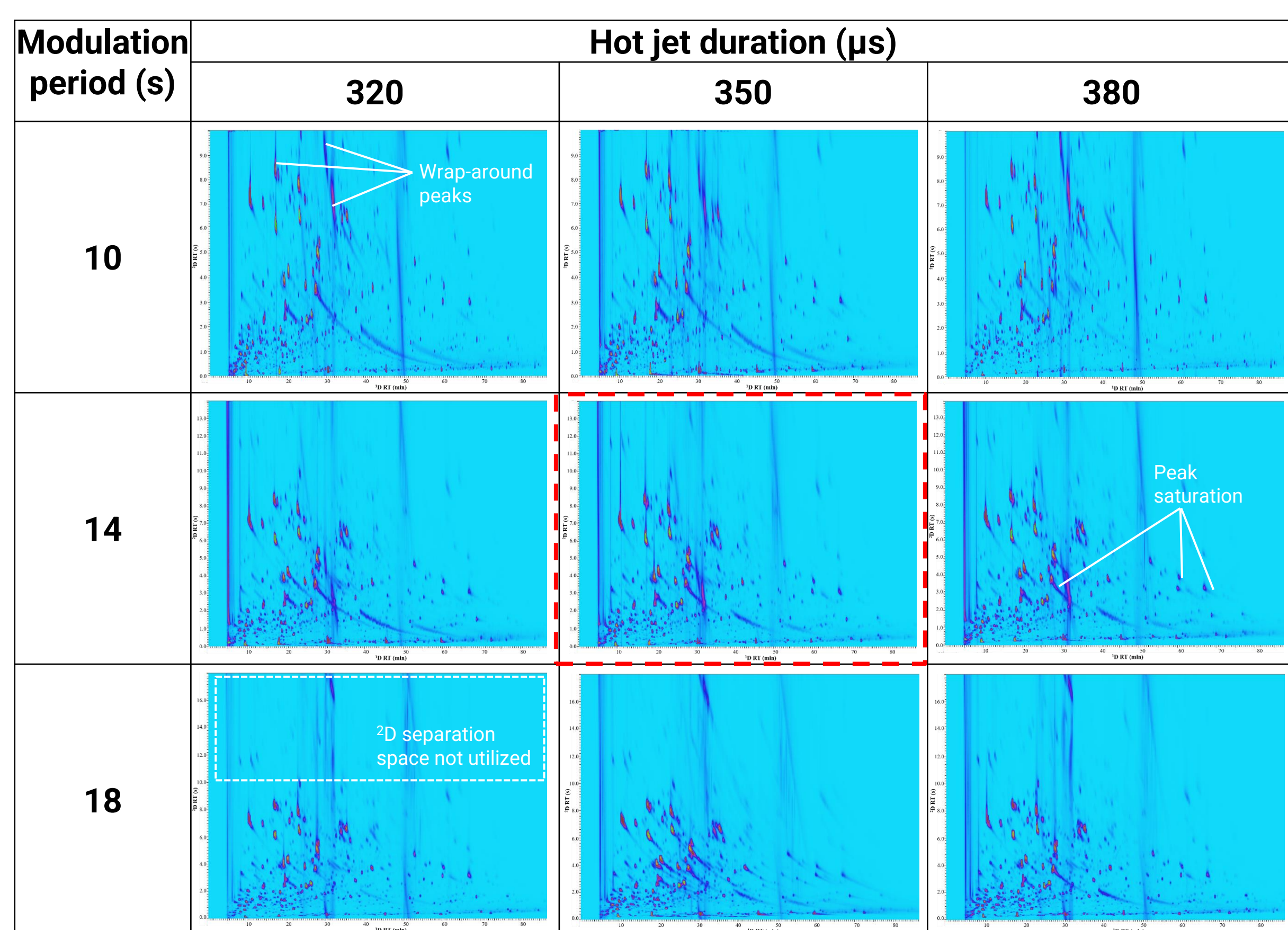


Figure 1. Optimization of GCxGC modulation period and hot jet duration

Table 1. CDCs detected in oolong tea

No.	Compound
1	6-Methyl-5-hepten-2-one
2	Isophorone
3	6-Methyl-trans-3,5-heptadien-2-one
4	Safranal
5	β -Cyclocitral
6	α -Damascone*
7	trans- β -Damasconone
8	β -Damascone*
9	α -Ionone
10	Geranylacetone
11	trans- β -Farnesene*
12	trans- β -Ionone
13	5,6-Epoxyde- β -ionone
14	trans- α -Farnesene*
15	Dihydroactinidiolide
16	trans-Nerolidol
17	cis-Nerolidol

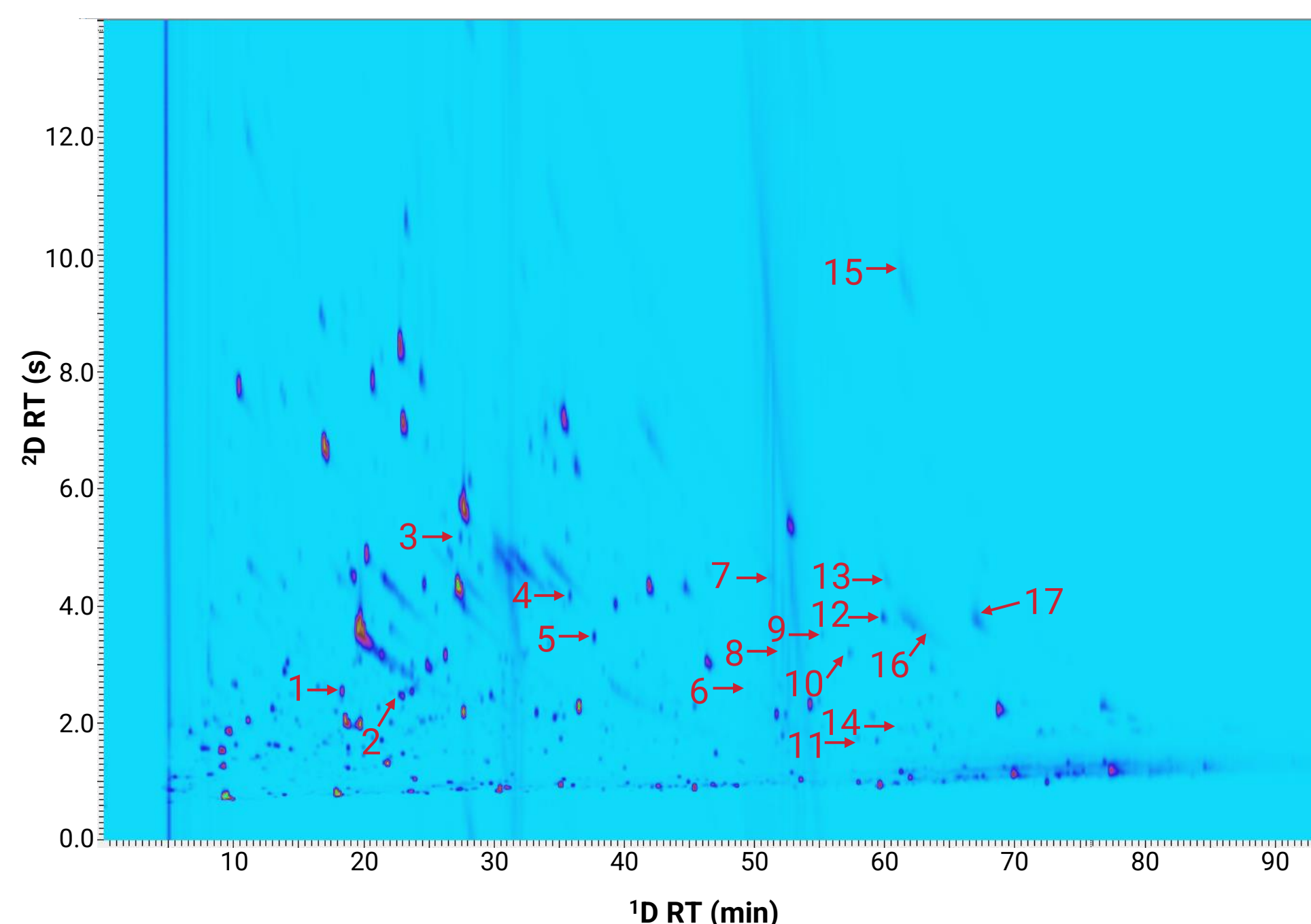


Figure 2. Separation of CDCs based on 2D GCxGC separation. The peak number corresponds to the compound numbers in Table 1.

*Trace CDCs which were only detected in GCxGC

ENANTIOMER DISTRIBUTION OF CDCs IN OOLONG TEA

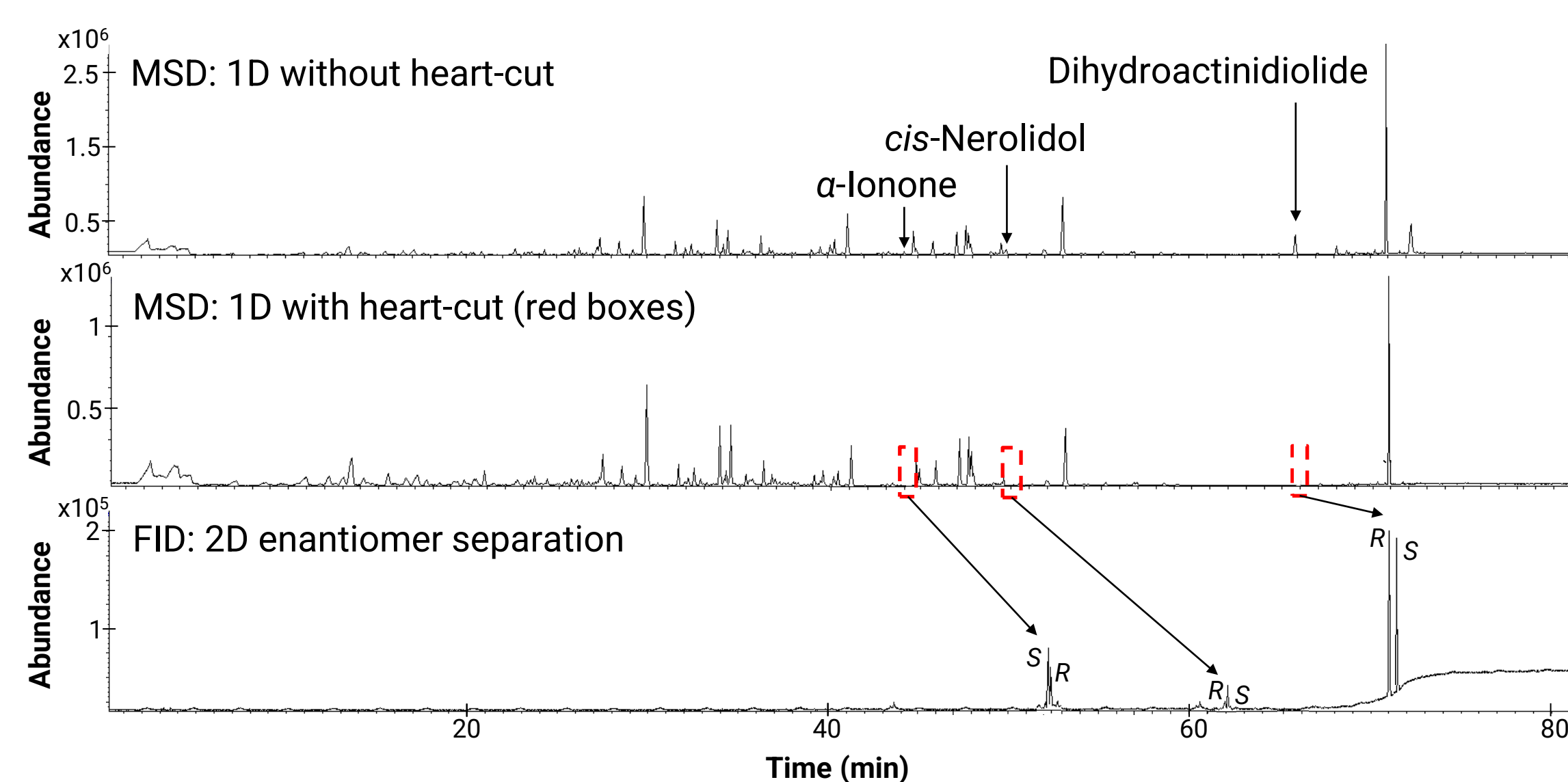


Figure 3. Chiral separation of α -ionone, cis-nerolidol and dihydroactinidiolide in oolong tea.

Table 2. Enantiomer ratio of α -ionone, cis-nerolidol and dihydroactinidiolide in different oolong teas.

Tea	Oxidation (%)	Roasting	Enantiomer ratio ^a		
			α -Ionone	cis-Nerolidol	Dihydroactinidiolide
ALS	20-25	Light	0.27	1.31	0.79
DD	30-35	Medium	0.89	1.51	0.64
OB	60-65	Heavy	0.26	5.83	1.27

^aEnantiomer ratio calculated as the ratio of area (R/S) within the enantiomer pair.

CONCLUSION

- The modulation period determines the time when the compounds are allowed to separate on 2D and should be optimized to avoid wrap-around of peaks while efficiently utilizing the separation space. On the other hand, hot jet duration determines the amount of compounds entering the 2D.
 - The optimized parameters for modulation period (14 s) and hot jet duration (350 μ s) were used.
- MD-GC can overcome the challenges faced by conventional GC in the separation of complex tea matrices.
 - GCxGC: improves detection limit due to cryogenic trapping of the modulation step.
 - GC-GC: removes interference from peaks of interest while improving quantification.
- Different cultivars and processing parameters result in different volatile compound compositions in oolong teas.

REFERENCES

- Shao, C.-Y.; Zhang, Y.; Lv, H.-P.; Zhang, Z.-F.; Zeng, J.-M.; Peng, Q.-H.; Zhu, Y.; Lin, Z., (2022) Aromatic profiles and enantiomeric distributions of chiral odorants in baked green teas with different picking tenderness. *Food Chemistry*, 388, 132969.
- Simkin, A. J., (2021) Carotenoids and apocarotenoids in plants: their role in plant development, contribution to the flavour and aroma of fruits and flowers, and their nutraceutical benefits. *Plants*, 10 (11), 2321.