Comprehensive Authentication of Commercial Berry Seed Oils Using FTIR and DSC Profiles Combined with Chemometrics

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INTRODUCTION

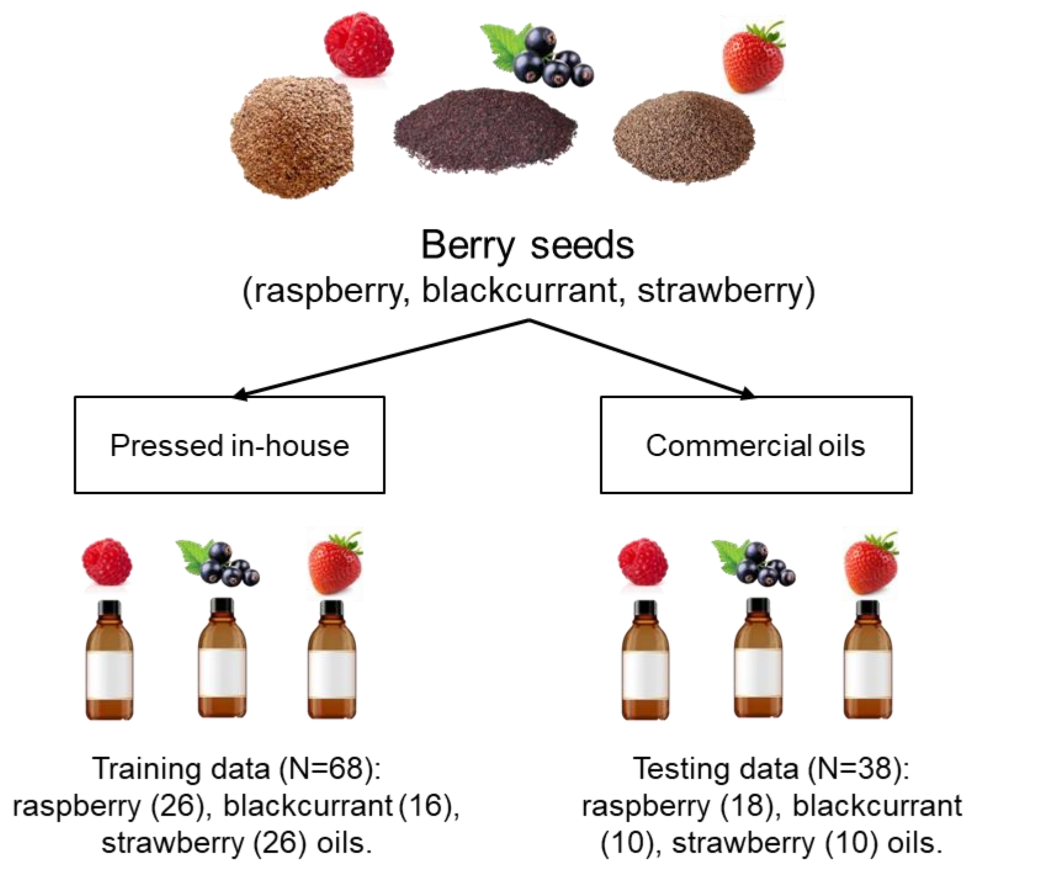
Production of juice from berry fruits generates large number of by-products, mostly in the form of pomace and seeds. The valorization of berry seeds to obtain oil is particularly important, due to its chemical composition and nutritional value. However, as a niche products, cold-pressed berry seed oils are sold at high prices, mainly by e-commerce, where the control of authenticity is rare. It is worth noting that these oils are susceptible to adulteration with lower-quality oils, which can have a detrimental effect on their nutritional value, safety, and sensory properties.

The aim of this study was to use the entire profiles of melting phase transition and FTIR spectra of selected berry seed oils (raspberry, strawberry, blackcurrant) for authentication purposes by applying the chemometrics.

MATERIALS AND METHODS

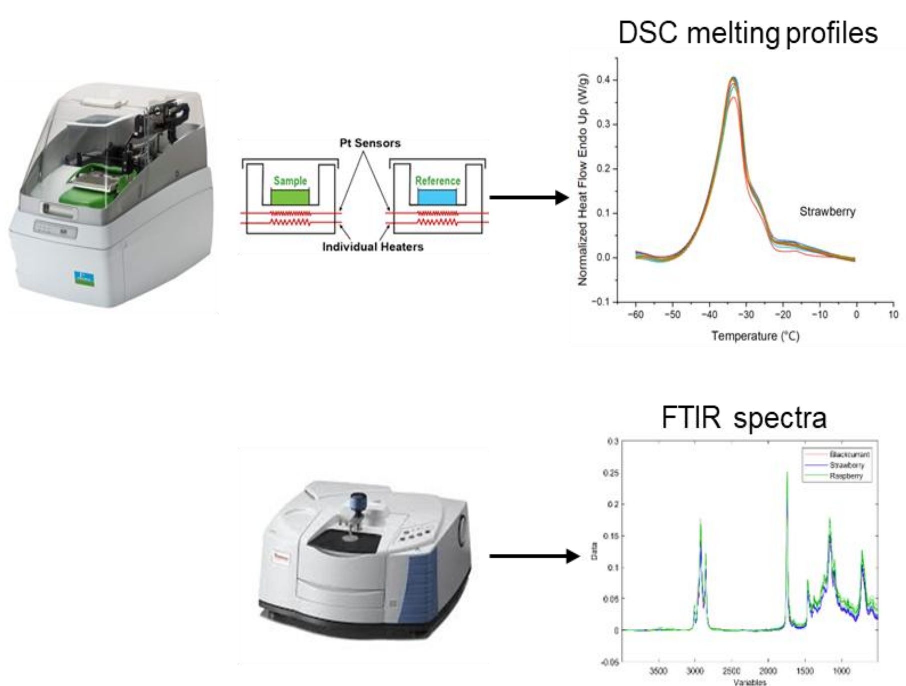
Materials

Three types of cold-pressed berry seed oils: blackcurrant (*Ribes nigrum*), strawberry (*Fragaria ananassa*) and raspberry (*Rubus idaeus*) pressed in-house (68 samples used to build the model for the authentication) and commercial oils purchased from the market (38 samples used for the authenticity assessment).



Methods

DSC melting phase transition profiles of berry seed oils were analyzed out using a PerkinElmer differential scanning calorimeter DSC 8500. The oil samples were first cooled with scanning rate 2°C/min from temperature 30 to −67 °C, and then heated from −67 to 30 °C at a heating rate of 5 °C/min. The FTIR spectra of berry seed oils were obtained using a Spectrum Two FT-IR spectrometer equipped with a Universal ATR with a diamond crystal (PerkinElmer). The data were collected over a spectral range of 4000-500 cm^{-1} at 4 cm^{-1} resolution in reflectance mode. All DSC and FTIR measurements were conducted in duplicate.



Data pre-processing was applied for DSC melting profile (mean centering) and FTIR spectra (SNV and mean centering). The group distribution was explored using Principal Component Analysis (PCA), then classified using Partial Least Squares Discriminant Analysis (PLS-DA), carried out using Solo +MIA v.9.3 software (Eigenvector Research, Manson, WA, USA).

RESULTS

The whole spectra of DSC melting profiles of raspberry, blackcurrant, and strawberry seed oils were analyzed in terms of fingerprinting (Fig. 1). The DSC profiles differed among oils types i.e. raspberry oils with two endothermic peaks detected at -40 and -20 °C (Fig. 1A), blackcurrant oils peaks were located at -37 °C and -26 °C (Fig. 1B), as well as strawberry oils with a major peak at -33 °C and a minor peak at -17 °C (Fig. 1C).

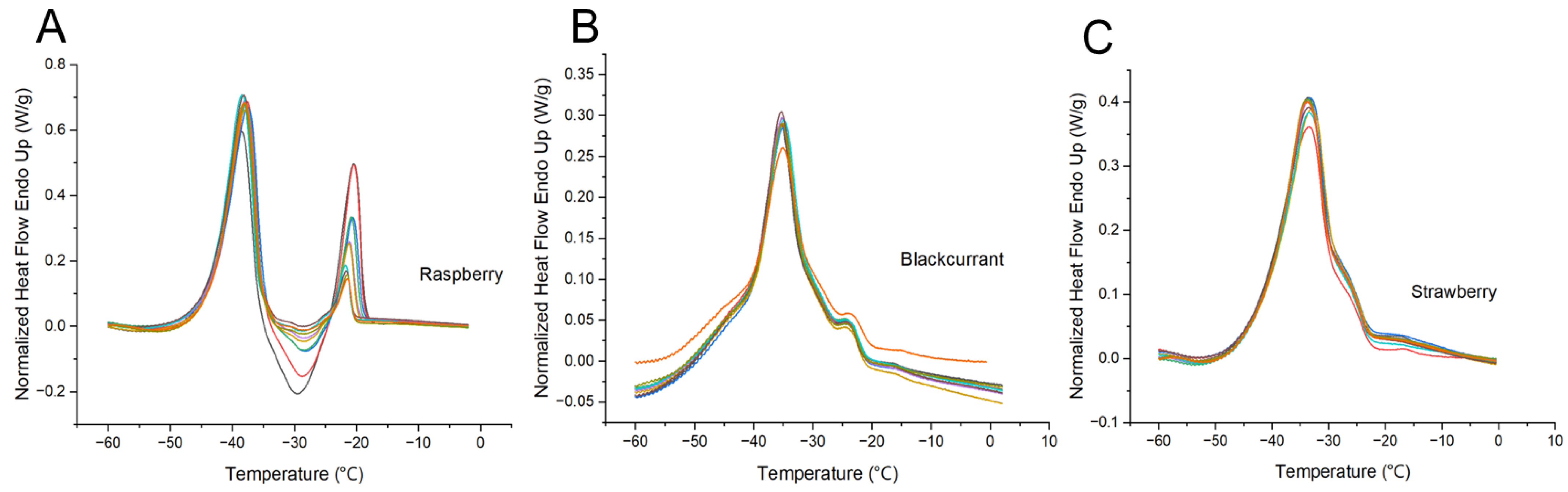


Figure 1. DSC melting profile of (A) raspberry, (B) blackcurrant, and (C) strawberry seed oil obtained at heating rate 5 °C/min.

Simultaneously, FTIR spectra from these oils were collected (Fig. 2). Three groups of oils showed distinctive FTIR spectra at several spectral regions i.e. 3010 – 2800 cm^{-1} (Fig. 2A), 1700 – 1650 cm^{-1} (Fig. 2B), and 1160 – 720 cm^{-1} (Fig. 2C). These differences at each spectral regions were contributed by C=, CH_2, and CH_3 (Fig. 2A), C=C and C=O (Fig. 2B), as well as cis, trans-HC (Fig. 2C). Hence, these distinctive characteristics from DSC melting profiles and FTIR were used to build the chemometrics model for rapid authenticity assessment.

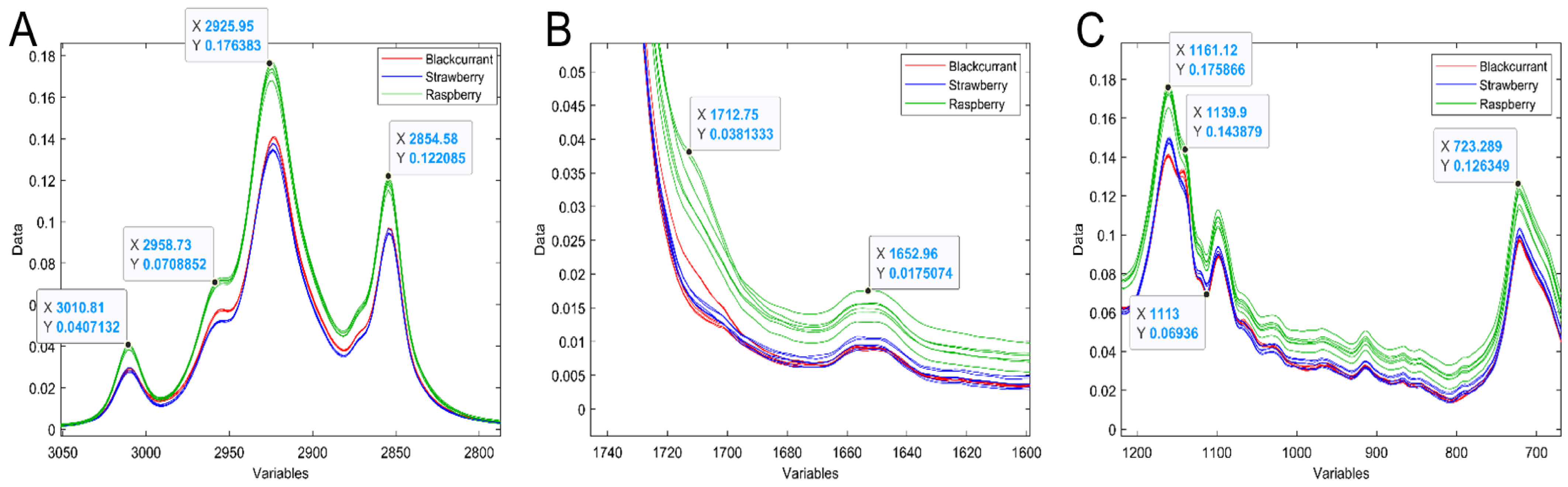


Figure 2. FTIR spectra of (A) raspberry, (B) blackcurrant, and (C) strawberry seed oil at three spectral regions.

Principal component analysis (PCA) in Fig 3, showed a clear separation trend based on the berry types from DSC dataset (Fig 3A). On the other hand, no meaningful separation between berry types was captured in FTIR spectra (Fig 3D). It indicates the need of pre-processing to amplify the presence of dominant variables in respective datasets of DSC (Fig 3B, 3C) and FTIR (3E, 3F).

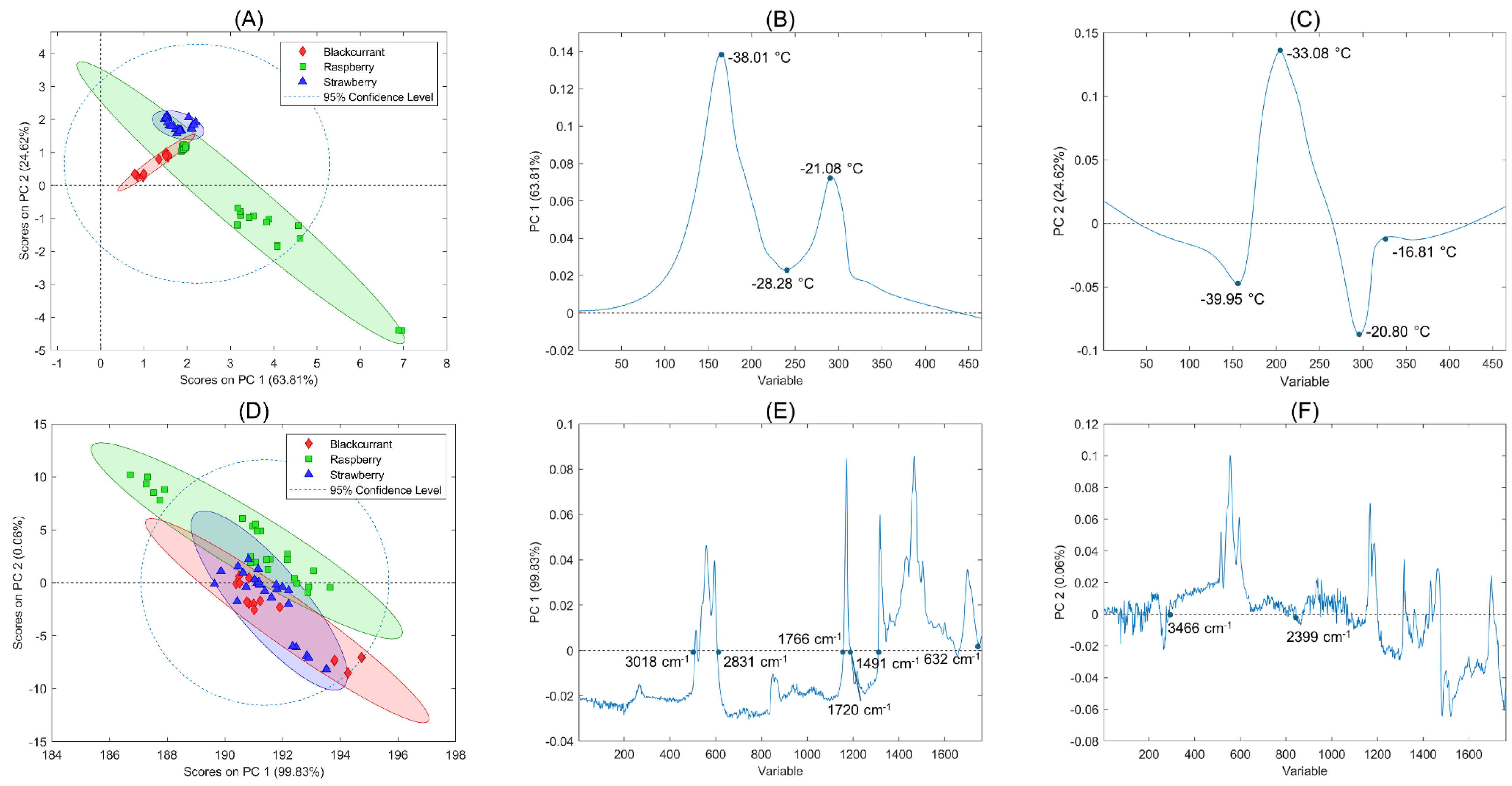


Figure 3. PCA scores and loading plots for (A, B, C) DSC curves and (D, E, F) FTIR spectra.

With supervised learning (PLS-DA) and personalised data processing (baseline correction and VIP for DSC; SNV, Pareto scaling, VIP selection for FTIR), the classification performance of both datasets were improved. During external validation using commercial oils, the DSC models demonstrated good predictive performance in classifying blackcurrant (F1 score = 0.55) and strawberry oils (F1 score = 0.91), while FTIR models were favoured for predicting the class of blackcurrant (F1 score = 0.91) and raspberry oils (F1 score = 0.89). Among the 38 commercial oils, 18 samples were misclassified by DSC and 6 samples by FTIR models, as they did not fit authentic characteristics.

CONCLUSIONS

1) A novel approach of using the entire DSC and FTIR spectra as an untargeted method for distinguishing three cold-pressed berry seed oils was successfully applied.
2) Principal component analysis (PCA) and partial least squares (PLS-DA) discriminant analysis revealed that the DSC profiles as well as FTIR spectra of oils differ by types (raspberry, strawberry, and blackcurrant) and the method could be used for authentication studies.
3) The study demonstrated great potential of an untargeted approach of using the large DSC and FTIR dataset with chemometrics for the discrimination of cold-pressed oils.

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