EXTRACTION AND CHARACTERIZATION OF MONTMORENCY (*PRUNUS CERASUS L.*) SOUR CHERRY PIT OIL

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INTRODUCTION

The United States produced 293.7 million pounds of Montmorency sour cherries (*Prunus cerasus L.*) in 2013[1] with an estimated pit production of 35.2-44.0 million pounds. The largest producing state is Michigan with Utah a far second. The cherry fruit is primarily consumed in the food industry in products such as pie and juice, while the pits remain an under-utilized byproduct. The pits are currently used as filler in cement manufacturing or are disposed of in a land-fill.

Cherry oil is similar to other natural oils and fats such as soybean, canola, peanut, or coconut oil and consists mainly of triacylglycerols (TAGs). The glycerol portion of TAG is constant in all oils and fats while the fatty acid structure and esterification position on glycerol differ with different oils (Fig.1).

The previous studies of cherry oil partially identified the composition and properties but lack comprehensive analysis and potential utility. The present study is directed towards full characterization and understanding of potential cherry pit oil applications.

The cherry pits were milled and extracted using a Soxhlet apparatus with the solvent hexane. The oil yield was 7% by weight from the uncracked pits.

FATTY ACID DISTRIBUTION AND TRIACYLGLYCEROL COMPOSITION

Table 1. Fatty Acid Distribution (FAD) of cherry oil of the current study compared with previous literature.

Fatty Acid	Current Study† (wt %)	2011 Study[3] (*wt %*)	2013 Study[4] (wt %)
C16 Palmitic	8.41	11	6.23
C18:3 Linolenic	5.74	-	5.06
C18:2 Linoleic (ω -6)	32.76	38.2	40.58
C18:1 Oleic (n-9)	48.20	42.9	46.80
C18 Stearic	2.51	6.4	1.33
C20 Arachidic	0.90	0.9	-
TOTAL	**98.52**	**99.4**	**100.0**

†Determined by liquid chromatography with mass spectrometry (LC/MS)
Values below 0.90% were excluded from this table.

Table 2. Triacylglycerol (TAG) composition as determined by liquid chromatography.

TAG	Current Study (mol%)
OOO	17.26
OLO	16.68
LLO	12.95
POL	7.47
OOP	6.84
LLLn	5.91
OLLn	4.64
LLL	3.62
LLP	3.60
OOS	2.66
PLLn	2.19
SLO	2.08
OOLn	2.04
TOTAL	**87.94**

Values below 2% were excluded from this table. O is oleic; L is linoleic; P is palmitic; Ln is linolenic; and S is stearic.

The cherry oil fatty acid distribution (FAD) and the triacylglycerol (TAG) composition were determined (Tables 1, 2). Both analyses correlated well and were used to predict the physical and function properties of the oil. A high concentration of oleic acid predicts a high level of oxidative stability, which was confirmed through the oxidative stability analysis. The fatty acid distributions reported earlier were similar to the current study (Table 1). The TAG analysis has not been reported previously.

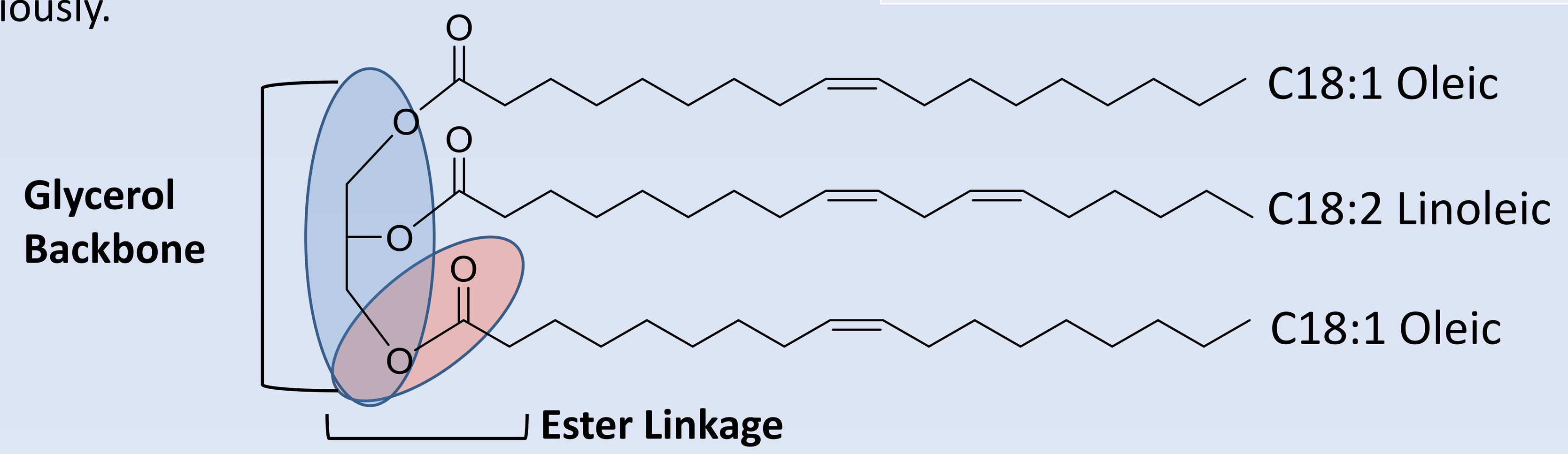


Figure 1. Typical OLO triacylglycerol (TAG) of cherry oil containing two oleic fatty acids and one linoleic fatty acid.

THERMAL BEHAVIOR

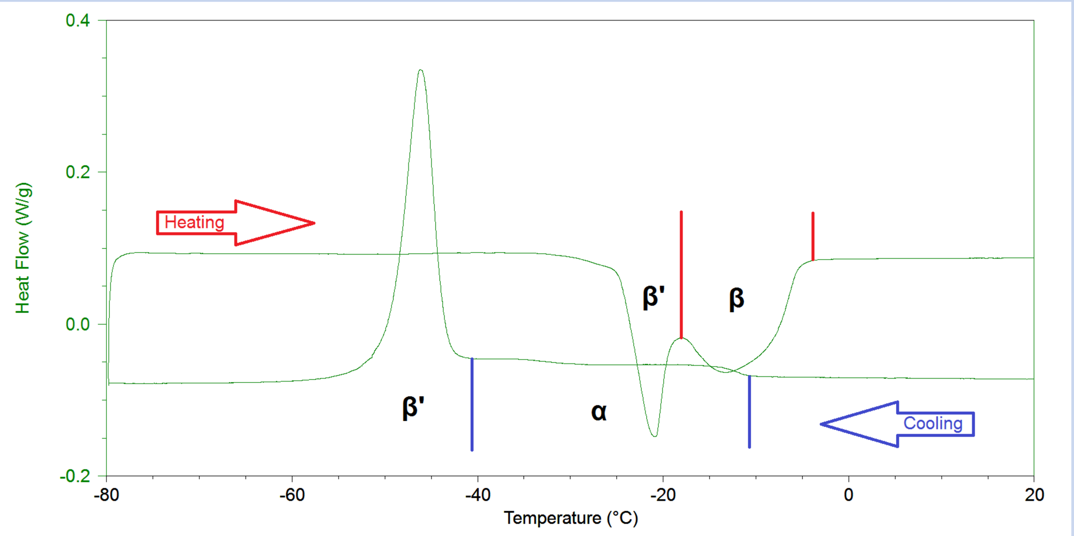


Figure 2. Thermal behavior of the cherry oil by differential scanning calorimetry (DSC), which measures characteristic heat flow patterns due to crystallization and melting of the polymorphs. This chromatogram shows crystallization of an unstable alpha (α) form and then transitions into the beta prime (β') form at -40°C during cooling. During heating the β' form melts and transitions into the β form at -18°C. Melting of β occurs at -4°C.

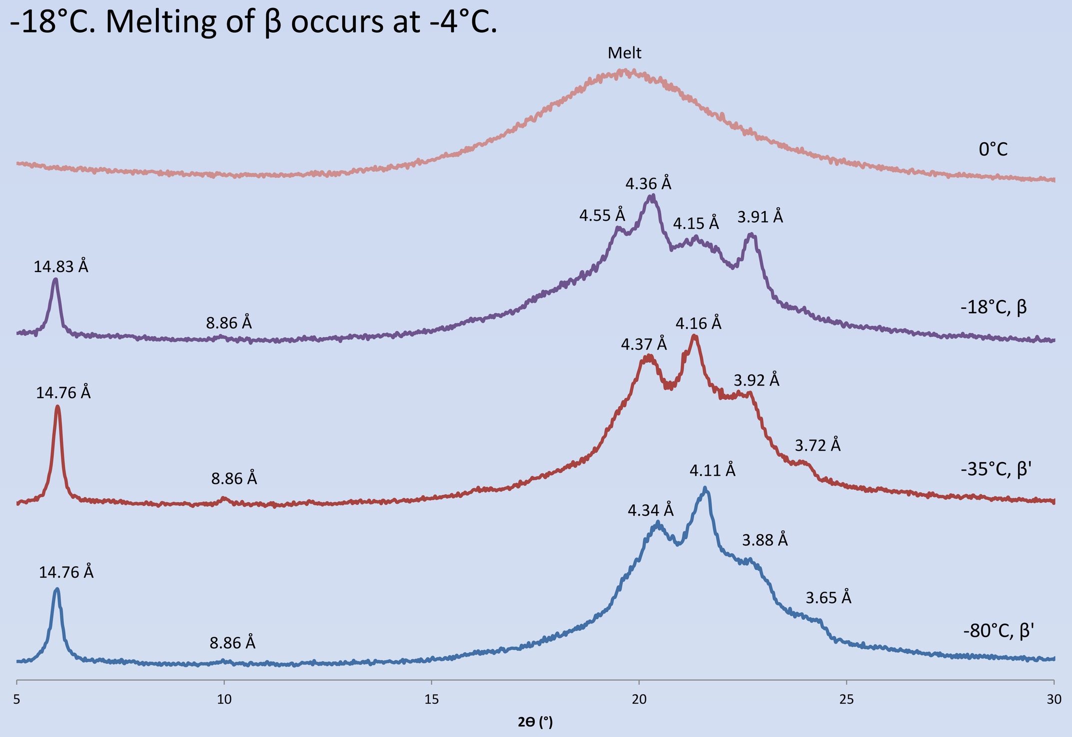
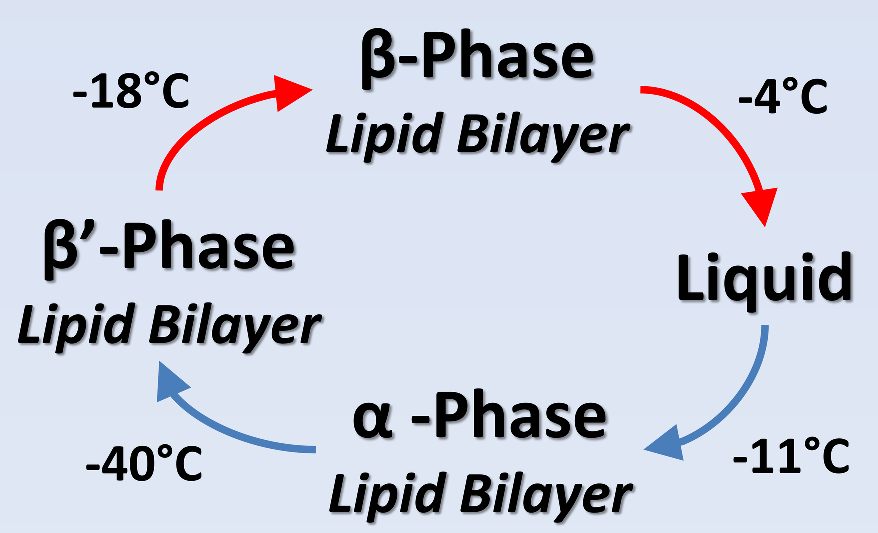


Figure 3. Wide angle x-ray powder diffraction (XRD) confirming the presence of β' and β polymorphs. The wide and narrow angle spacings (Å) are identified above each peak and were used to identify different polymorphs. The temperatures at which the XRD recorded are listed to the right.

The oil was characterized by differential scanning calorimetry (DSC) and wide angle x-ray diffraction (XRD). XRD confirmed the presence of β' and β polymorphs (Fig. 3). The α polymorph is observed in the cooling run on the DSC thermogram (Fig.2), but is unconfirmed by XRD as it is unstable and transforms into β' without an endotherm.

Figure 4. The phase behavior order and phase transition temperatures of the cherry.



OXIDATIVE STABILITY

Table 3. Thermal decomposition temperatures and oxidative induction times of sour cherry oil compared to commercial oils.

	Crude Cherry Oil	Purified Cherry Oil	High Oleic Soybean Oil	Regular Soybean Oil	Canola Oil
Onset of Decomposition[a] (°C)	352.80	354.27	317.95	344.27	314.97
Oxidative Induction Time[b] (min.)	29.97	18.09	260.67	63.21	34.01

[a]Determined by TGA.[b]Determined by DSC.

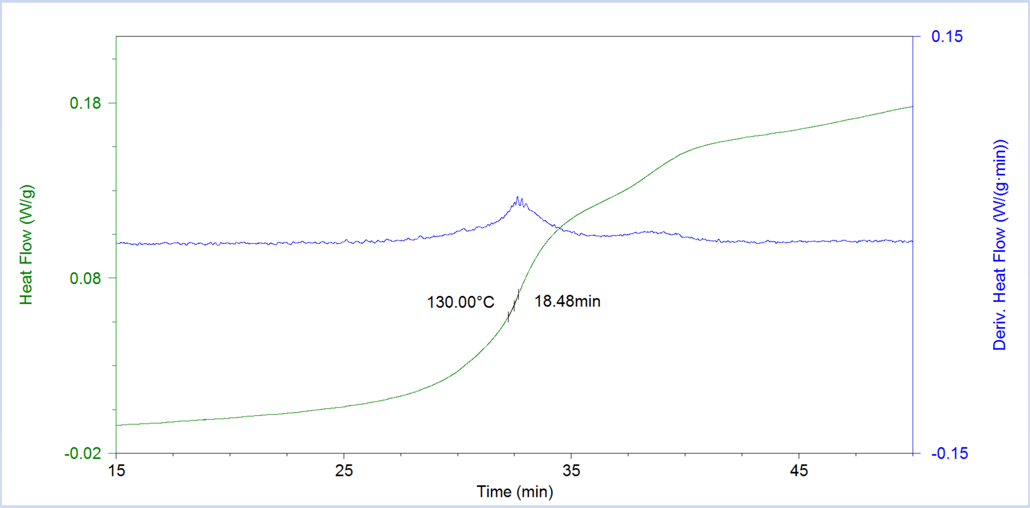


Figure 5. The oxidation induction time (OIT) as determined by DSC. A derivative of the heat flow from oxidation was calculated to determine OIT.

The thermal decomposition temperature of the cherry oil as determined by TGA was found to be very high at 353°C (Table 3, Fig. 6), similar to earlier reports[4]. The oxidative induction time (OIT) analysis is an indication of the oxidative stability of the oil with longer times being better. The OIT of the cherry oil is comparable to canola oil (Table 3).

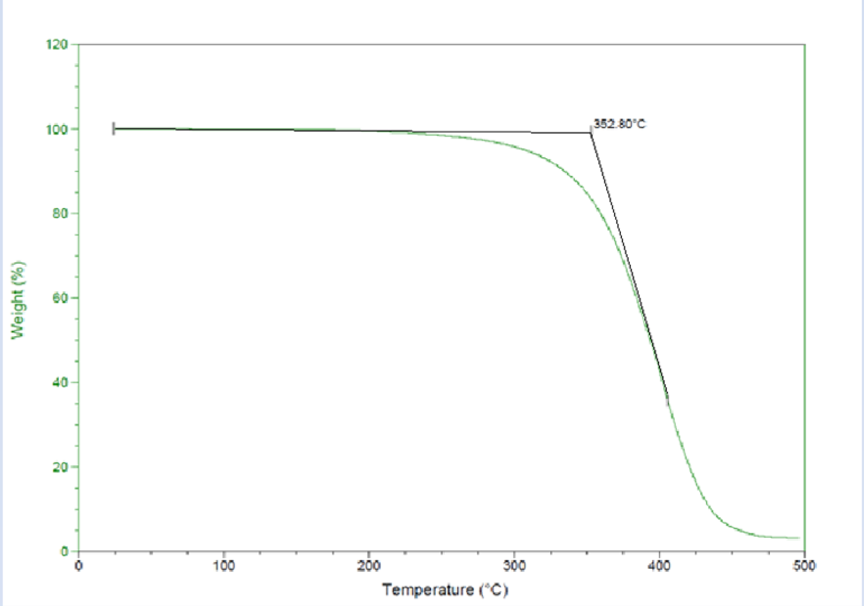


Figure 6. The thermal decomposition temperature was determined by thermogravimetric analysis (TGA), with the weight loss measured as a function of temperature.

Conclusion

The cherry pits are an under utilized resource that need value-added applications. This study is directed to fully characterize and understand the applications of the cherry oil. The FAD and TAG compositions compared well. The cherry oil contained a large percentage of oleic acid indicating a relatively high oxidative stability as confirmed by a long oxidative induction time and high thermal decomposition temperature, similar to canola oil. The thermal behavior analysis confirmed the presence of α, β' and β polymorphs. Based on the composition and properties the oil shows potential for both edible and cosmetic applications.

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