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Oxidative stability assessment of *Bauhinia purpurea* seed oil in comparison to two conventional vegetable oils by differential scanning calorimetry and Rancimat methods

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ABSTRACT

The differential scanning calorimetry (DSC) and oxidative stability index (OSI) techniques were applied for evaluating the oxidative stability of *Bauhinia purpurea*, rice bran and cotton seed oil. The DSC cell temperature was adjusted at four isothermal temperatures (110, 120, 130, and 140 °C) and oxidative DSC curves were obtained under oxygen flow rate of 50 ml/min. During the oxidation reaction the increase of heat was observed with sharp exothermic curve. T_0 was the oxidative induction time determined by the downward extrapolated DSC oxidative curve to time axis. The oxidation times (T_0) acquired from each oil demonstrated a good correlation, $r > 0.99$, with the oxidative stability measured by Rancimat method. DSC method is concluded to be useful by consuming shorter time with lesser amount of sample.

1. Introduction

The protection of oil quality, which remains suitable to consumers for longer time, is an important objective of quality control in the oil and fat industry. Shelf life of vegetable oils is the main characteristic that influence its suitability and market value [1]. The consequence of lipid oxidation leads to decrease in shelf life and has been recognized as the big problem in the food industry [2]. Oxidative stability is one of the most important indication for maintaining the quality of the vegetable oils [3]. The resistance to oxidation is recognized as oxidative stability under different conditions and is expressed as the period of time necessary to accomplish an end point which can be selected according to diverse criteria, but typically leads to rapid increase in the rate of lipid oxidation is a measure of oxidative stability and is known as induction time [4,5]. A number of methods have been developed for the assessment of oxidative stability. There are various accelerated stability tests to quickly check the stability of oils and fats as oxidation is the major cause of oil degradation [6,7]. Usually, the Schaal oven test and the active oxygen (AOM) have been the most generally used tests to evaluate oil stability [8]. It can also be determined by oxidative stability index (OSI) method as recommended by AOAC [9], which is widely used in the fat and oil industry by using two commercially available instruments, the Rancimat from Metrohm Ltd. (Herisau, Switzerland) and the Oxidative Stability Instrument from Omniom Inc. (Rockland, MA) [10]. Recently, differential scanning calorimetry (DSC) has been used to determine the oxidative stability. Cross [11] was the first investigator who applied DSC, used isothermal conditions with flow of oxygen. The induction period was taken as the time where a fast exothermic reaction between oil and oxygen occurred. Several researchers have used the application of thermal analysis for accelerated oil stability test [12,13]. Hassel's results showed that oil samples, which required 14 days via AOM, were evaluated in less than 4 h by DSC [14]. Kowalski with his coworkers and other researchers have also determined the oxidative stability of vegetable oils by DSC [15–18]. *Bauhinia purpurea* is a very valuable tree and has numerous traditional uses. Naturally it is found in the sub-Himalayan tract and outer hills and valleys from the river Indus in Pakistan eastwards to Assam and Myanmar, ascending to altitudes of 1500–1830 m [19]. In Pakistan the trees are cultivated in plains and sub-mountainous tracks, the fresh and dried flower buds of bauhinia are used as a food material. The leaves, stems and roots are widely used in Pakistan and in other countries for the treatment of several diseases especially infections, pain, diabetes, jaundice, leprosy, cough and also used in several medicine formulations [20]. Phytochemical and pharmacological studies of the plant revealed that the ethanol extract of leaves are used for analgesic, antipyretic, anti-inflammatory, antispasmodic and antimicrobial activity [21]. Several types of bioactive compounds were isolated from different parts of *B. purpurea* [22], and characterization of fatty acids of Kachnar (*B. purpurea* L) seed oil has been done by Ramdan et al. [23]. The objective of the present work was to evaluate and compare the

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oxidative stability of *B. purpurea* with rice bran and cotton seed oil by DSC and OSI techniques.

2. Materials and methods

B. purpurea, rice bran and cotton seed oil were used in the present study. The rice bran and cotton oil samples were obtained from local oil industry, Hyderabad, Sindh, Pakistan. Seeds from *B. purpurea* tree were collected from the campus of Sindh University, Jamshoro, Pakistan. The oil was extracted from seeds using hexane as a solvent through Soxhlet apparatus. All chemicals and reagents used were of the highest purity (Analytical grade) purchased from Merck (Darmstadt, Germany).

2.1. Oxidative stability index

Oxidative stability index was evaluated by OSI instrument (automated Metrohm Rancimat model 679) following AOCS Official Method Cd 12b-92 AOCS 1997 [9]. The instrument was run at 110 °C and an air flow rate of 20 l/h was bubbled through the oil (2.5 g). The volatile degradation products were trapped in distilled water, increasing the water conductivity. The oxidative stability index was the time necessary to reach the conductivity curve inflection point.

2.2. Differential scanning calorimetry analysis

The oxidative stability of conventional oils was determined by a Mettler Toledo differential scanning calorimeter DSC-820 (Schwerzenbach, Switzerland). The instrument was calibrated with pure indium and the baseline was obtained with an empty open aluminum crucible. The weighed amount of samples (5.0 ± 0.25 mg) were taken into open aluminum DSC crucible and placed in the sample compartment of the instrument. The four different isothermal temperatures were used (110, 120, 130, and 140 °C) and purified oxygen (99.99%) was passed through the sample at 50 ml/min.

2.3. Statistical analysis

Statistical data were analyzed by using SAS 8.2 software (SAS institute, Cary, NC, USA). Duncan multiple range test to compare differences among means and SAS REG procedure was used between DSC T_0 and OSI values. The relationship between DSC T_0 and DSC isothermal temperature was also determined by the SAS REG procedure which is used for a simple linear equation. All the experiments were carried out in triplicate and reported as mean ± standard deviation.

3. Results and discussion

Straight line was observed with the stream of nitrogen (99.99%) flowing at 50 ml/min by the differential scanning calorimetry for *B. purpurea* oil at 130 °C as shown in Fig. 1, curve A clearly indicates that peak is not exothermic. While exothermic oxidation curve obtained when oil samples were run under oxygen atmosphere (99.99%) flowing at 50 ml/min (Fig. 1, curve B). Oxidation process is a principally exothermic reaction which occurs in between the oil and oxygen. The comparative stability of the *B. purpurea*, rice bran and cotton seed oil towards oxidation was analyzed by the extrapolated T_0 values. Differential scanning calorimetry (DSC) oxidative induction time (T_0) and oxidative stability index (OSI) values of *B. purpurea*, rice bran and cotton seed oils are depicted in Table 1. OSI instrument at the isothermal temperature (110 °C) gave significantly ($P < 0.05$) higher oxidative induction time than DSC technique. This variation may be due to a smaller sample size which was used in the DSC analysis as compared to OSI instrument (5 mg vs. 5 g). The results of oxidative stability measured as induction time (IT) value by Rancimat assay for *B. purpurea* (Table 2) shows oxidative stability up to 1339.31 min, higher than rice bran (217.34 min) and cotton seed oil (427.28 min). The extraordinary stability of *B. purpurea* oil may be due to the presence of higher amount of tocopherols [24,25]. Each DSC isothermal temperature was found to have a significant effect ($P < 0.01$) on the DSC T_0 (Table 1) measurements. For the analyzed oils, with increasing isothermal temperature a significant ($P < 0.05$) decrease was observed for T_0. Generally, with an increase in 10 °C from 110 to 140 °C, the T_0 value was reduced approximately to half of its earlier appraisal (Table 1). This detail is in agreement with Q_{10} law for the association among the rate of chemical reaction and temperature [3,26]. An excellent coefficient correlation was found between the DSC T_0 and OSI measurements as shown in Table 2. The coefficients of correlation were also highly significant ($P < 0.01$) for each evaluation. In observation of the high association between DSC T_0 and OSI time linear regression equations were calculated (Table 3). The regression equations of logarithm DSC T_0 values against DSC isothermal temperature were established and given in Table 4. The coefficient of the determination (R^2) for analyzed oils was above 0.9956, showing good linear regression which revealed that oxidative stability of the oils can be accurately determined by DSC in a short time as compared to OSI method.

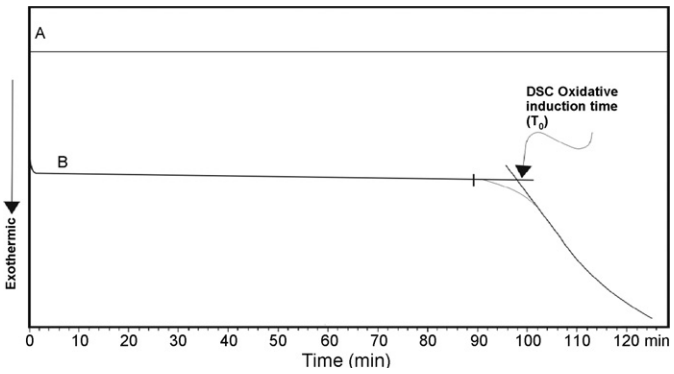

Fig. 1. A representative differential scanning calorimetry oxidation curve of *B. purpurea* oil: (A) isothermal curve at 130 °C with nitrogen (99.99%) flowing at 50 ml/min; and (B) isothermal curve at 130 °C with oxygen (99.99%) flowing at 50 ml/min.

Table 1
Differential scanning calorimetry (DSC) oxidative induction time (T_0) and oxidative stability index (OSI) values of *B. purpurea*, rice bran and cotton seed oils.

Oil	DSC T_0 (min)				OSI (min)
	110 °C	120 °C	130 °C	140 °C	110 °C
B. purpurea	483.33	269.77	99.11	48.44	1339.31
Rice bran	132.89	72.74	36.06	18.66	217.34
Cotton seed	172.41	92.00	42.74	20.30	427.28

Table 2
Pearson correlation coefficient matrix between differential scanning calorimetry (DSC) and oxidative stability index (OSI) methods.[a].

	DSC110	DSC120	DSC130	DSC140
DSC110	–	–	–	–
DSC120	0.998	–	–	–
DSC130	0.985	0.994	–	–
DSC140	0.977	0.999	0.987	–
OSI 110	1.000	0.987	0.981	0.999

[a] Significance at 0.01 level ($P < 0.01$). DSC at isothermal temperature 110 °C, DSC120; DSC at isothermal temperature 120 °C, DSC 130; DSC at isothermal temperature 130 °C, DSC140; DSC at isothermal temperature140 °C, OSI 110 °C.

Table 3
Relationships between oxidative stability index (OSI) values and differential scanning calorimetry (DSC) oxidative induction time (T_0) at four different isothermal temperatures.

Indicator (Y)	Indicator (X)[a]	Regression equation	*P*-values
OSI 110	DSC110	$T_0(\text{OSI110}) = 0.4899T_0\,(\text{DSC110}) - 129.89$	0.0001
	DSC120	$T_0(\text{OSI120}) = 0.4834T_0\,(\text{DSC120}) - 333.95$	0.0001
	DSC130	$T_0(\text{OSI130}) = 0.3276T_0\,(\text{DSC130}) - 313.46$	0.0001
	DSC140	$T_0(\text{OSI140}) = 0.4668\,T_0\,(\text{DSC140}) - 538.8$	0.0001

Table 4
Relationship between logarithm of DSC T_0 values ($\log_{10}\,T_0$) and DSC isothermal temperature (T) of *B. purprea*, rice bran and cotton seed oils.

Oil	Regression equation	Coefficient of determination
B. purpurea	$T = 54.323 - 0.0351\,\log_{10}\,T_0$	0.9997
Rice bran	$T = 12.273 - 0.0487\,\log_{10}\,T_0$	0.9996
Cotton seed	$T = 14.789 - 0.0305\,\log_{10}\,T_0$	0.9956

4. Conclusion

The results of present study for the determination of the oxidative stability of *B. purpurea* along with two conventional vegetable oils have shown a high correlation between DSC T_0 values and OSI values. Both methods confirmed that *B. purpurea* oil is very stable oil when compared to rice bran and cotton seed oil. Due to considerable oxidative stability, *B. purpurea* oil may find some appropriate applications in future. Furthermore, the DSC method offers simplicity without using any chemical and time saving nature. Therefore, DSC method can be easily used as an alternative technique for the measurement of oxidative stability in edible oil processing industries where mostly OSI technique is used.

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