A Simple and Rapid Method for Assessing Rancidity of Oils Based on the Formation of Hydroperoxides

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ABSTRACT

A new colorimetric method is reported for determining rancidity of oil based on the complex formation between titanium and lipid hydroperoxides present in the oil. This method was highly correlative with peroxide value (PV) and thiobarbituric acid (TBA) methods as well as with odor intensity value (OIV).

INTRODUCTION

The determination of hydroperoxides as outlined by Frenkel and Eskin (in preparation) suggested to these authors the possibility of adapting this method to assess rancidity of oils, since lipid hydroperoxides are among the first compounds formed during the course of rancidity (1). The hydroperoxide method is based on complex formation between the titanium ion and hydroperoxide resulting in a colored complex that can be measured spectrophotometrically at 415 nm. In the present study the hydroperoxide method was compared with other methods for rancidity determination including thiobarbituric acid (TBA), peroxide values (PV) and odor intensity values (OIV).

EXPERIMENTAL PROCEDURES

Materials

Rapeseed oil (RSO) samples from low erucic acid seed were obtained directly from the processor and were all finished for the consumer market, i.e., alkali refined, deodorized and bleached, commercial antioxidants added. Titanium tetrachloride was purchased from British Drug Houses (Toronto, Canada).

Method

A set of duplicate samples of oil (50 ml) were placed in uncovered red pyrex glasses and incubated for up to 16 days at 65 C. Duplicate samples were removed at 0, 2, 5, 8, and 16 days; covered with foil; and stored at -40 C until analyzed.

Odor Evaluation

The panel consisted of 12 persons some of whom had prior experience in odor evaluation. The odor of the oils was evaluated in a standard sensory testing room with sensory booths and slight positive atmospheric pressure and controlled light. Approximately 50 ml of each oil sample in red Pyrex glasses were examined at 50 C, the AOCS standard temperature for oil odor testing (2). In order to maintain a constant temperature, the red glasses were placed in water baths on small electric warmers in each panel booth (3). Each panelist determined the strength of the overall odor for each sample compared to the unheated rapeseed oil sample frozen at -40 C at zero time. A semistructured scale was used to evaluate the odor intensity of the oil as illustrated in Table I. No set divisions were placed on the scale with the exception of the beginning and end point, so that the panelist was free to place his mark anywhere along the line. A numerical value was derived by measuring the distance in centimeters from the bland reference point to the panelist's mark. All samples of oil were coded and presented in a random order.

Objective Methods

Thiobarbituric acid values (TBA) were determined on the oil samples according to the modified procedure described by Dobbs (3). Oil (0.5 g) was weighed into a 15 ml screw top glass tube to which was added 5 ml hexane. The tubes were capped and mixed on a vortex for 15 sec, and 5 ml of 0.02M TBA solution was added to each tube which was capped and shaken well. The tubes were placed in a boiling water bath for 40 min, cooled, and the absorbance read at 528 nm in a Coleman Junior Spectrophotometer against an equivalent hexane blank. Peroxide values (PV) were obtained following the procedure of Pearson (4).

Lipid hydroperoxides were assayed by using a modification of the method described by Frenkel and Eskin (in preparation) for the determination of hydroperoxides. Oil sample (0.5 g) was dissolved in 10 ml acetone in a Pyrex centrifuge tube followed by the addition of 0.5 ml titanium reagent (20% $TiCl_4$ in conc. HCl). The solution was mixed thoroughly and the titanium hydroperoxide complex formed was precipitated by the addition of 2 ml conc. NH_4OH. The mixture was then centrifuged at full speed for 5 min on an International Model HN Centrifuge and the supernatant discarded. The precipitate was then redissolved in 4N HNO_3 with the final volume adjusted to 10 ml with acid and the absorbance read at 415 nm against an equivalent blank.

RESULTS AND DISCUSSION

The hydroperoxide values (HV) were compared with the

TABLE I

Semistructured Scale for Determining Odor Intensity Values

Name_____ Booth #_____ Date:_____

You have been given a BLAND reference sample. Smell the reference and then smell each of the other samples. Mark the intensity of the overall ODOR of each sample.

CODE:		
	bland _____	strong
	bland _____	strong
	bland _____	strong
	bland _____	strong

TABLE II

Objective Measurements for Rancidity Determination in Rapeseed Oil Samples Using Thiobarbituric Acid (TBA), Peroxide Value (PV), and Hydroperoxide Methods

Storage at 65 C (days)	TBA 528 nm	PV (Me/Kg)	Hydroperoxide 415 nm
0	0.05	3	0.01
2	0.15	6	0.02
5	0.43	53	0.26
8	0.60	86	0.37
16	0.88	198	0.68

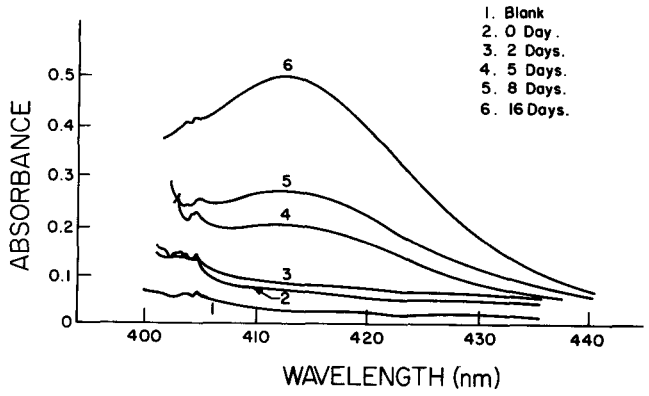

FIG. 1. Change in absorbance spectra for hydroperoxide formation in rapeseed oil samples over 16 days storage at 65 C.

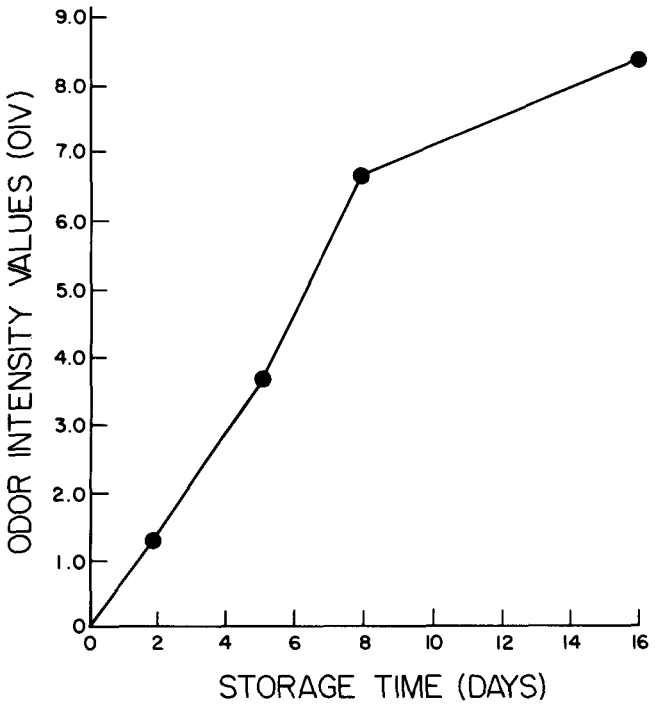

FIG. 2. Odor intensity values (OIV) of rapeseed oil samples stored at 65 C over 16 days.

TABLE III

Regression Equations and Coefficients of Determination (r^2) for Methods Used for Assessing Rancidity of Rapeseed Oil

Methods[a] compared	Linear regression $y = a_1x + a_0$	Coefficient of determination (r^2)
PV and HV	HV = 0.003 PV + 0.03	0.98
PV and TBA	TBA = 0.004 PV + 0.14	0.93
PV and OIV	OIV = 0.04 PV + 1.14	0.87
HV and TBA	TBA = 1.20 HV + 0.10	0.98
HV and OIV	OIV = 12.16 HV + 0.70	0.93
TBA and OIV	OIV = 10.27 TBA - 0.38	0.98

[a]TBA = thiobarbituric acid, PV = peroxide value, HV = hydroperoxide value, OIV = odor intensity value.

results obtained by using the TBA and PV methods and are summarized in Table II. The data show that TBA, PV, and HV all changed little during the first 2 days of storage but increased markedly after 5 days. The change in absorbance spectra using the hydroperoxide assay on oil samples over the sixteen days of storage is shown in Figure 1. It indicates a well-defined peak with an absorbance maximum at 415 nm characteristic of hydroperoxide formation (Frenkel and Eskin, in preparation).

The panel data obtained from the sensory evaluation is shown in Figure 2. With storage time there is an increase in OIVs which becomes more marked after 5 days. To test for possible correlations between the various methods used in this study, linear regression equations were derived for all possible combinations. The results tabulated in Table III indicate a high degree of correlation among all methods used. The results for TBA and PV were in agreement with those reported by Fioriti et al. (5) who found good correlation between flavor scores and TBA and PV values for high oleic sunflower and corn oil stored up to 16 days at 60 C. This study establishes the HV as a new and effective procedure for assessing rancidity of oils which is far simpler and quicker than either the TBA or PV assays.

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