EFFECT OF MINOR CONSTITUENTS OF CRUDE RAPESEED OIL ON THE STABILITY OF REFINED OIL AGAINST THE OXIDATIVE DETERIORATION

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INTRODUCTION

Rapeseed (canola type) oil belongs to less stable vegetable oils because of its relative high content of linolenic acid. In oil processed from unripe or damaged seeds the enzymic activity further deteriorates the stability, mainly due to oxidation and hydrolysis products. Rapeseed lipoxygenases are active in producing hydroperoxides (Meshehdani et al.,1990) which are rapidly decomposed, especially during some processing operations (Meshehdani et al.,1990), but the oxygen containining decomposition products, remaining in deodorized oil, catalyse the development of oxidative rancidity on storage.

Another deteriorative process is the hydrolysis of triglycerides into free fatty acids, and of phospholipids into phosphatidic acids. Free fatty acids catalyse the autoxidation of triacylglycerols, and phosphatidic acids may bind heavy metals into compounds not discarded during the degumming.

Good indicators of the quality of crude rapeseed oil are the content of free fatty acids, phosphatidic acid, and chlorophyll pigments (Campbell, 1984), mainly pheophytins (Holasová et al.,1990). Chlorophyll pigments are typical for unripe or damaged seeds, where the enzymic activity is also high. Therefore, we tried to correlate the content of these minor substances with the stability of refined rapeseed oils produced from zero-erucic rapeseed grown recently in Czechoslovakia under climatic conditions common in Central Europe.

MATERIALS AND METHODS

Material

Czechoslovak zero-erucic winter rapeseed grown in the years 1988 - 1990, and stored for 2 - 10 months, was used for processing. Both mixtures of high glucosinolate cultivars (Belinda, Germany; Silesia, Solida, Czechoslovakia) and low glucosinolate cultivars (Darmor, France; Ceres, Germany;

Sonáta, Czechoslovakia) were studied. The water content was up to 12 % at the time of cropping, and between 7 - 9 % before the processing.

Processing Conditions

The seed crushing was accomplished in two-high roll crushing rolls; the cooking took place in a seven-high stack conditioner SKET heated from 60 °C to 90 - 105 °C, jacketted for steam heating on the bottom and on the sides, with direct steam injected into the second and the seventh kettles. The layer of materials was 250 - 300 mm high on every stack, the overall time of conditioning was about 35 - 60 min. The moisture content changed from the initial 70 - 75 % to the final 6.4 - 6.6 %.

The expressing was carried out in continuous worm expellers Krupp SVP-3 or SKET HSP-18, the temperature of oil reaching 85 - 100 °C. Cakes were crushed, the flakes produced were smaller than 5 mm (the fraction of particles smaller than 0.5 mm should not exceed 15 %). The flakes were extracted in a carrousel extractor Extraktionstechnik (Germany), diameter 6.25 m, layer of extracted material 1.8 m deep. The carrousel consists of 18 cells; the extraction is countercurrent at 50 °C. Light petroleum (iso-hexane) boiling in the range of 60 to 72 °C was used for the extraction; the capacity ranged between 600 - 750 $t.d^{-1}$ (time of extraction about 100 min).

The five-high tray toaster had the diameter of 3.5 m, was jacketted, and equipped with jets of live steam into the two highest trays. The bed depth and the temperature varied between 300 - 350 mm, and 84 - 87 °C, 80 - 90 °C, 112 - 115 °C, 102 - 115 °C, and 105 - 120 °C in the succeeding trays, respectively. The average toasting temperature was 100 - 110 °C, the average toasting time 35 - 40 min. Meals from the toaster were crushed, transported with hot (100 °C) air into meal dryers and coolers.

The conditions of degumming, alkali refining, bleaching, and deodorization were reported in another place (Pokorný et al.,1989; 1987).

Analytical Methods

Chlorophyll and carotenoid pigments were determined by spectrophotometry and spectrofluorimetry (Pokorný et al., 1989); the peroxide value, iodine value, acid value, phosphorus were determined after the standard methods (IUPAC, 1987); the phospholipid classes were determined by HPLC after IUPAC; tocopherols were determined by HPLC (Pocklington, Dieffenbacher, 1988), the content of volatile glucosinolate decomposition products by the capillary GLC (Velíšek et al.,1990); the ionic iron content spectrophotometrically (Čoupková et al., 1986); the content

of total oxidation products by reverse-phase HPLC (Pánek et al., 1989), and the stability against oxidative rancidity by the Schaal test at 20 and 60 °C (the induction period was the time necessary to attain weight increase of 500 mg and 200 mg, respectively).

RESULTS AND DISCUSSION

Since 1988 we have analysed 18 series of samples taken at various stages of rapeseed processing, and rapeseed oil refining. There were only small differences in the contents of minor components between expressed and extracted crude rapeseed oils (Tab.1). The extracted oils contained slightly more total tocopherols, carotenoids, phospholipids, volatile glucosinolate decomposition products (both nitriles and isothiocyanates), and ionic iron. Their stability against autoxidation was substantially higher.

In case of crude expressed oils the stability against autoxidation was related to the content of phospholipid phosphorus, and total pheophytins. Similar relations were found with both Schaal stability values (weight increase of 500 mg and 200 mg, respectively), and the two values were significantly interrelated. The content of total tocopherols was negatively correlated with the content of phospholipid phosphorus. No such statistically significant ralationships were detected in the set of crude extracted oils. No correlation existed between the iron content and the oxidative stability.

The interrelationships between the stability and the phospholipid content is explained by the well known moderate antioxidant activity of phospholipids in vegetable oils (Nasner, 1985), especially in higher concentrations (Pokorný et al., 1982). The chelating capacity and the activity to non-radical decomposition of lipid hydroperoxides may have an effect.

The majority of minor compounds are removed during rapeseed oil refining, and the oxidative stability deteriorated during the process. Crude oils contained 1.0 - 2.5 % polar oxidation products, the content decreasing considerably during the alkali refining. Moderate increase was observed during the subsequent bleaching and deodorization. Prooxidative effect of these substances cannot be excluded. The peroxide value of crude oils varied between 5.4 - 20.2 $mval.kg^{-1}$ and the acid value between 1.39 - 2.26. The peroxide content decreased during alkali refining, bleaching, and deodorization but even the remaining non-peroxidic oxidation products may catalyse the subsequent oxidation of refined oils (Yoon et al., 1988). No significant correlations were detected between minor substances in crude oils and the oxidative stability of refined oils; probably, many factors contributed to the final oxidative stability.

CONCLUSIONS

Only small differences were observed between crude expressed and extracted rapeseed oils but nevertheless, the extracted oils were more stable against oxidation. The stability was correlated with the content of phospholipids.

Refined oils were much less stable against oxidation, and the final stability was not correlated with any minor component of crude oils. Oxidation products present in crude oils and remaining in refined oils could contribute to low stability of refined rapeseed oils. Therefore, the lipoxygenase activity should be controlled during the storage and processing of seeds.

Table 1. Differences between crude expressed and extracted oils

Characteristic [$mg.kg^{-1}$]	Expressed oil range	Expressed oil median	Extracted oil range	Extracted oil median
Total tocopherols	516.0-785.0	689.0	635.0-814.0	734.0
α- Tocopherol	312.0-469.0	384.0	372.0-477.0	399.0
δ - Tocopherol	11.0- 36.0	29.0	10.0- 35.0	29.0
Chlorophylls	1.3- 8.2	2.95	2.4- 11.5	2.86
Pheophytins	26.4- 49.2	33.8	27.1- 48.6	35.9
Carotenoids	39.5- 60.6	49.3	36.8- 69.6	54.8
Total phospholipids P	79.0-545.0	365.0	127.0-513.0	403.0
Phosphatidylcholine P	33.0-329.0	114.0	21.0-288.0	129.0
Phosphatidylethanolamine P	30.0-320.0	191.0	28.0-248.0	148.0
Nitriles	5.4- 16.2	9.4	6.9- 81.2	21.0
Isothiocyanates	1.1- 21.6	2.6	2.5- 21.9	6.5
Iron	1.6- 8.1	3.1	1.6- 5.6	4.2
Schaal (500 mg)[d]	15.8- 24.2	20.0	19.8- 45.1	30.6
Schaal (200 mg)[d]	8.3- 18.8	9.6	11.2- 23.7	18.4

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