Oxidative stability of “fragile” virgin oils

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Summary : The oxidation of virgin borage oil, linseed oil, walnut oil and sunflower oil was followed during storage in the dark at room temperature, either in closed or opened glass bottles. Peroxide value (PV), anisidine value, volatile components, Rancimat value, polymer and tocopherol contents were measured regularly during an 18-month period. Because of a rather high value before the storage, the variation of peroxide value showed the highest increase for the sunflower oil samples, while the PV evolution was the lowest in linseed oils. Indeed, linseed seemed to be the most stable oil under these storage conditions and according to the classical oxidation parameters. A correlation was observed between the absolute PV variation after 9 months and the amount of linoleic acid in the oil, but not with the tocopherol content. This very surprising behaviour of linseed oil stored in the dark, is however very different when the oil is exposed to light, revealing an important difference between auto-oxidation and photo-oxidation for this oil.

Introduction

Auto-oxidation is very intense in highly unsaturated oils however the exact rate of increase is not very well known in the case of virgin oils. The aim of this study is to complete the knowledge of these products.

Material and methods

Oils : virgin walnut, linseed, borage and sunflower oil

Storage : 18 months at room temperature in the dark :

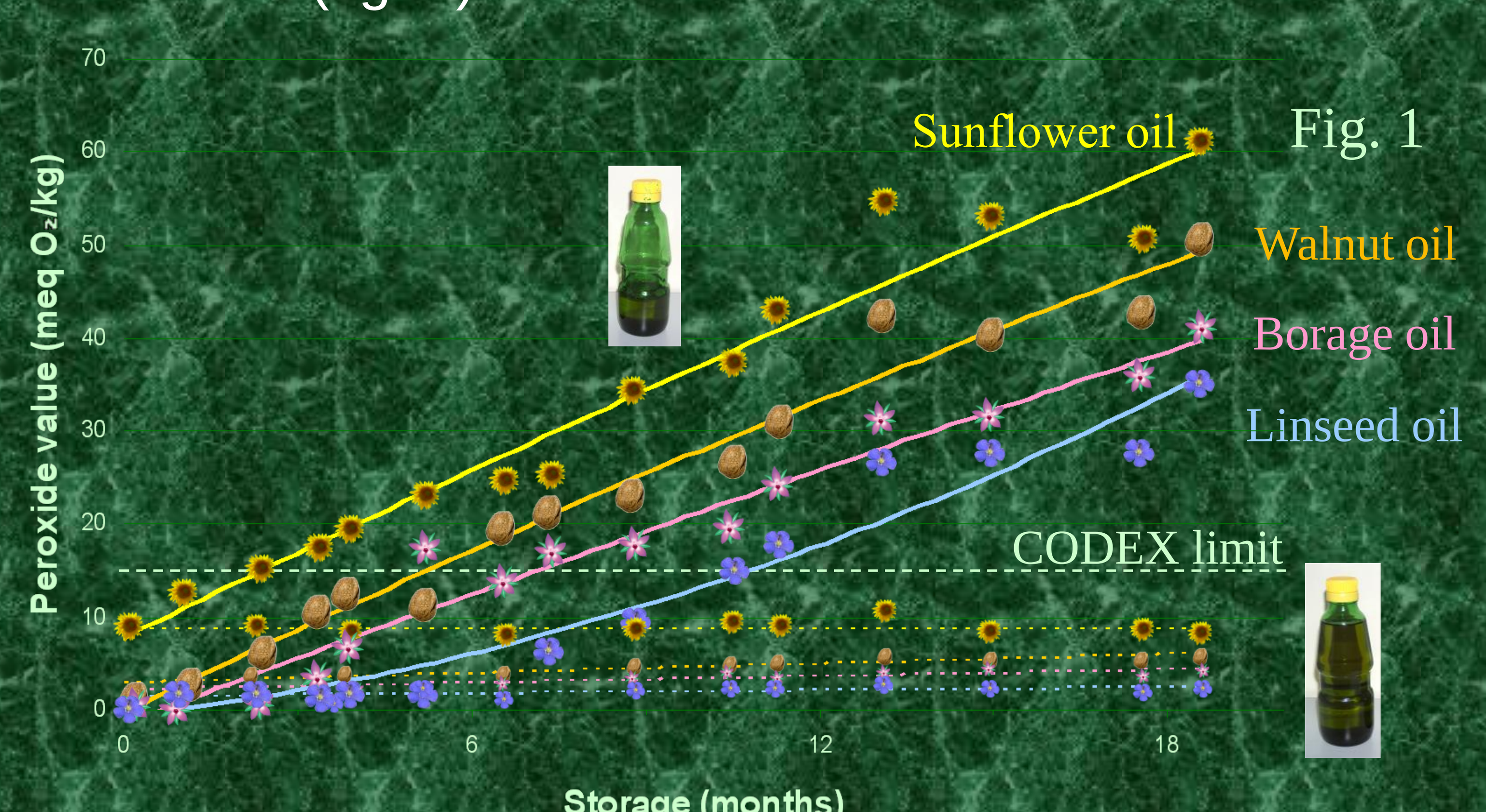
- Commercial conditions (closed bottles)
- Consumer conditions (removal of 20 ml/month, bottles opened once a month)

Analysis : peroxide & anisidine values, Rancimat, tocopherols, polymers by standardised methods

Results

- Peroxide value

The lowest variations were logically observed in closed bottles but, more surprisingly, linseed oil was apparently the most stable of all the oils in both storage conditions (fig. 1).

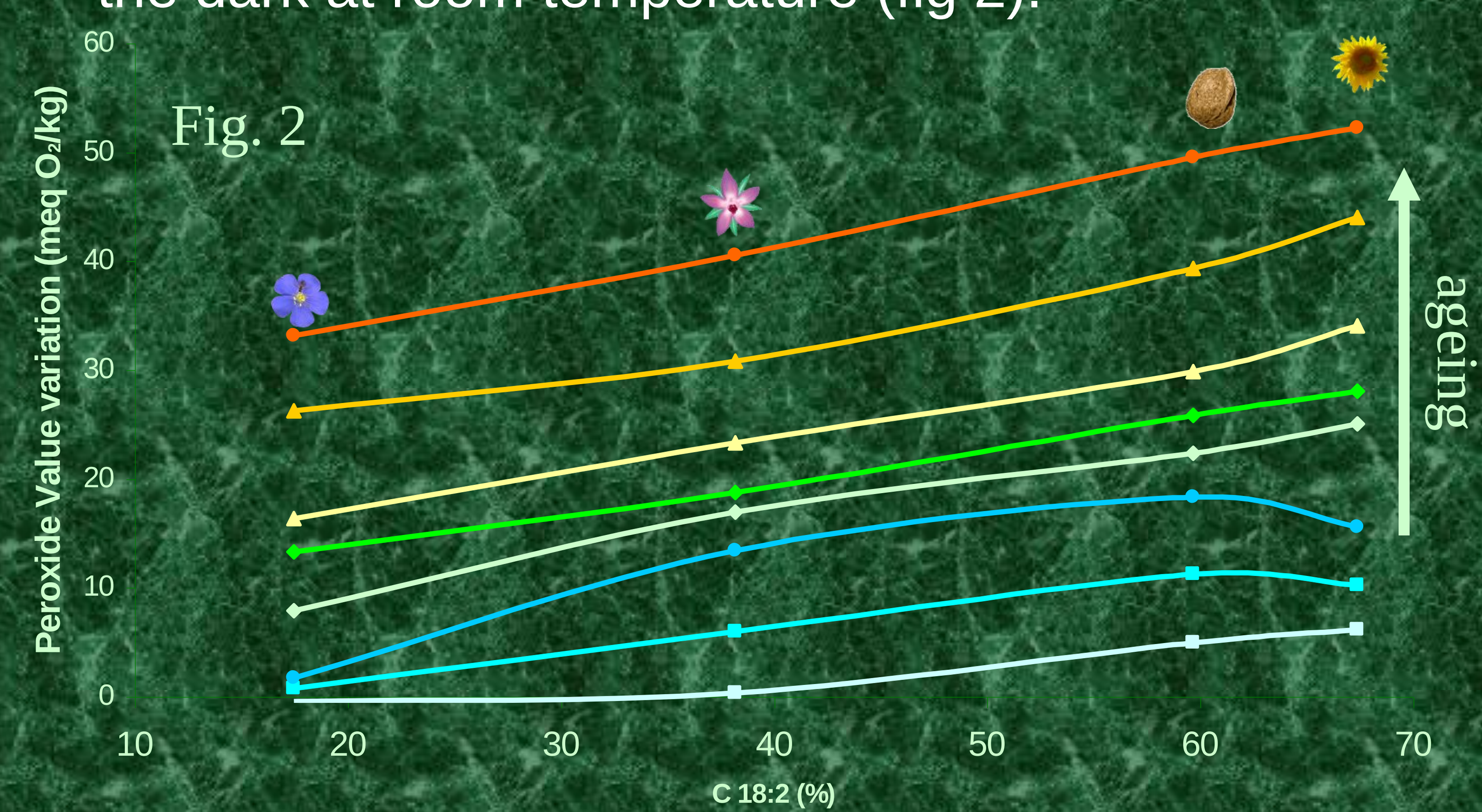


Sunflower oil showed the highest peroxide value (PV) increase, but the lowest variation of polymer content and anisidine value, indicating that primary oxidation is intense, but transformation to secondary oxidation products is slower than in the 3 other oils.

Borage and walnut oils exhibited intermediate behaviours.

Exposition to light of the same linseed oil led to very rapid increase of PV, indicating the significant susceptibility of this oil to photo-oxidation.

A correlation was observed between linoleate (C18:2) level and PV variation in opened bottles, in the dark at room temperature (fig 2).



- Anisidine value increase in 18 months

Oil type	Walnut	Sunflower	Linseed	Borage
Opened bottles	3,9	0,3	3,6	5,2
Closed bottles	0,5	0,0	0,7	0,8

- Polymer variation in 14 months (% m/m)

Oil type	Walnut	Sunflower	Linseed	Borage
Opened bottles	0,25	0,09	0,22	0,29
Closed bottles	0,05	0,09	0,07	0,07

- Tocopherols

Tocopherols could not explain the differences observed as linseed and walnut tocopherol content were similar.

- Copper and iron

Iron and copper were respectively under 0.9 and 0.01 mg/kg in all the samples, no correlation with peroxide evolution rate was observed.

Conclusion

The surprisingly slow evolution of peroxide value (PV) of virgin linseed oil stored in opened bottles at room temperature could be explained by its specific fatty acid composition. Indeed, PV showed a good correlation with linoleic acid content indicating that linoleic acid is primarily implicated in the auto-oxidation process in the dark (auto-oxidation) which is not the case for linolenic rich oil. One hypothesis to explain this behaviour could be that hydroperoxydes formed in these conditions could be readily transformed in other molecules which were not quantified by classical oxidation control methods.