S & D SHORT COMMUNICATION

Oxidation of Rapeseed Oil: Effect of Metal Traces

B. Benjelloun*, T. Talou, M. Delmas and A. Gaset
Laboratoire de Chimie des Agroressources, Ecole Nationale Supérieure de Chimie (INPT), 118 route de Narbonne 31077 Toulouse Cedex, France

Traces of heavy metals in edible oils are known to have an effect on the rate of oil oxidation. In this investigation we studied the effect of trace metals by excluding instead of adding them. Three supports were used to fix trace metals: grafted cellulose, cationic resin and absorbent resin. Cationic resin and grafted cellulose allowed copper (Cu) and iron (Fe) to be fixed. The measurement of peroxide value and variation of linolenic acid with temperature indicate good oxidative stability of oil processed on cellulose and cationic resin. These results confirm the effect of metals, particularly Fe and Cu, on oil oxidation.

KEY WORDS: Ion exchanger, metals, oil stability, oxidation, rapeseed oil.

The problem of oxidative deterioration is critical for the use and storage of oils. Indeed, oxidation of unsaturated fats and oils not only produces offensive odors and off-flavor limiting their use, but can also decrease nutritional quality through the formation of secondary reaction products (1). Traces of heavy metals in edible oils are well known to have serious deteriorating effects on the stability of these oils. It was observed that unsaturated fats and oils develop rancidity when metal traces such as iron, copper, cobalt or nickel are added. In this investigation, we have fixed metals on different supports to confirm the effect of heavy metal traces by excluding instead of adding them (2). The oil used is rapeseed oil. Rapeseed oil contains a high amount of unsaturated fatty acids, and its oxidative stability decreases rapidly, particularly with temperature.

MATERIALS AND METHODS

Commercially refined rapeseed oil provided by Organisation Nationale Interprofessionelle Des Oleagineux (ONIDOL) (Paris, France) does not contain antioxidants or stabilizers. Supports used were absorbent resin Duolite ES861 (Duolite Ltd., Paris, France), cationic resin Lewatit S100 (Bayer Ltd., Paris, France) and grafted cellulose AC3. The oil to be treated was passed through a resin column or a grafted cellulose column. Mineral determination: A ten-gram sample of each oil was weighed in a crucible covered by a Pyrex watch glass and charred on a hot plate at 300°C. When the sample stopped smoking, ashing was continued in a muffle furnace at 500°C for about 15 hr. Ashes were directly analyzed by EDAX (spectrometric analysis by X-ray energy dispersion) on a Jeol spectrometer JSM 25.

Linolenic acid variation with temperature was determined after heating 125 mL of oil sample, at 180°C, for 8 hr (3). Every two hours, the oil composition, particularly linolenic acid content, is determined by gas chromatography, after microesterification. A Carlo Erba chromatograph Fractovap 6180, equipped with a fused capillary column (Carbowax 20M, 50 m × 32 mm i.d.) is used, with an oven temperature program: isothermal for 2 mn at 50°C, and then from 50°C to 180°C at 10°C/mn. Peroxide number was determined according to the Association of Official Analytical Chemists (AOAC) (4), after heating oil at 120°C for 8 periods of 15 min and cooling it for about 15 min between each period.

*To whom correspondence should be addressed.

RESULTS AND DISCUSSION

Metals detected by EDAX in untreated rapeseed oil were iron and copper with 6.2% and 93.8% respectively (relative percent in weight versus total metal content). After each treatment, the metal content was determined using EDAX. Two supports of the three supports, namely resin S100 and grafted cellulose fixed copper and iron, respectively. According to Lundberg (5), copper and iron are the strongest prooxidizers in fats and oils. Because of the fatty acid content, rapeseed oil oxidizes rapidly with temperature and develops off-flavor (6). Effect of trace elements on oil oxidation can be represented by peroxide value. Figure 1 displays the effectiveness of each treatment on the oxidation. Best results were obtained with grafted cellulose and resin S100. In fact, the peroxide value of cellulose-treated oil is 70% lower than that of untreated oil. Peroxide values obtained using resin S100 and cellulose are almost the same. There was no change in peroxide value when using resin Duolite ES861. Peroxide value measures whole oxidation. Because of high linolenic acid content in rapeseed oil, oxidation can be represented by linolenic acid

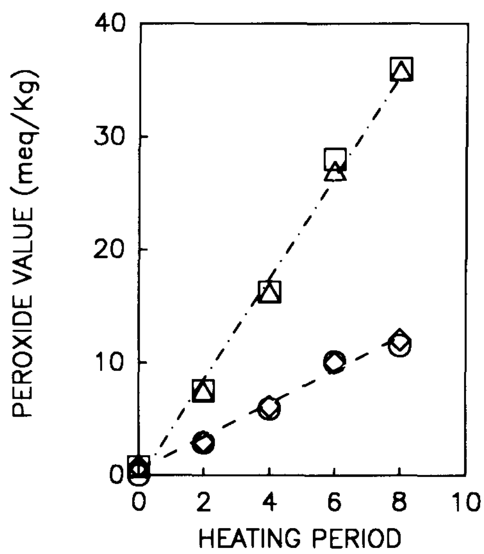

FIG. 1. Variation of peroxide value with heating periods for untreated oil (□), cellulose-treated oil (○), Lewatit S100-treated oil (◇) and Duolite ES 861-treated oil (△).

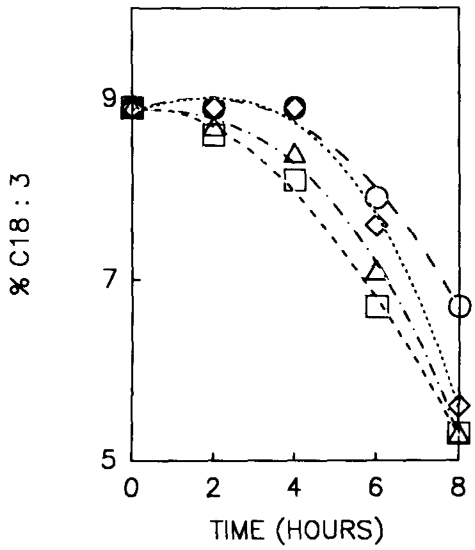

FIG. 2. Variation of C18:3 with time of heating for untreated oil (□), cellulose-treated oil (○), Lewatit S100-treated oil (◇) and Duolite ES 861-treated oil (△).

variation with temperature (7). Figure 2 shows linolenic acid variation with heating time. The C18:3 degradation decreases with temperature after each treatment. According to next results, resin S100 and grafted cellulose leads to an oil with good oxidative stability. This confirms the important activity of metals such as iron and copper on lipid oxidation. Metal traces increase formation rate of peroxides and catalyze reactions between unsaturated fatty acids and oxygen. But if metals contribute to oil and fat oxidation, they are not exclusively responsible. Other minor compounds can be responsible for oil deterioration as for instance polar compounds (8) which can be absorbed on silica gel column (B. Benjelloun, PhD thesis, in preparation).

ACKNOWLEDGMENT

This work was supported by ONIDOL (Organisation Nationale Interprofessionelle Des Oleagineux, Paris, France).

REFERENCES

1. Frankel, E.N., *J. Am. Oil Chem. Soc. 61*:1908 (1984).
2. Dutton, H.J., and A.W. Schwab, *Ibid. 11*:385 (1948).
3. Gomes, T., and M. Catalano, *Agrochimica 29*:281 (1985).
4. AOAC (Association of Official Analytical Chemists), Washington, D.C. (1980).
5. Lundberg, W.D., *Autoxidation and Antioxidants*, Interscience Publishers, New York, NY, 1962, p. 451.
6. Eskin, N.A.M., and M. Vaisy-Genser, *J. Am. Oil Chem. Soc. 66*:1081 (1989).
7. Dobarganes, M.C., and J.J. Rios, *Grasas y Aceites 37*:61 (1986).
8. Mistry, B.S., and D.B. Min, *J. Food Sci. 52*:786 (1987).

[Received July 23, 1990; accepted October 30, 1990]