MOLECULAR ORIGIN, PHASE TRANSITIONS, AND FORMATION MECHANISM OF SEDIMENT IN REFINED CANOLA OIL

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ABSTRACT

The major components of the haze-causing material in refined canola oil are wax esters of saturated long chain fatty acids and alcohols from C16:0 to C32:0. The physical behaviour of the waxy sediment dictated the crystallization of the hazy substances which is influenced by temperature, sediment content and phospholipid content, etc in the oil.

INTRODUCTION

Precipitation of high-melting substances causes a hazy appearance in vegetable oils such as sunflower (Chulu *et al.*, 1989). Canola oil is known to contain a low amount of high-melting substances and therefore normally does not require winterization for clarity. Occasionally, however, some batches of refined canola oil develops floc haze or a sediment on storage (Liu *et al.*, 1993; Hu *et al.*, 1993; Gao and Ackman, 1994). Research on canola sediment revealed unique chemical and physical properties of the material. This paper reviews the recent findings on the chemical composition, the phase transition behaviour, the macromelecular structure of the sediment, and the crystallization kinetics of sediment formation in canola oil.

CHEMICAL COMPOSITION OF CANOLA SEDIMENT

TLC-FID analysis of canola sediment showed that canola sediment contained mainly wax esters (80%) of saturated long-chain fatty acids and fatty alcohols (Liu *et al.*, 1994a). Other components were also identified including free fatty alcohols, free fatty acids, hydrocarbons, and mono- and diglycerides (Hu *et al.*, 1993; Gao and Ackman, 1994). In some reports, triglycerides (TG) were also reported to be a component in canola oil sediment with a similar fatty acid profile to that of oil (Hu *et al.*, 1993). Clearly a more efficient method for separating the trace solid sediment from liquid oil contamination is necessary before fully understanding the role of TG particularly saturated TG in sediment formation especially in winterized/dewaxed oil. Canola sediment was also found to contain unidentified compounds (Liu *et al.*, 1994b; Gao and Ackman, 1994). These compounds could not be separated by normal solvents for simple triglycerides and phospholipids and therefore could not be identified by TLC-FID technique. Further studies indicated that it showed no colour reactions with phospholipid spray, nor did it release any methyl esters by transesterification treatments. The exact composition of these substances and their roles in sediment formation are not known. Polar complex carbohydrate derivatives (Liu *et al.*, 1994b) or excess long-chain wax esters have been suggested (Gao and Ackman, 1994).

Detailed studies of the fatty acid and fatty alcohol composition of canola waxes established the structures of wax esters of saturated long-chain fatty acids (FA) and fatty alcohols (FAL). The majority of FA and FAL have even-number carbon atoms from C16:0 to C32:0. The most generous FA's are C20:0 (35%) and C22:0 (20%) (Liu *et al.*, 1993), but Hu *et al.* (1993) reported that the major FA's were C16:0, C18:0 and C20:0. Gao and Ackman (1994) found C24:0, C26:0 and C28:0 in abundance. Variations in the relative proportions of FA in canola sediment were also reported in sediments isolated from different batches of oil and appeared to be significant in sediment formation (Liu *et al.*, 1994b). The FA composition of canola sediment reported by various workers is similar and C24:0, C26:0, C28:0 and C30:0 were found to be the principle fatty alcohols (Przybylski *et al.*, 1993). Compared to sunflower oil waxes (Kleiman *et al.*, 1969), canola sediment contains a higher amount of longer chain FA's.

PHYSICAL PROPERTIES OF CANOLA SEDIMENT

X-ray diffraction (XRD) of canola sediment showed an XRD pattern with d-spacings of 4.13, 3.72, 2.98 and 2.49 Å, typical of waxes (Liu *et al.*, 1993). This indicates that the formation of haze in canola oil involves crystallization of wax esters which may be influenced by other components. DSC crystallization and melting curves of fatty species often exhibit complex features due to polymorphic phenomenon, but simple DSC thermal curves were recorded for canola sediment (Liu *et al.*, 1993; Gao and Ackman, 1994). This further suggests that polymorphism could not be a factor in the formation of sediment. The surface free energy of the waxy sediment crystals in the oil was estimated to be 5-10 erg/cm^2, similar to that for long-chain hydrocarbons. Polarized light microscope revealed that canola sediment often crystallized in rod-like crystals in the oil (Liu *et al.*, 1993).

FACTORS INFLUENCING THE FORMATION OF SEDIMENT IN CANOLA OIL

Formation of sediment in canola oil is thus viewed as crystallization in metastable oil solution (metastable supersaturated solution). Studies on the kinetics of crystallization of sediment in mixtures of canola oil/sediment showed dependence of crystallization and melting transitions on sediment concentration and the rate of cooling (heating). The crystal size and shape were also influenced by the cooling rate. Phospholipids (lecithin) were found to retard the growth of sediment crystals but not to effect the transition temperatures (Liu *et al.*, 1994a). Gao and Ackman (1994) found a significantly higher amount of phospholipids in the oil labelled hazy and suggested that it may be a factor in haze formation.

Storage tests indicated that canola oil that contained 50 ppm sediment may pass the cold test (0°C, 24h) but would develop a sediment in two days even at 25°C (Liu *et al.*, 1993). This is consistent with reports that about 60-70 ppm waxy sediment was found in oils that were later found hazy (Hu *et al.*, 1993; Gao and Ackman, 1994). In contrast, sunflower oil containing 100 ppm was reported to remain stable at 25°C for more than a week (Chulu *et al.*, 1989). Canola oil that contained 25 ppm sediment remained clear at 25°C for more than a month (Liu *et al.*, 1993). Further studies indicated a power law type relationship may exist between the clouding time and sediment concentration (Liu *et al.*, 1994b) which may be useful for predicting sedimentation tendency in canola oil.

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REFERENCES

Chulu, C.L., Barlow, P., and Hole, M. (1989). Cloudiness in Zambian sunflower oil: effect of storage temperature and wax levels. *Tropical Science*, **29**, 33-38.

Gao, Z., and Ackman, R.G. (1994). Gradient density isolation and fraction of haze-causing solids of canola oil. *Journal of Science of Food and Agriculture* (in press).

Hu, X., Daun, J.K., and Scarth, R. (1993). Characterization of wax sediments in refined canola oils. *Journal of American Oil Chemists' Society*, **70**, 535-537.

Kleiman R., Earle, F.R., and Wolff, I.R. (1969). Wax esters from sunflower oil tank settlings. *Journal of American Oil Chemists' Society*, **46**, 505.

Liu, H., Biliaderis, C.G., Przybylski, R., and Eskin, N.A.M. (1993). Phase transitions of canola oil sediment. *Journal of American Oil Chemists' Society*, **70**, 441-448.

Liu, H., Biliaderis, C.G., Przybylski, R., and Eskin, N.A.M. (1994a). Effects of crystallization conditions on sedimentation in canola oil. *Journal of American Oil Chemists' Society*, **71**, 409-415.

Liu, H., Biliaderis, C.G., Przybylski, R., and Eskin, N.A.M. (1994b). Physical behaviour and composition of low- and high-melting fractions of sediment in canola oil. *Food Chemistry* (in press).

Przybylski, R., Biliaderis, C.G., and Eskin, N.A.M. (1993). Formation and partial characterisation of canola oil sediment. *Journal of American Oil Chemists' Society*, **70**, 1009-1015.