

Solid phase microextraction analysis of volatile constituents of heated palm olein and selected oils

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ABSTRACT

Effect of heating on the development of volatile aroma constituents of palm olein and selected oils was studied. The aroma constituents of heated oils were collected using a solid-phase microextraction (SPME) headspace technique with an adsorbent of a divinylbenzene/carboxen (50/30 μ m) on polydimethylsiloxane (PDMS) fibre. The extracted volatiles were desorbed from the fibre in the injection port of the gas chromatograph at 250°C and the aroma constituents were identified by GC-MS. The analytical data showed that compounds responsible for the rancidity, i.e. hexanal, 2E,4E-heptadienal and 2E,4E-decadienal increased significantly when the oils were heated above 100°C while there were no significant changes in their amounts when heating below 60°C. Meanwhile, the volatile contents were slightly increased when the oils were heated at 80°C. In palm olein, the hexanal content before heating (1.5 μ g/g) was similar with its content (1.6 mg/g) after heating at 60°C. However, when palm olein was heated between 100°C and 180°C the hexanal content increased to 6.4 μ g/g and 8.7 mg/g respectively. Similar patterns were also observed when soybean, sunflower and corn oils were heated. In soybean oil, the hexanal content before heating was 3.2 μ g/g and rose to 13.2 μ g/g after heating at 180°C. The concentration of hexanal in sunflower oil increased from 3.6 μ g/g to 12.7 mg/g when the oil was heated at 40°C and 180°C respectively. Meanwhile in corn oil, the hexanal contents before heating and after heating at 180°C were 2.8 μ g/g and 13.5 μ g/g respectively.

Key words: Aroma constituents, rancidity, vegetable oil.

INTRODUCTION

Vegetable oils are easily degraded via autoxidation process when exposed to heat and light. The degradation process occurs due to the presence of unsaturated constituents which lead to the formation of secondary products. Some of the degraded compounds lead to the development of various volatile constituents such as aldehydes and ketones which are responsible for the rancidity/off-flavour of vegetable oils¹⁻⁴. Several volatile

constituents, i.e. hexanal and pentanal, have been commonly used as indicators of lipid oxidation, since these off-flavour components have very low threshold values^{5,6}. Other volatiles, such as 1-penten-3-one, 4-(Z)-heptenal, 2,4-(E,E)-heptadienal and 2,6-(E,Z)-nonadienal, have been characterized as contributors to the fishy off-flavour in fish oil and fish products⁷⁻⁹.

Volatile constituents can be trapped from the oil by static, dynamic and adsorption headspace

techniques. Among the adsorption techniques, solid-phase microextraction (SPME) trapping, which is developed by investigators at the University of Waterloo¹⁰⁻¹², is widespread in the field of environmental chemistry and toxicology¹³⁻¹⁴. Recently, a septum-free SPME injector device is introduced to detect the presence of aldehyde in oxidized lipids¹⁵. Until now, information on the utilization of the SPME techniques for characterizing the origin and oxidative state of vegetable oils based on the determination of the aroma and volatile compounds is limited¹⁶⁻¹⁹. The main purpose of the present study is to evaluate the SPME technique in analyzing volatile constituents during heating of palm olein and other selected vegetable oils.

MATERIAL AND METHODS

Palm olein, soybean oil, sunflower oil and corn oil were obtained from the local stores in mid-December 2008 and analyses were carried out between January and June 2009 at Food Bioprocess and Biotechnology Laboratory, the International Islamic University Malaysia (IIUM). The volatile constituents were collected using a SPME technique with a divinylbenzene/carboxen (50/30 μ m) on polymethylsiloxane (PDMS) on a stable-flex fibre (Supelco, Bellefonte, USA) as an adsorbent. The gas chromatographic (GC) and gas chromatography-mass spectrophotometric (GC-MS) analysis were carried out using a HP5890 Gas chromatograph (Agilent, Palo Alto, USA) and a HP 5971A mass selective detector (Agilent, Palo Alto, USA).

Headspace extraction of volatiles

The oil sample (5 g) was subjected to accelerated oxidation by heating at 40°, 60°, 80°, 100°, 120°, 140°, 160° and 180°C in a 15-ml open vial. The internal standard solution, i.e. n-dodecane (5 μ g/g) was injected into the headspace vial for the purpose of quantification of the volatile constituent. After heating the sample for 30 min., the volatiles from the oil were collected using a SPME headspace sampling system as previously described¹³. The PDMS fibre was placed in the headspace vial 3 mm above the surface of the oil.

Gas chromatographic analysis

The polydimethylsiloxane (PDMS) fibre

was injected into a HP5890 Gas Chromatograph (Agilent, Palo Alto, USA) equipped with a fused silica capillary column (Ultra 1, 50m x 0.32 mm x 0.52 mm; μ Agilent, Palo alto, USA) and FID detector. Helium was applied as a carrier gas at a constant flow rate of 1.0 ml/min and the peak areas were calculated by a HP3396B integrator (Agilent, Palo Alto, USA). Quantitative analysis of the volatile constituent was calculated using n-dodecane as an internal standard according to method previously reported (20-21). Operating condition: Injector and detector temperatures were 230°C and 250°C respectively; the oven temperature was programmed from 70°C to 220°C at a rate of 4°C/min.

GC-MS analysis

A HP 5890 model gas chromatograph equipped with the same column as GC analysis was directly interfaced to the ion source of a HP 5971A mass spectrometer (Agilent, Palo Alto, USA). Working condition: GC as above with He column head pressure 25 kPa, MS: transfer line temperature 280°C, ion source temperature 182°C, and MS identification of the compounds was made according to the mass spectra of the standards and by applying NIST 98 library.

RESULTS AND DISCUSSION

Volatile constituents of heated palm olein

Fig. 1 shows the GC chromatogram of the SPME headspace volatiles collected from palm olein after heating at 100°C for 30 min. It was found that at least 21 volatile constituents have been identified using a GC-MS spectroscopic technique. The major compounds collected in the headspace of heated palm olein were 2-butanone (peak 3), 3-methylbuten-1-ol (peak 6), hexanal (peak 8), 2E,4E-heptadienal (peak 16) and 2E,4E-decadienal (peak 19). As comparison, the volatile constituents of other oils, i.e. soybean oil, sunflower oil and corn oil, were also analyzed. Hexanal and 2E,4E-decadienal were found in high amounts in all heated samples.

Effect of heating on volatile constituents of palm olein

The study on the effect of heat treatment on the formation of volatile aroma compounds in

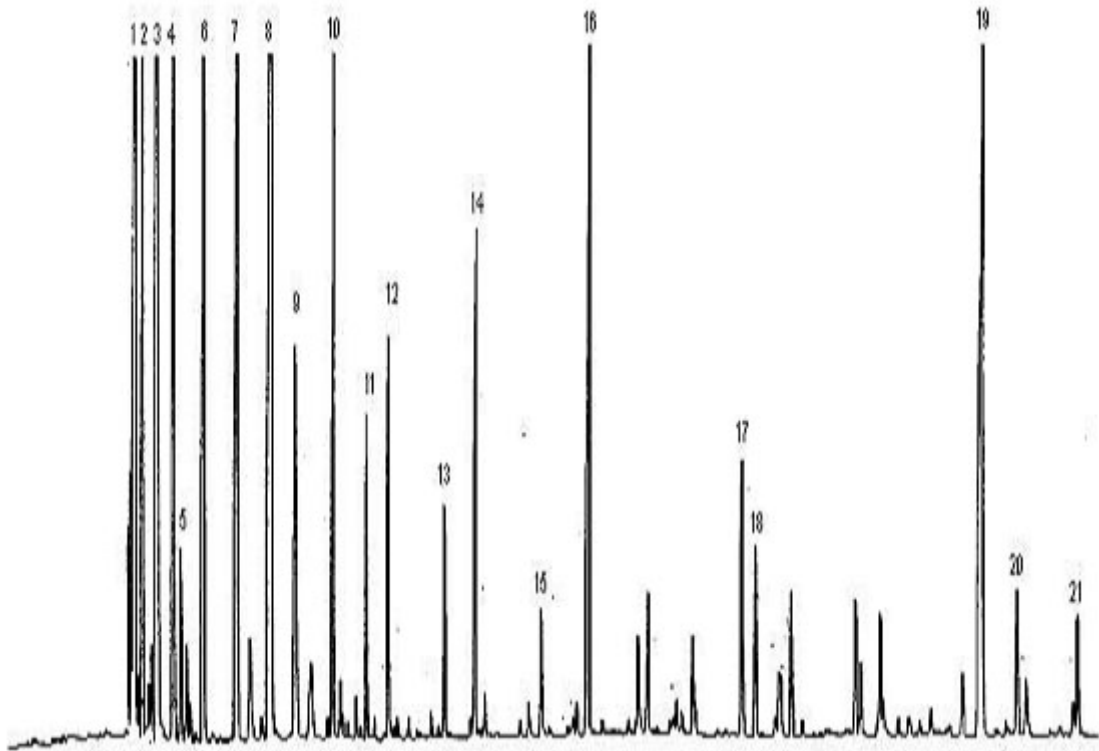


Fig. 1: GC chromatogram of the SPME headspace volatile aroma of heated palm olein

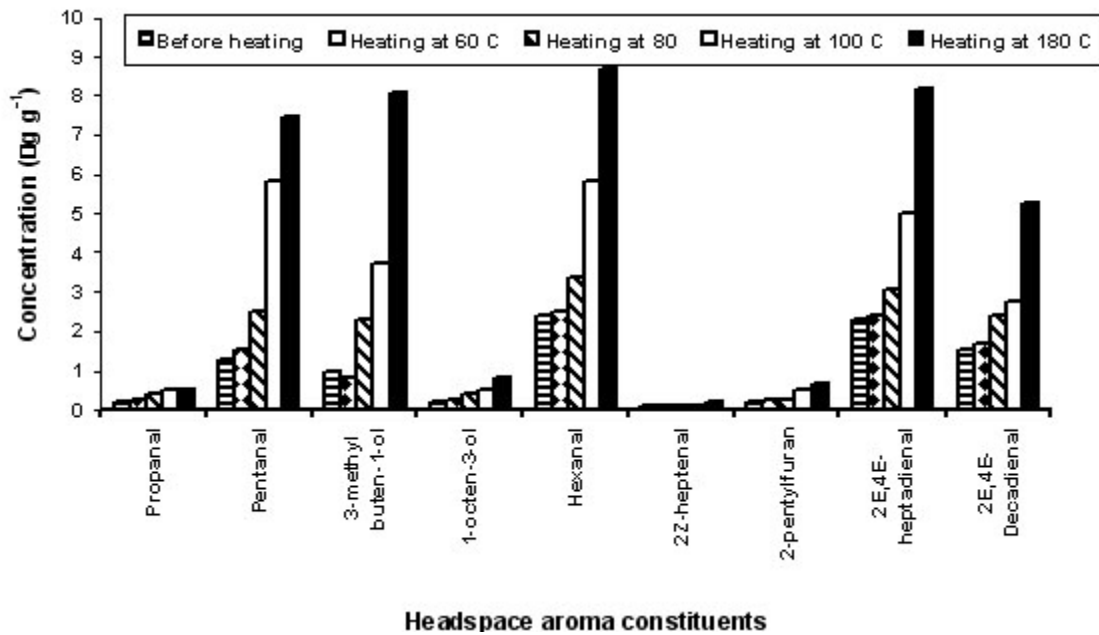


Fig. 2: Changes of headspace volatile constituents of heated palm olein

palm oil was carried out. It was found that there was no significant changes in the volatiles formed in the headspace of the palm olein before and after heating at 60°C. This indicated that, no oxidation/

degradation process had taken place when the oil was heated at and below 60°C. A similar result was also obtained by Snyder and co-workers in their storage study on vegetable oils and found that there

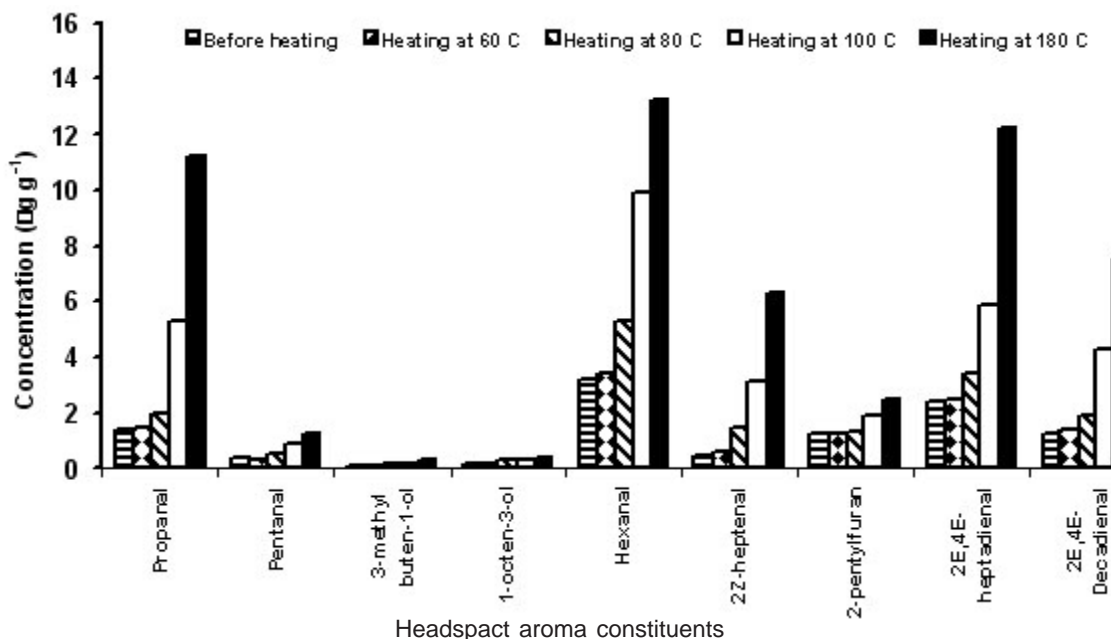


Fig. 3: Changes of headspace volatile constituents of heated soybean oil

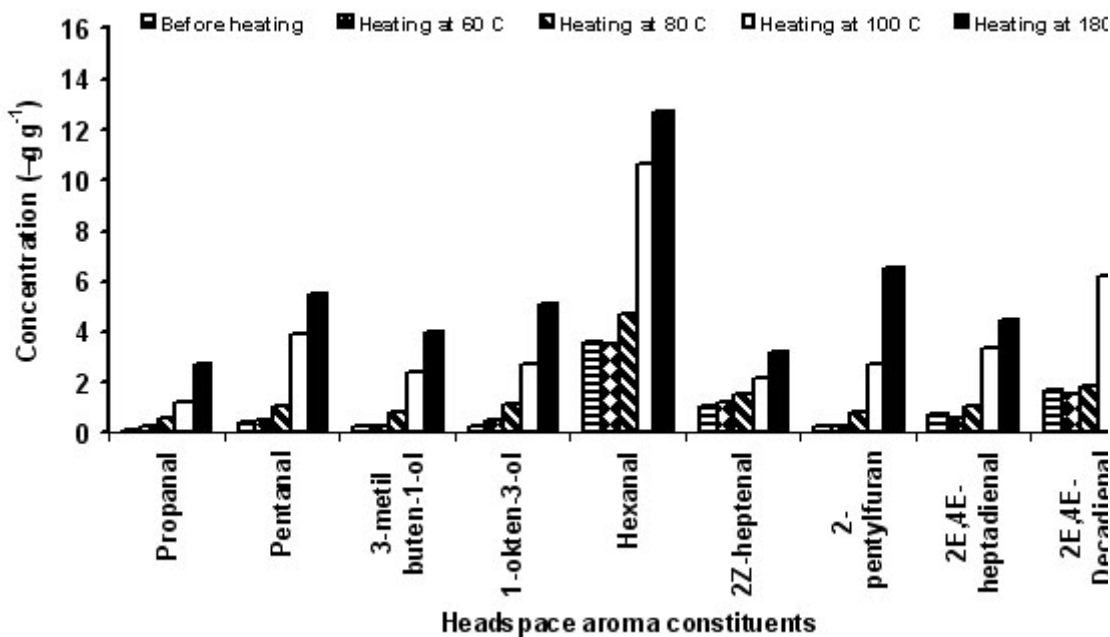


Fig. 4: Changes of headspace volatile constituents of heated sunflower oil

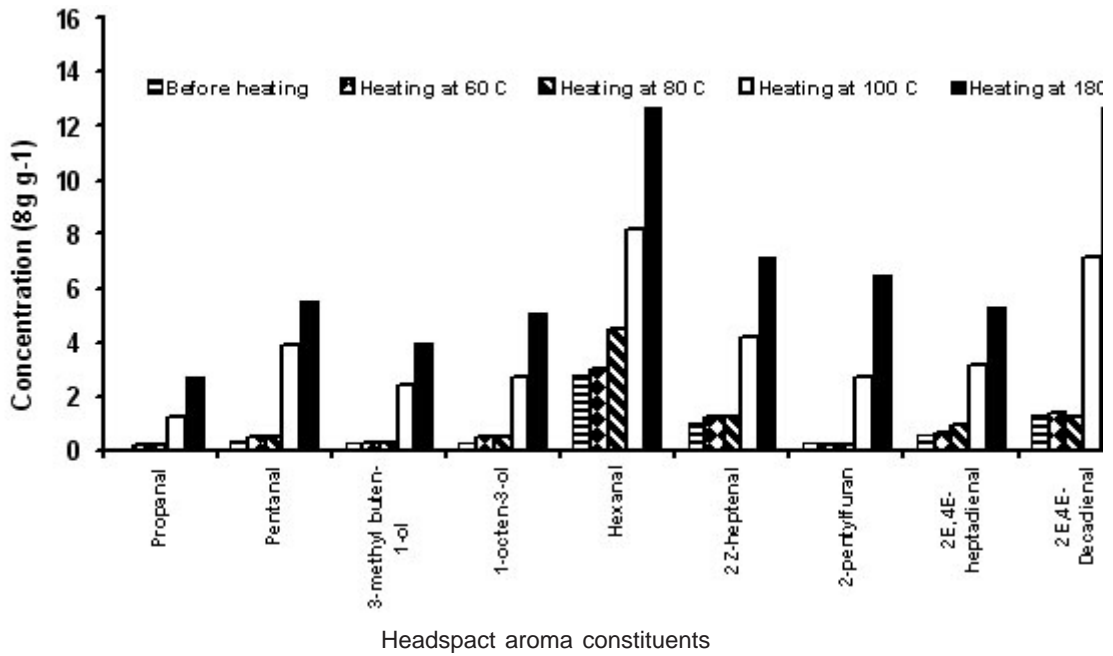


Fig. 5: Changes of headspace volatile constituents of heated corn oil

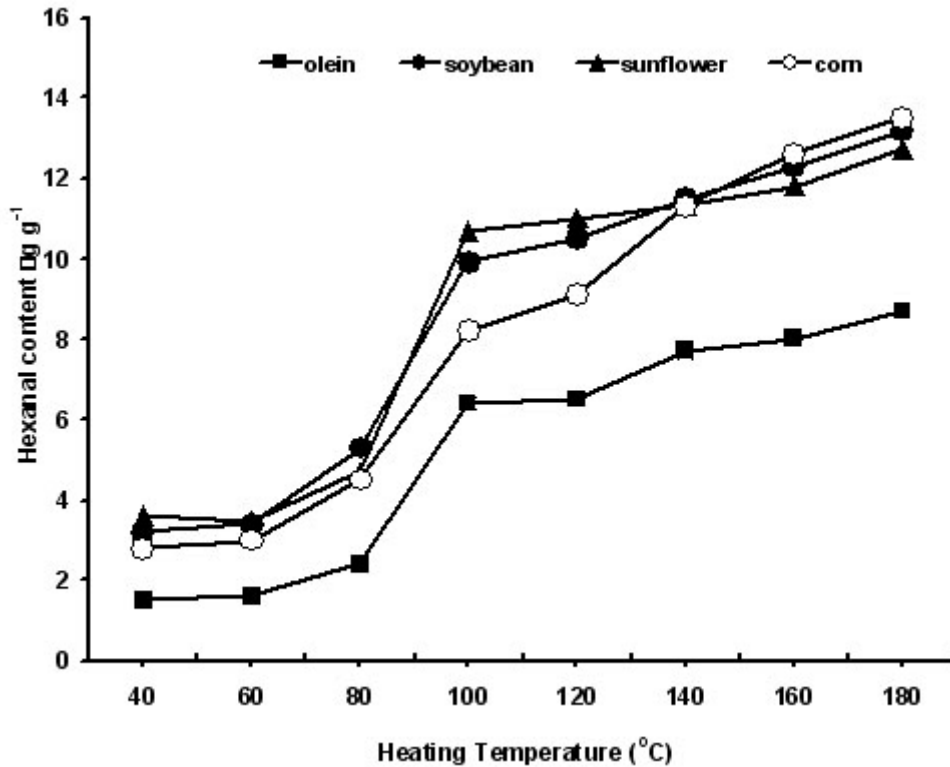


Fig. 6: Hexanal content of heated palm olein and selected oils

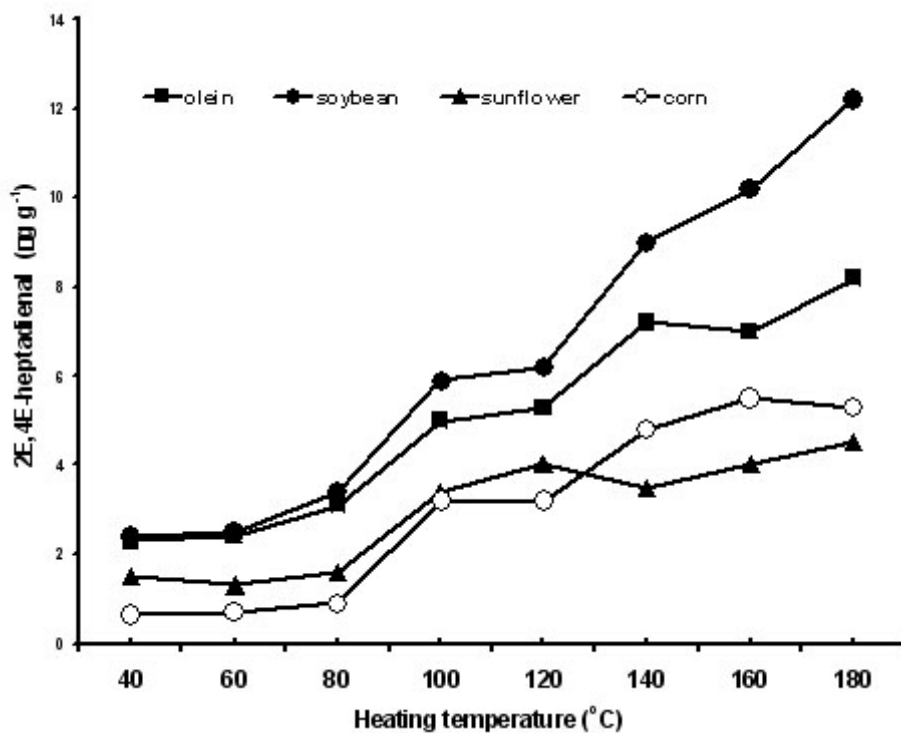


Fig. 7: 2E,4E-heptadienal content of heated palm olein and selected oils

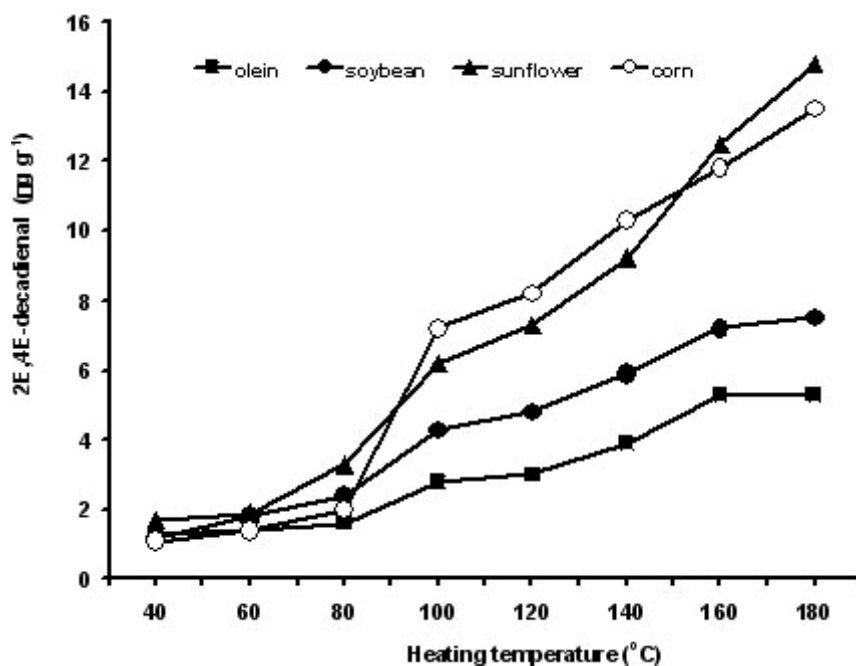


Fig. 8: Concentration of 2E,4E-decadienal in heated palm olein and selected oils

was no decomposition products developed when the oils were stored at 60°C for 8 hr²¹. Meanwhile, the volatile contents were slightly increased when the oil was heated at 80°C. However, the formation of the volatiles showed a significant increase when the oil was heated at and above 100°C (Fig 2). For example, n-hexanal was rapidly increased from 1.5 µg/g (before heating) to 8.7 µg/g after heating at 180°C (frying temperature) whilst 2E,4E-heptadienal rose from 2.3 µg/g to 10.3 µg/g. A similar pattern also occurred when soybean and sunflower oils were heated (Fig. 3, & 4). In soybean oil, the hexanal content increased from 3.2 µg/g to 13.3 µg/g after heating at 180°C whilst 2E,4E-heptadienal increased from 2.4 µg/g to 12.2 µg/g after heating at frying temperature. Meanwhile, in sunflower oil, the hexanal content increased from 3.6 µg/g to 12.7 µg/g after heating at 180°C whilst 2E,4E-heptadienal increased from 0.7 µg/g to 4.5 µg/g after heating at frying temperature. Selke and co-worker obtained a similar trend during their study on headspace volatiles of heated soybean oil²². However the changes of volatiles in heated corn oil was slightly different (Fig. 5). Although the hexanal content increased, the concentration of 2E,4E-heptadienal was unchanged. A similar result was also observed by other researchers when analyzing headspace volatiles of heated corn oil²⁰.

Fig. 6 shows that the hexanal concentration of heated palm olein was significantly low compared to other selected oils. This indicated that palm olein was more stable towards oxidation at higher temperature due to lower concentration of linoleic acid²³.

Other rancidity constituent, i.e. 2E,4E-heptadienal showed a different trend. Corn oil and

sunflower oil contained less concentration of 2E,4E-heptadienal compared to palm olein and soybean oil (Fig 7). Its content in corn oil was significantly unchanged while in sunflower oil the change was rather small.

Fig. 8 shows that the 2E,4E-decadienal concentration of heated palm olein was significantly low compared to other selected oils when heating at and below 100°C and 180°C. It showed that the quantity of this compound was closely related to the unsaturation degree of the oils. Palm olein was expected to produce lower quantity of decadienal as compared to other liquid oils²³.

CONCLUSION

Volatile flavour constituents of heated palm olein has been characterized and identified using the SPME headspace adsorption technique followed by GC-MS analysis.

The analytical data showed that the compounds responsible for the off-odour (rancid), i.e hexanal, pentanal, 2E,4E-heptadienal and 2E,4E-decadienal increased rapidly when the oils were heated above 100°C while at 60°C and below there were no significant changes in amount of the compounds. Nevertheless, the amount of the volatile contents increased slightly when the oil was heated at 80°C.

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