Rancidity Development in Macadamia Kernels As Determined by Head-space Hexanal Concentration

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Lipids in Macadamia Oil

- Macadamia nut high in oil (>72%)
- Macadamia oil is
  - High in mono-unsaturated fatty acids (>80%)
  - Low in poly-unsaturated fatty acids (PUFA)
  - similar to olive oil in FA profile
- Hydroperoxides (ROOH) from the oxidation of PUFA further decomposed to a complex variety of secondary oxidation products.
- Volatiles at very low concentrations cause rancidity and decrease the quality of oils and lipid-containing foods.

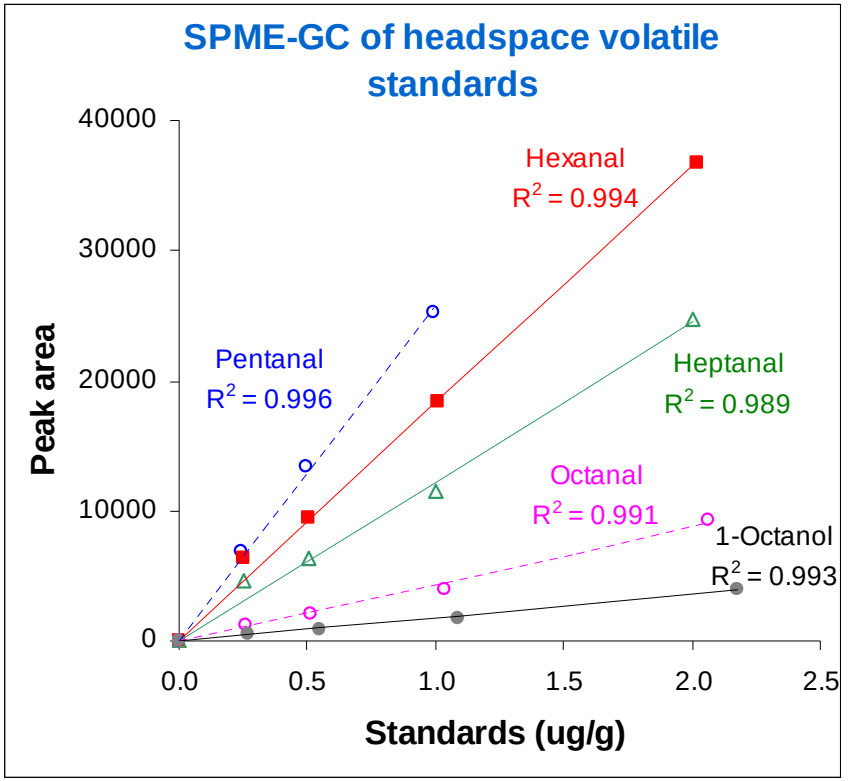
	Macadamia oil	Olive oil
Palmitic (c16:0)	7	9
Stearic (C18:0)	2-4	3.6
Palmitoleic (C16:1)	15.5	2.4
Oleic (C18:1)	65	80
Linoleic (C18:2)	1.5	5
Linolenic (C18:3)	0.1-0.2	0.5

Methods monitoring rancidity development

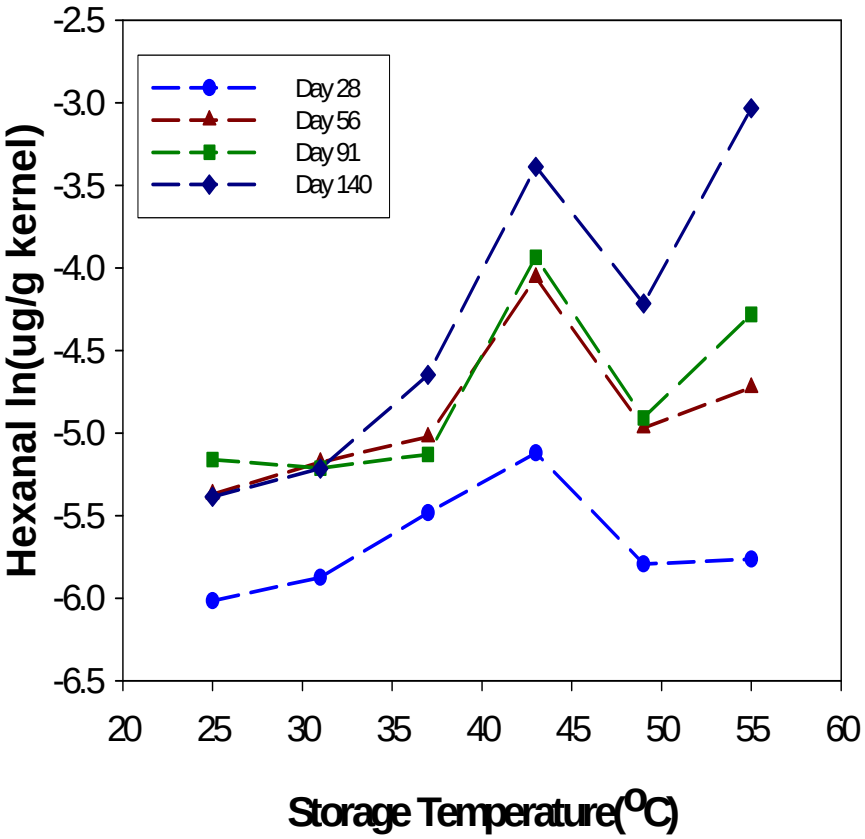
- For initial (primary) oxidation products – hydroperoxides
  - Conjugated dienes (CDHP)
  - Peroxide Value (PV)
  - Chromatography
- For secondary oxidation products – carbonyl compounds
  - *p*-Anisidine Value (*p*AV)
  - Conjugated trienes
  - TBA or TBARS (Thiobarbituric acid reactive substances)
- Free fatty acids (FFA)
- For volatiles attributing to the off-flavour
  - GC, GC-MS: specific and total volatiles
  - HPLC, HPLC/MS
  - Sensory

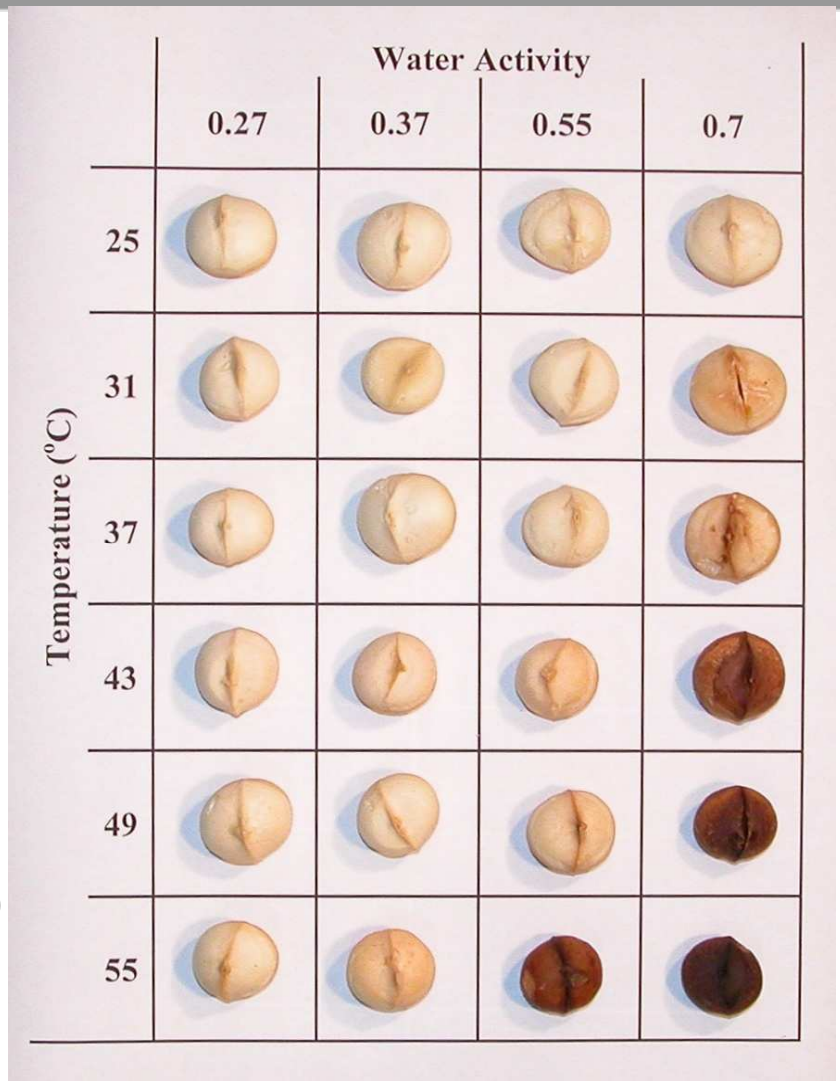
Volatiles

- Cause rancid flavour at ppm levels
- Closely correlated with sensory and consumer acceptability
- Major volatiles contributing to rancid flavour
  - Hexanal: from C18:2 (1.5%)
  - Octanal: from C18:1 (65%)
- Measured on GC or GC/MS
  - Solid-phase micro-extraction (SPME)-GC: simple, sensitive, quantitative
  - Linear response for major volatiles contributing to rancidity



Effects of storage temperature and duration on hexanal production (Salter et al 2005)

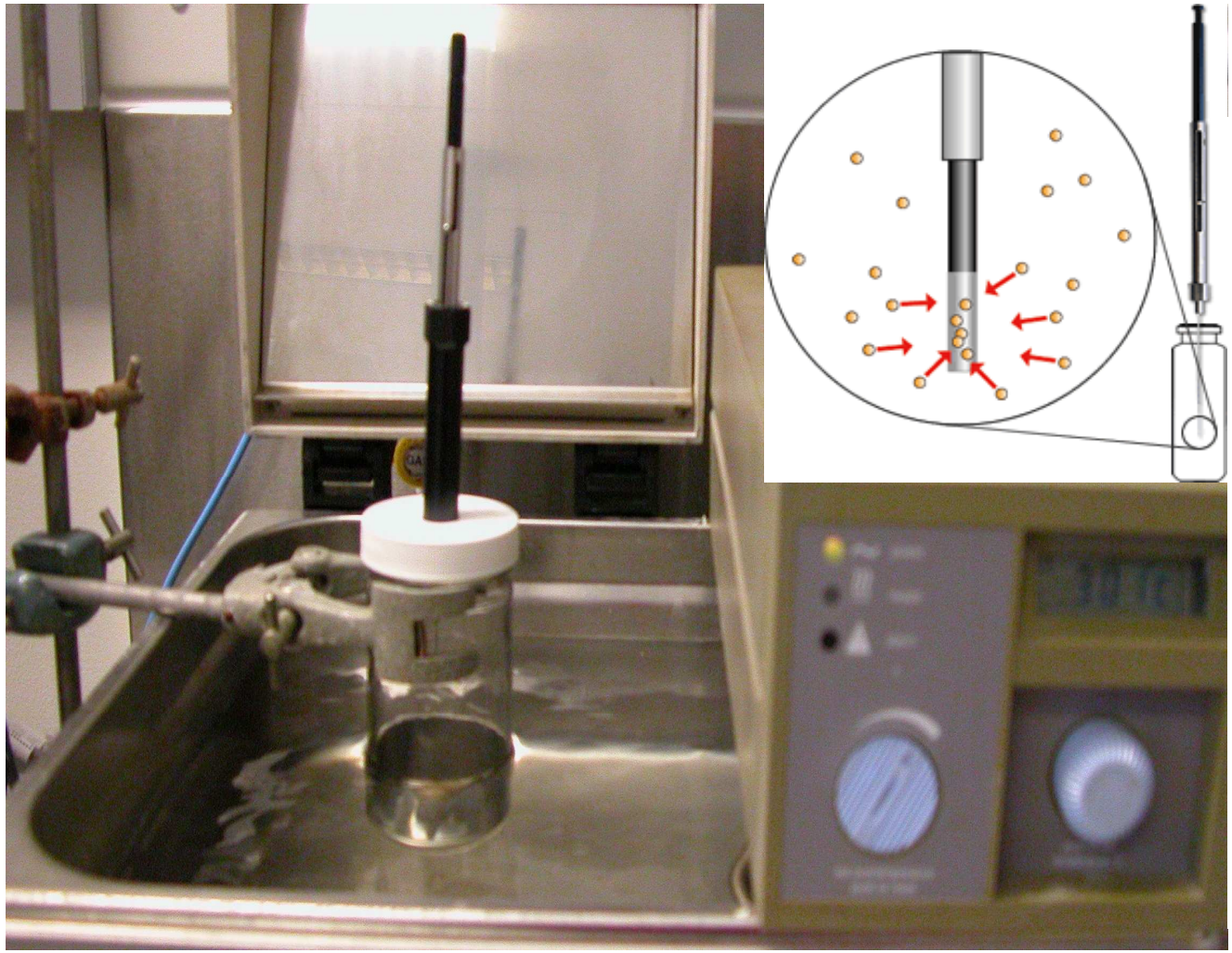


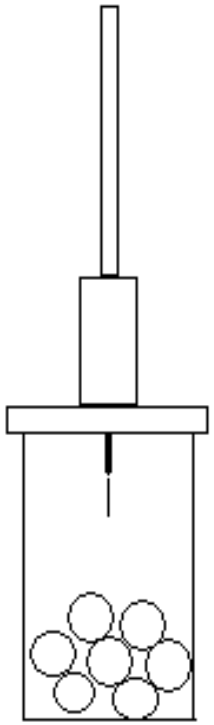


Accelerated Aging Trial

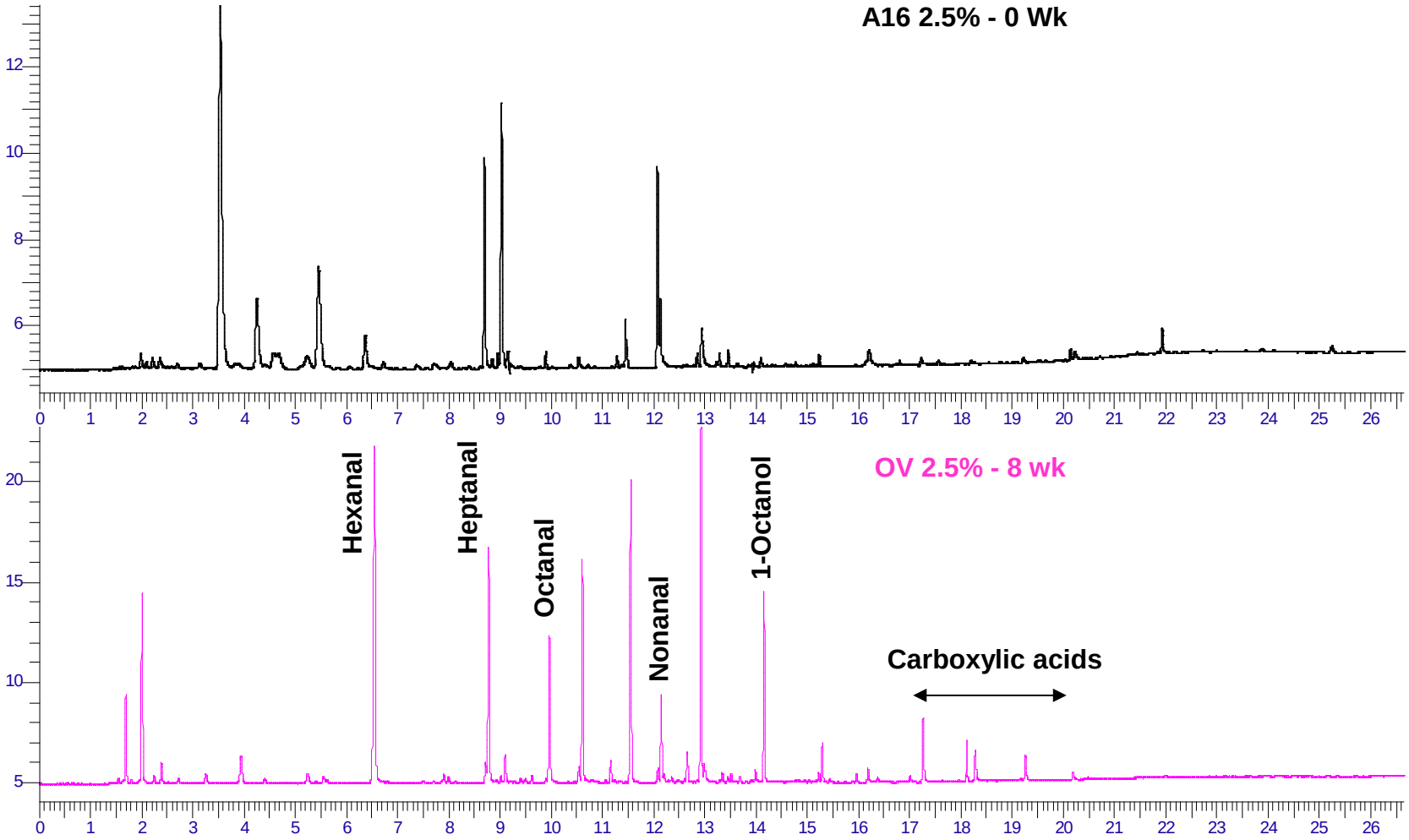
- Determine rancidity development in
  - raw and roasted kernels stored at 40 or 22^{o}C
  - 3 roasting regimes (temperature/duration)
  - 2 moisture content (1.5 and 2.5%)
  - 2 cultivars (A16 and OV)
- Rancidity determined during storage using SPME headspace volatiles from whole kernels
  - Septum jars with kernels warmed in 30^{o}C water bath for 5 min
  - SPME fibre (PDMS/DVB, 65 µm) exposed to sample for 20 min
  - Fibre then desorbed at 220^{o}C in injector port for 3 min (splitless)
  - Column: SGE BP20 (30 m x 0.25 mmm ID x 0.25 µm film)
  - Oven program: 40^{o}C 5 min → 12C/min to 240^{o}C → 240^{o}C 5 min
  - Detector: flame ionisation detector (FID), 280^{o}C

Headspace volatiles – SPME for GC

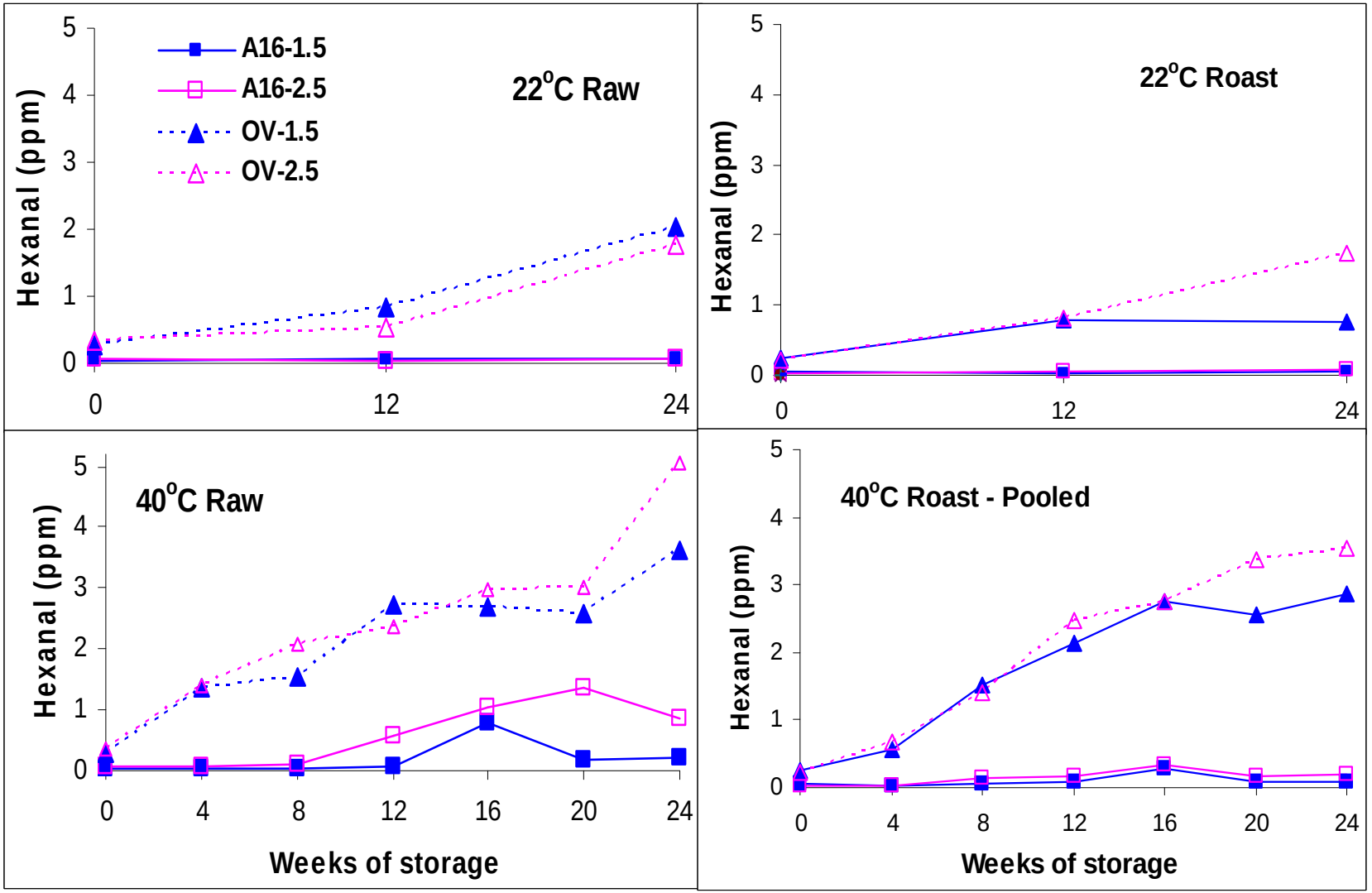




Headspace volatile profile in raw kernels stored at 40°C



Hexanal in raw and roasted kernels stored for 24 weeks



Results

- Higher hexanal levels in OV than A16 at the beginning.
- At 22^{o}C
  - negligible change in hexanal levels in A16
  - progressively higher level of hexanal detected in OV.
- At 40^{o}C, hexanal levels
  - increased rapidly in OV within 4-8 weeks and continue to increase until 24 weeks
  - stable in A16 until after 8 weeks when started to increase.
- Similar differences and trends between cultivars and moisture contents for roasted kernels, with slower increase in hexanal production in OV.

Summary

- Kernels with poor initial storage properties deteriorates more rapidly.
- Roasting has minimal effects on the rate of deterioration.
- Similar ranking of deterioration for kernel source and treatments at ambient and accelerated storage conditions.
- Head-space hexanal levels determined using SPME-GC
  - responsive to the aging treatments
  - sensitive method for monitoring rancidity development
  - application as sensitive indicators of kernel stability under accelerated aging treatments
- Further research proposed to relate head-space hexanal levels to consumer perceptions of kernel quality.