RECOVERY AND ISOMERIZATION OF CAROTENOIDS FROM TOMATO PROCESSING BY-PRODUCTS

Irini Strati and Vassiliki Oreopoulou

Food Chemistry and Technology Laboratory
School of Chemical Engineering
National Technical University of Athens

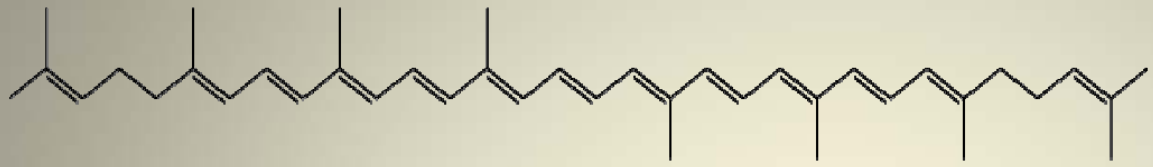
TOMATO PROCESSING BY-PRODUCTS

- Total quantity of industrial tomatoes used by Greek tomato processing industry: 470,000 tonnes (2014 data)
- Approximately 5-10% of the raw material is removed as industrial waste, consisting mainly of skins and seeds (23,5-47x10^3 tonnes of byproducts)
- Industrial waste is intended for animal feed or fertilizer without any further valorization

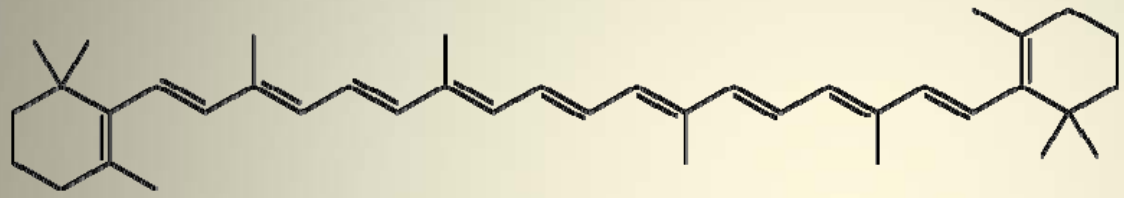
Bioactive phytochemicals in industrial tomato processing byproducts (mg / kg dw)

Compounds	Al-Wandawi et al., 1985		Knoblich et al., 2005		Riggi & Avola,2008	Kalogeropoulos et al., 2012	Shao et al., 2013
	Skins	Seeds	Skins	Seeds			
Carotenoids							
lycopene	119.8	0.4	734.0	130.0	20.5-75.7	413.7	98.2-172.1
b-carotene	3.0	1.4	29.3	14.4	4.1-12.0	149.8	
lutein			14.5	6.5			
zeaxanthin			3.7	1.0			
a-carotene			0	0.4			
cis-b-carotene			11.7	5.6			
Tocopherols						177.93	
Sterols						833.5	
Terpenes						312.2	
Simple polyphenols						517.5	

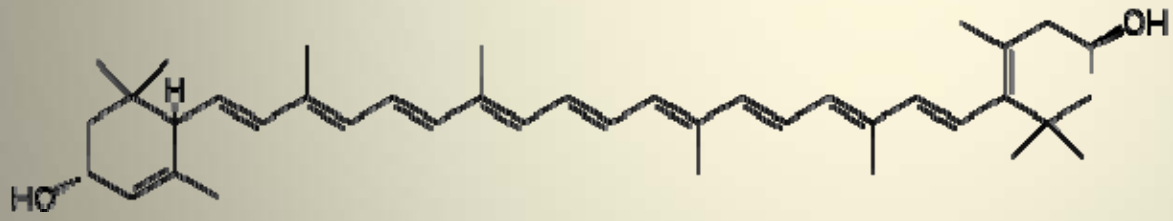
Tomato carotenoids



lycopene



b-carotene

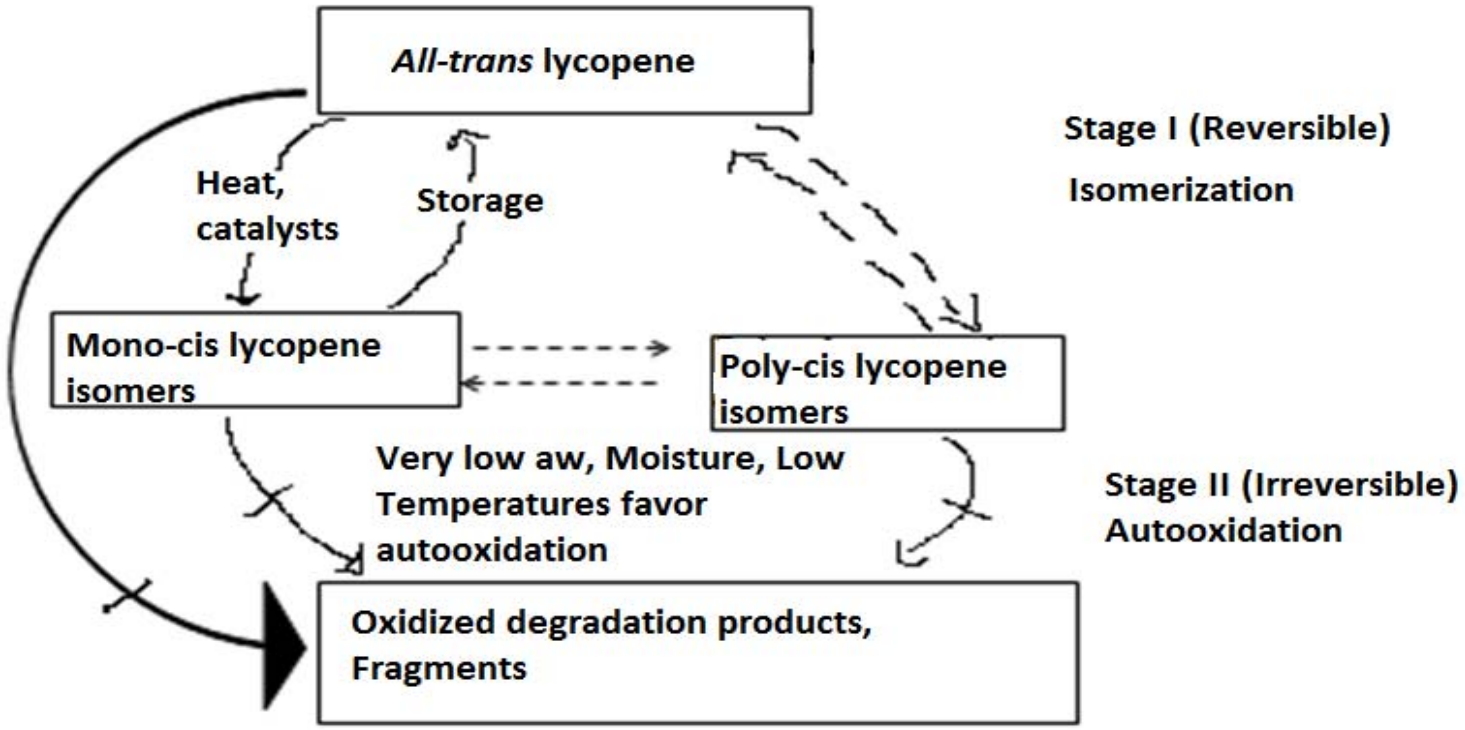


lutein

Uses:

- natural pigments
- additives for functional foods
- natural antioxidants

Isomerization



Proposed reaction pathway (Boskovic, 1979)

About 94-96 % of total lycopene in tomato fruit

⟹ *all-trans* configuration

Processing ⟹ formation of *cis*-isomers

Cis-isomers

- susceptible to oxidation
- may present lower bioactivity than *all-trans* isomers

However, *cis*-lycopene isomers are considered to be more bioavailable than the *all-trans* isomer

Methods of recovery for carotenoids

➢ Organic Solvent extraction

Combined action assisted by:

- Enzymes
- Ultrasound
- Microwaves
- Extraction at High Pressure
  - ✓ Pressurized Liquid Extraction
  - ✓High Hydrostatic Pressure Extraction

➢ Supercritical Fluid Extraction (CO_2)

Advantages:

- High selectivity
- Environmentally safe technology
- Use of non toxic organic solvents

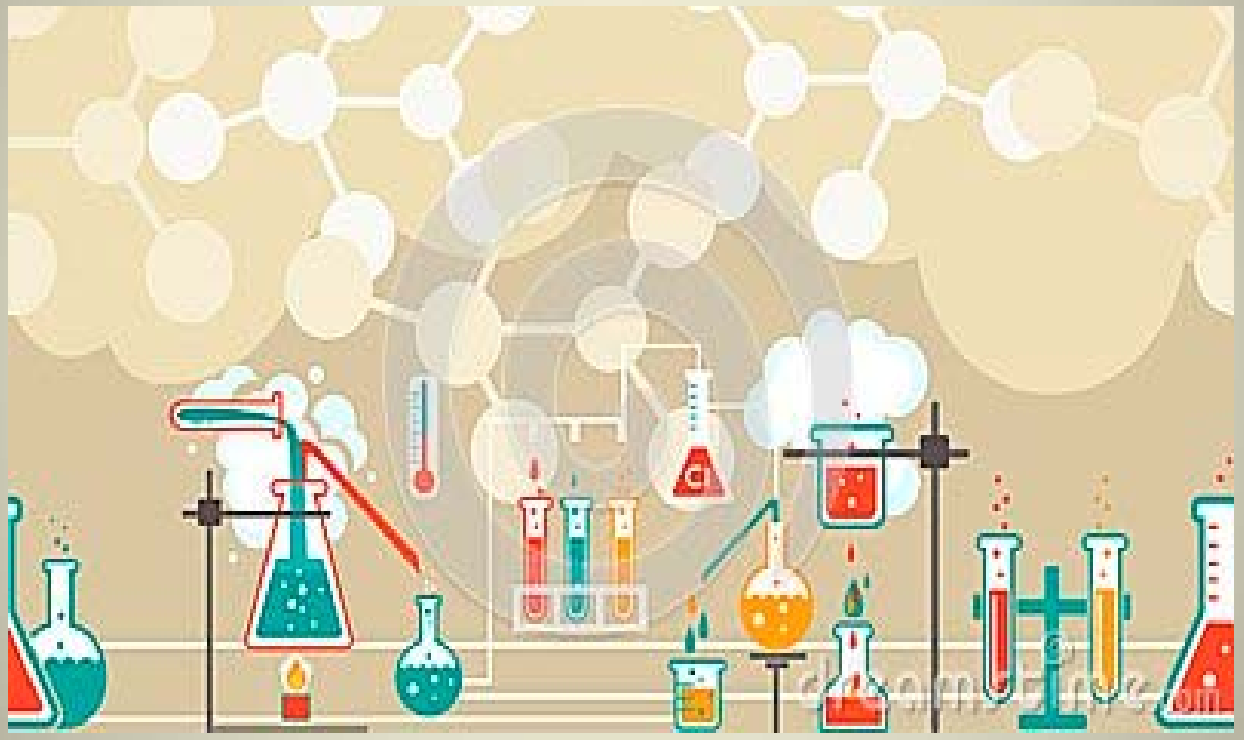
Disadvantage: High investment cost

Objectives of the study

- Examine the extraction efficiency and degree of isomerization of carotenoids from tomato processing by-products after organic solvent extraction

- Explore the stability of carotenoids (lycopene), when tomato processing by-products are subjected to various drying and storage conditions before extraction for carotenoid recovery

Experimental part



Raw material handling

- Tomato processing by-products
  - Storage at -20°C 60 days
  - Freeze drying at -55 °C
  - Vacuum oven drying at 70 °C
  - Drying in air circulation oven at 70 °C
    - Milling 0.5 mm
    - Extraction / Analysis
  - Air drying in open space at 25-30 °C

Organic Solvent Extraction

- **Solvents:** hexane, ethanol, acetone, ethyl acetate, ethyl lactate and solvent mixtures
- **Extraction time:** 30 min
- **Extraction temperature:** 25 °C - 70 °C
- **Extraction steps:** 3
- **Solvent : dry tomato by-products** = 10:1 (v/w)

(Strati and Oreopoulou, 2011)

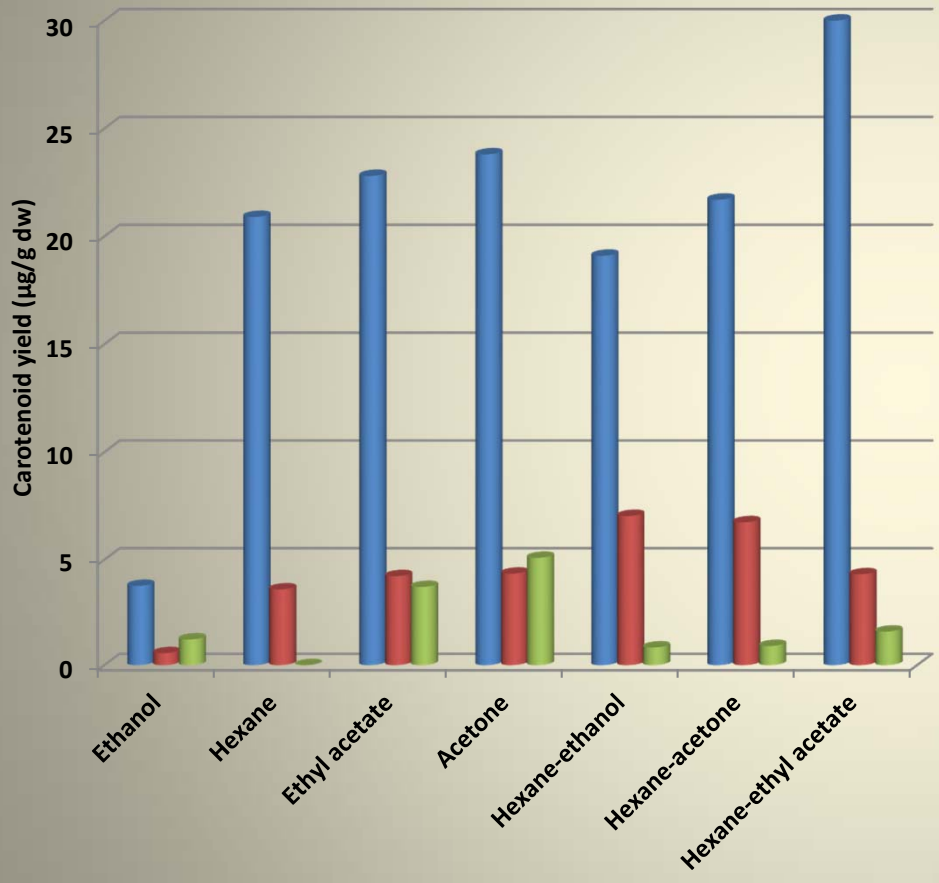
Carotenoid analysis

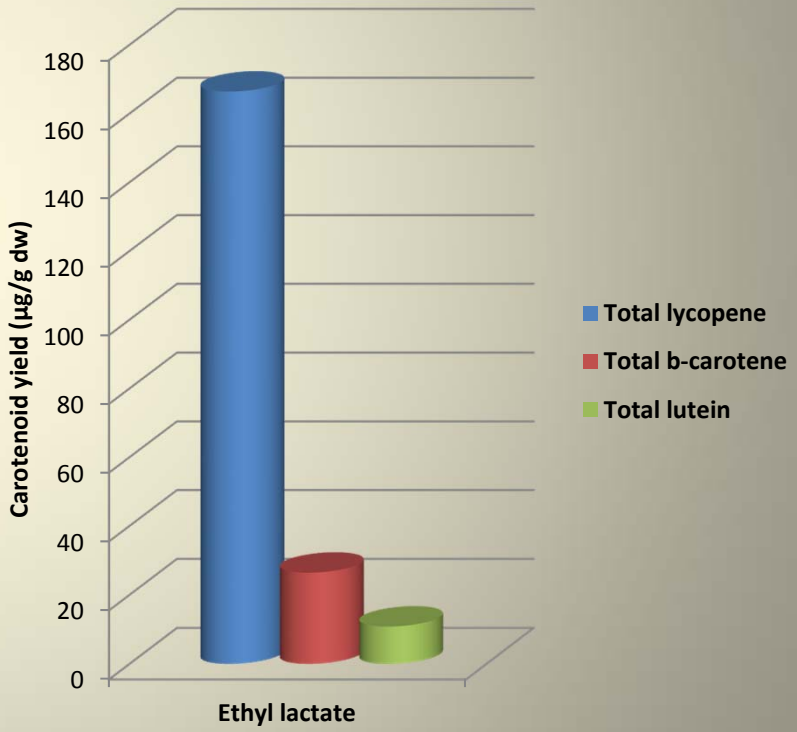
Determination of carotenoids and their cis-isomers by HPLC-DAD method

(Strati et al., 2012)


RESULTS

The effect of organic solvents on the recovery of total carotenoids



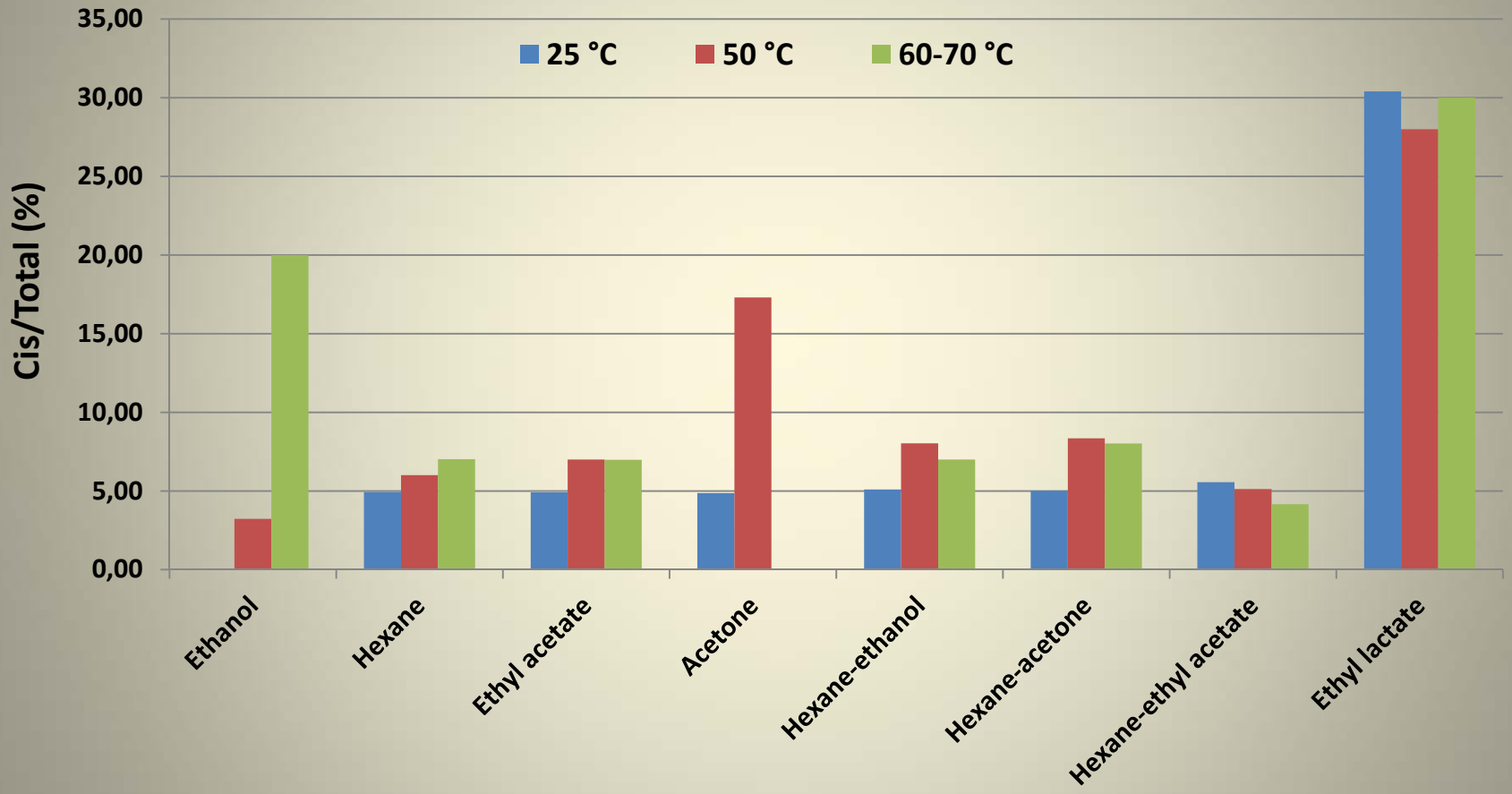


The effect of organic solvents on the isomerization of carotenoids

SOLVENTS	LYCOPENE (µg/g dw)			β-CAROTENE (µg/g dw)			LUTEIN (µg/g dw)		
	Cis-isomers	*All*-trans	Total	Cis-isomers	*All*-trans	Total	Cis-isomers	*All*-trans	Total
Ethanol	nd	3.8±0.0	3.8	nd	0.6±0.0	0.6	0.5±0.1	0.7±0.0	1.2
Hexane	1.0±0.1	19.9±0.2	20.9	0.9±0.1	2.7±0.0	3.6	nd	nd	nd
Ethyl acetate	1.1±0.2	21.7±0.2	22.8	1.1±0.3	3.2±0.5	4.3	1.6±0.2	2.1±0.0	3.7
Acetone	1.2±0.1	22.6±0.3	23.8	1.4±0.3	2.9±0.1	4.3	2.3±0.3	2.8±0.0	5.1
Hexane-ethanol (50:50, v/v)	1.0±0.1	18.1±0.3	19.1	1.8±0.2	5.3±0.3	7.1	nd	0.8±0.1	0.8
Hexane-acetone (50:50, v/v)	1.1±0.2	20.6±0.2	21.7	1.6±0.3	5.1±0.2	6.7	nd	0.9±0.1	0.9
Hexane-ethyl acetate (50:50, v/v)	1.7±0.2	28.5±0.3	30.2	1.1±0.2	3.2±0.2	4.3	0.7±0.0	0.9±0.1	1.6
Ethyl lactate	50.6±0.8	115.8±1.9	166.4	8.7±0.5	17.7±0.8	26.4	4.8±0.2	6.0±0.8	10.8

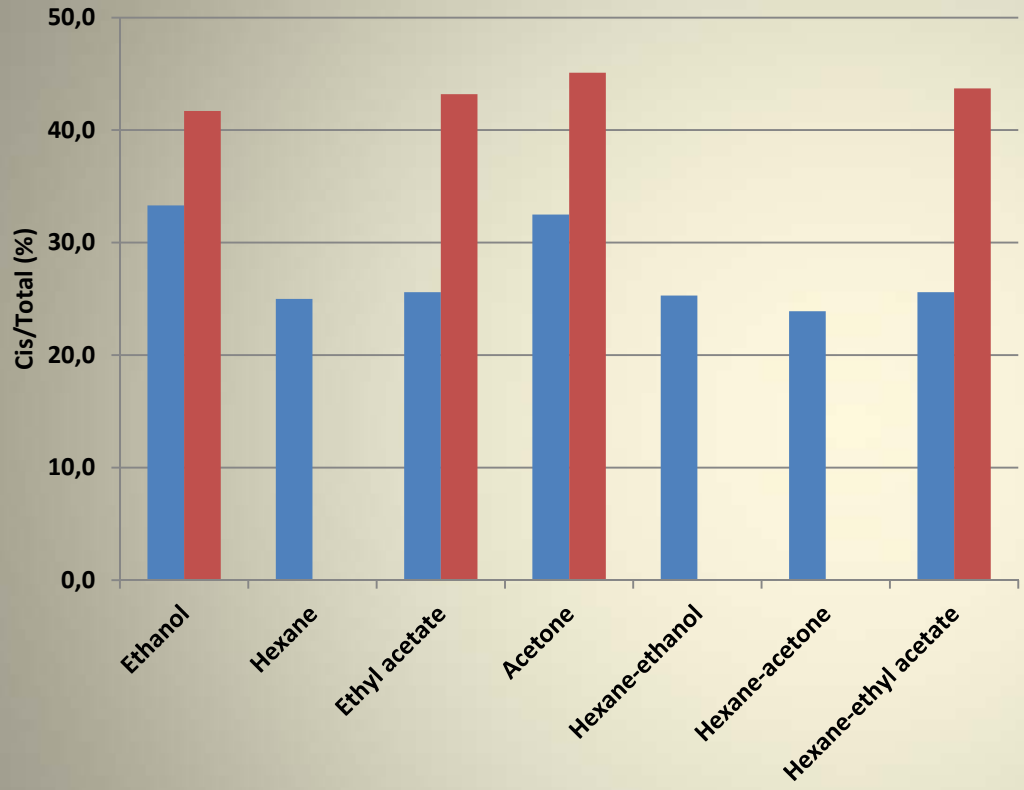
Extraction conditions: T=25 °C, solvent: dry tomato by-products=10:1 (v/w), particle size=0.5 mm, 3 extraction steps of 30 min each

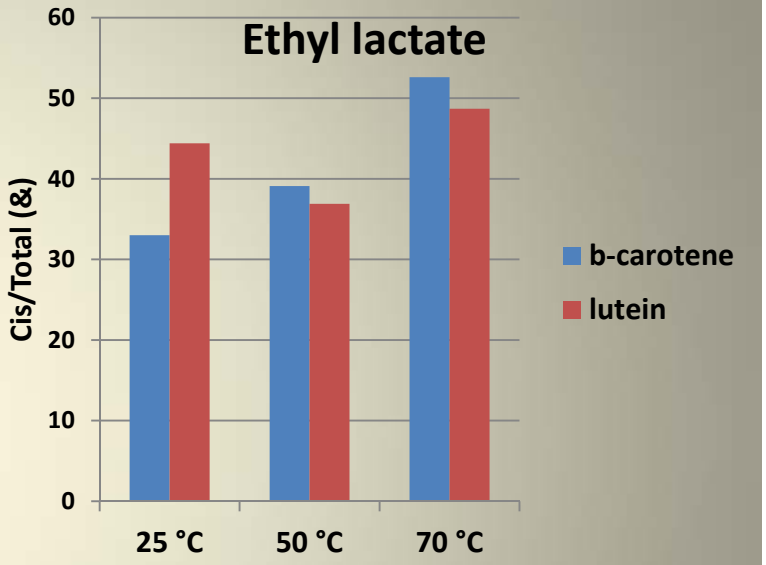
The effect of extraction temperature on the isomerization of lycopene



Extraction conditions: solvent: dry tomato by-products=10:1 (v/w), particle size=0.5 mm, 3 extraction steps of 30 min each

Isomerization of b-carotene and lutein





Extraction conditions: solvent: dry tomato by-products=10:1 (v/w), particle size=0.5 mm, 3 extraction steps of 30 min each

The effect of drying and storage conditions on lycopene loss and isomerization

Drying/Storage conditions	Moisture content (g /100 g ww)	Total lycopene (µg/g dw)	Lycopene loss (%)	All-trans isomers (%)	Cis-isomers (%)
Fresh tomato processing by-products	80.48±0.35	39.1±0.25	0	99.7 %	0.3 %
Air drying	5.65±0.21	30.2±0.61	22.8	94.4 %	5.6 %
Oven drying	4.86±0.19	28.8±0.52	26.3	84.4 %	15.6 %
Vacuum oven drying	4.41±0.11	32.7±0.34	16.4	91.4 %	8.6 %
Freeze drying	3.87±0.32	35.2±0.20	10.0	95.5 %	4.5 %
Storage -20°C/60 days	81.21±0.17	33.8±0.17	13.5	97.6 %	2.4 %

Extraction conditions: hexane-ethyl acetate mixture (50:50, v/v), T=25 °C, solvent: tomato by-products =10:1 (v/w), particle size=0.5 mm, 3 extraction steps 30 min each

Conclusions

- The *all-trans* configuration of lycopene, *b*-carotene, and lutein predominated in all solvent extracts

- The yield and isomerization of carotenoids was affected by the extraction solvent

- The use of non polar or medium-polarity solvents for the extraction of carotenoids resulted in limited isomerization, even at relatively high extraction temperatures

- Ethyl lactate affected significantly the isomerization of lycopene (30.4 %), *b*-carotene (33.0 %) and lutein (44.4 %)

- Considerable isomerization of *b*-carotene and lutein during extraction at 25 °C; however, increase of temperature caused degradation of *cis*-isomers

Conclusions

- Carotenoids recovered from fresh tomato processing by-products are maintained relatively stable after industrial processing treatments

- The drying method affected significantly lycopene isomerization, with the following order:

  freeze-drying (4.5 % *cis*-isomers)
  < air drying (5.6 % *cis*-isomers)
  < vacuum drying (8.6 % *cis*-isomers)
  < oven drying (15.6 % *cis*-isomers)

- Significant loss of carotenoids after the different drying methods and after storage of tomato processing by-products at -20 °C for 60 days

- **Suggestions:** Direct extraction of carotenoids from tomato processing by-products in situ or drying at low temperatures in the absence of air

Thank you very much for your attention !