

Aroma compounds of coloured carrots (*Daucus carota* L. ssp. *sativus* Hoffm.)

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Summary

Seven carrot varieties with different colours, orange, white, purple with orange core, purple, yellow, and red, were examined for their content of essential oils, oil components and sugars as aromarelevant compounds. Influence of high global radiation during growing period on total amount of essential oil could be demonstrated except for the red cultivar. White, red and yellow carrots contained the highest amounts of essential oil. The quantitative composition of essential oils differed not only between orange cultivars but also between new coloured ones. The results were discussed with regard to antioxidative capacity of selected oil components. Sucrose was the dominant sugar, also in white, purple, yellow and red carrots. New coloured cultivars were recommended to increase vegetable consumption.

Introduction

The carrot (*Daucus carota* ssp. *sativus*) is an relatively important vegetable, consumed fresh or prepared, not only in Germany but also worldwide. In 2004, carrots were cultivated on 1,076,909 ha totally in the world (9,100 ha in Germany) with 23,607,214 t (420,000 t in Germany; FAO, 2005). Nutritional value is based for example on vitamins (β -carotene), dietary fibre and minerals. And consumers are interested in a pleasant flavour and attractive colour.

Besides organic acids and other non-volatile chemical constituents, sugars and volatiles are responsible for the characteristic flavour. The essential oil is mainly composed by mono- and sesquiterpenes (HABEGGER et al., 1996; HABEGGER and SCHNITZLER, 2000; SIMON et al., 1982; SIMON, 1982a; SIMON, 1982b; SIMON et al., 1980).

In general, for raising the consumption of vegetables new colours of known vegetables, as a part of diversification, may play an important role. Recent developments in carrot breeding present new root colours. These are mainly traced back to origin species. Carrots were first described in the 10th century in Afghanistan with purple and yellow colours. Probably white coloured carrots resulted from cross-breeding of the Mediterranean carrot (ssp. *maximus*) with the Central European wild carrot (ssp. *carota*). During the 16th to 18th centuries yellow carrots were the most frequent cultivation and consumption form in Central Europe. The orange-coloured cultivars, rich in β -carotene, were developed end of 17th century in the Netherlands (KÖRBER-GROHNE, 1987). A variety with red roots has long tradition in China and Japan (KOST, 2003).

The objective of this study is the comparison of new coloured with orange-coloured cultivars for the composition of essential oils and sugars as the most important aroma compounds. The results are discussed with regard to possible antioxidative capacity of selected oil components.

Materials and methods

In 2003 and 2004 seven different coloured carrots were cultivated in a research field of the Chair of Vegetable Science – Quality of Vegetal

Foodstuff at Dürnast, State of Bavaria, Germany according to good agricultural practice: 'Napoli' F₁ (orange; bejo), 'White Satin' F₁ (white; bejo), 'Purple Haze' F₁ (purple with orange core; bejo), 'bejo 01-0102' (purple; bejo), 'Mello Yello' F₁ (yellow; bejo), 'Nutri Red' (red, Seminis) and 'Boloro' F₁ (orange, Nickerson Zwaan). Climate of 2003 was characterized by higher temperature and higher global radiation compared with 2004 (Tab. 1).

Tab. 1: Climate parameters during cultivation period

month	Average daily temperature (°C)	
	2003	2004
March	4.9	2.7
April	8.3	9.2
May	14.9	11.0
June	20.5	15.4
July	18.6	17.1
August	21.3	18.3

sum of global radiation from April to August in 2003 882,880 Wh/m²
sum of global radiation from April to August in 2004 804,750 Wh/m²

Carrots were harvested at optimal ripening stage. After washing roots were sorted according to European Union external quality standard; a representative sample was taken and deepfrozen. At analysis date the deepfrozen material was crushed and mixed. The essential oils were extracted by simultaneous steam distillation and pentane extraction (SDE, Likens-Nickerson-apparatus). Octanol was added as internal standard and in order to prevent foaming. The amount of essential oil was determined gravimetrically. Separation of components was carried out by HRGC (Fisons Instruments Mega 5360) on a Supelco-Wax capillary column (60 m, i.d. 0.32 mm, f.d. 0.25 μ m) with He as carrier gas (0.8 ml/min) and a temperature programme: 50 °C (3 min), 10 °C min⁻¹, 120 °C (2 min), 2 °C min⁻¹, 155 °C (0 min), 8 °C min⁻¹, 240 °C. The essential oil was diluted by acetone (pa), the sample amount was 1 μ l, split 1:50. The separated components received the same number for all chromatograms. Analyses were done with 5 replications.

The mass spectra were collected by GC-MS (quadrupole mass spectrometer HP 5971 A) on the same column and with the same temperature programme. Data were evaluated by comparison with retention time and mass spectra (ANDERSEN and FALCONE, 1969; WILEY, 1990; ADAMS, 1989; JENNINGS and SHIBAMOTO, 1980) and with commercially obtained standards. Trans- γ -bisabolene (m/z 93, 107, 119, 135) was tentatively identified.

Sabinene, β -myrcene, α -terpinene, γ -terpinene and β -ionone (Carl Roth GmbH), R-(+)-limonene and terpinolene (Fluka Chemie) were quantified using multipoint external standard calibration curves under identical chromatographic conditions. Quantitation was performed using peak area. For interpretation of the other components, peak areas were calculated into relative substance amounts by using the internal standard.

Sugar was analysed in four replications from frozen-dried and ground carrot powder by HPLC after extraction by methanol and filtering (PB column 300 mm x 7,8 mm Phenomenex Rezex RPM Mono-saccharid; column temperature 85 °C; distilled water as eluent with a flow of 0,6 ml min⁻¹; injection volume 20 µl; refractive index detector Varian RI 4). Sucrose, glucose and fructose were quantified on the basis of peak areas and comparison with a calibration curve obtained by the corresponding standards.

Analysis of variance was calculated by SAS, multiple mean comparison by Tukey-Test at 95 % probability.

Results

Total amount of essential oil

In 2003 and 2004 the total amounts of essential oil in roots of 'Nutri Red' and 'White Satin' were significantly higher than in roots of orange coloured cultivars. Independently of the cultivation year, the purple cultivars 'bejo 01-0102' and 'Purple Haze' had significantly lower amounts of essential oil than the new white, yellow and red carrots. Every year 'Napoli' produced higher amounts of essential oil than 'Bolero'. In 2003 with higher global radiation, the climate had an increasing effect on oil production, except for 'Nutri Red' and 'bejo 01-0102' (Fig. 1).

Composition of essential oils

The essential oil of carrot roots consists mainly of mono- and sesquiterpenes, alcohols and aldehydes (HERRMANN, 1995). About 400 components were detected in root oils, about 110 were positively and

tentatively identified. The composition of essential oils of the different coloured cultivars was qualitatively nearly the same. But there were some important differences in quantitative manner (Fig. 2).

'Napoli' and 'Bolero' represented orange coloured cultivars with β -caryophyllene, terpinolene and sabinene as dominant substances in the essential oil. The same major components were analysed in 'White Satin'. The purple coloured carrots, 'Purple Haze' and 'bejo 01-0102', and 'Nutri Red' had significantly lower levels of sabinene (Tab. 2). Terpinolene was the major component in essential oils of purple, yellow and red carrots; followed by *trans*- γ -bisabolene, β -myrcene and γ -terpinene in 'bejo 01-0102', sabinene and *trans*- γ -bisabolene in 'Mello Yello' and α -pinene, γ -terpinene, β -pinene and *trans*- γ -bisabolene in 'Nutri Red'.

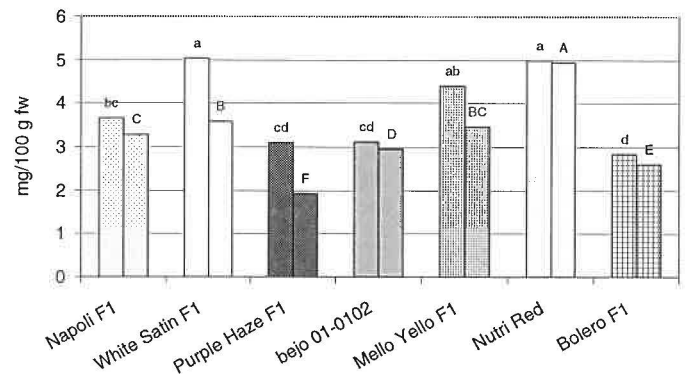


Fig. 1: Total amount of essential oil in different carrot cultivars in two years (2003 column left; 2004 column right)

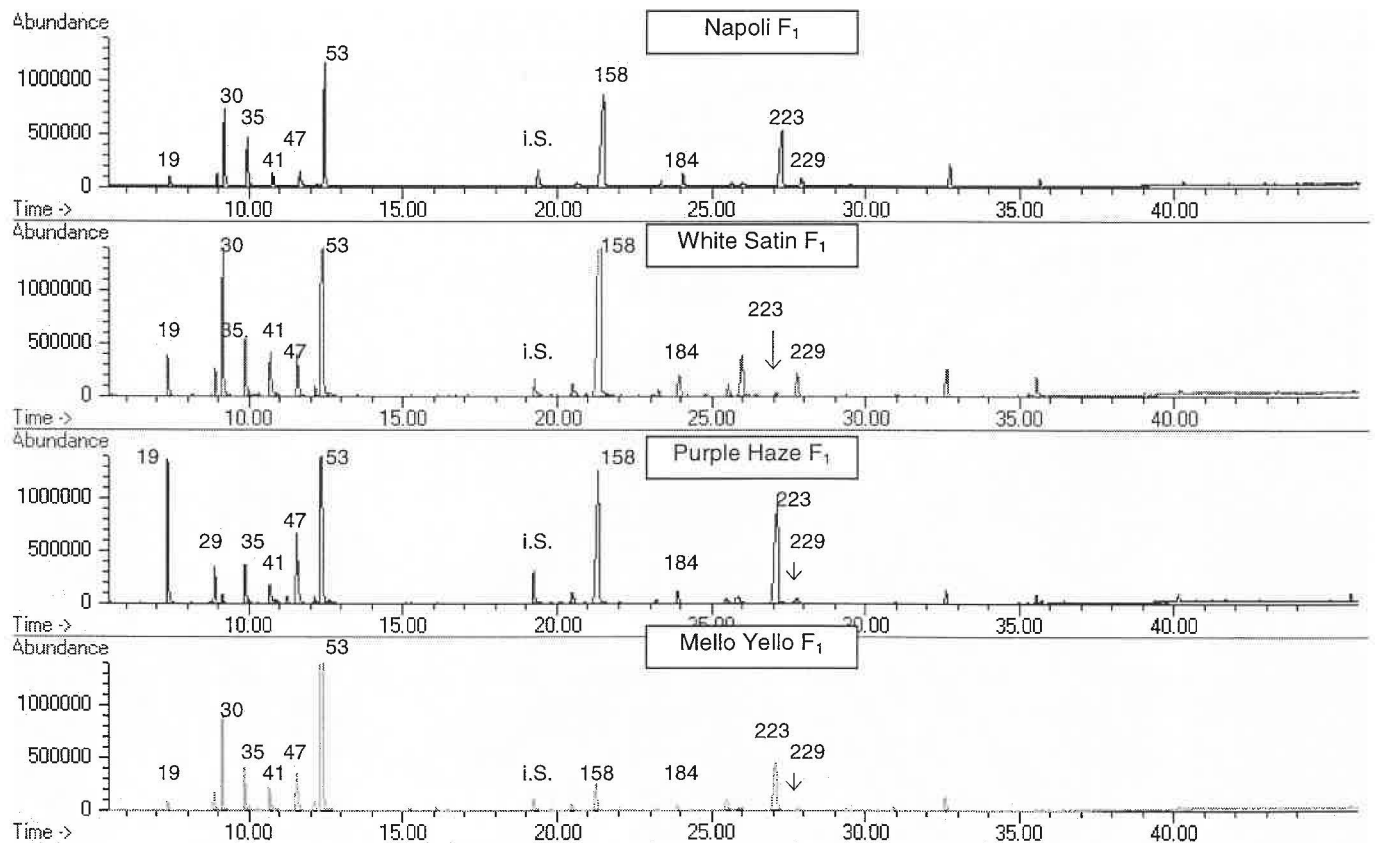


Fig. 2: GC-MS-Total ion chromatograms of selected carrot cultivars (peak numbers see Tab. 2 and 3)

Tab. 2: Levels of compounds in essential oil of different carrot cultivars (mg/100 g fw)

2003								
peak	compound	Napoli F ₁	White Satin F ₁	Purple Haze F ₁	bejo 01-0102	Mello Yello F ₁	Nutri Red	Bolero F ₁
30	sabinene	0.328 c*	0.629 a	0.020 e	0.002 e	0.423 b	0.007 e	0.106 d
35	β-myrcene	0.71 a	0.226 b	0.098 d	0.142 c	0.209 b	0.065 de	0.059 e
37	α-terpinene	0.006 b	0.012 a	0.002 c	0.002 c	0.011 a	0.003 c	0.003 c
41	limonene	0.072 cd	0.155 a	0.052 e	0.086 bc	0.076 c	0.099 b	0.054 de
47	γ-terpinene	0.060 d	0.105 c	0.104 c	0.146 b	0.192 b	0.225 a	0.066 cd
53	terpinolene	0.743 c	0.685 c	0.615 c	0.589 c	1.379 b	1.688 a	0.741 c
293	β-ionone	0.00068 b	nd	0.00014 d	nd	nd	0.00121 a	0.00048 c
2004								
peak	compound	Napoli F ₁	White Satin F ₁	Purple Haze F ₁	bejo 01-0102	Mello Yello F ₁	Nutri Red	Bolero F ₁
30	sabinene	0.327 a*	0.352 a	0.012 c	0.001 c	0.332 a	0.008 c	0.068 b
35	β-myrcene	0.217 a	0.157 c	0.070 e	0.116 d	0.183 b	0.074 e	0.057 e
37	α-terpinene	0.004 c	0.006 b	0.001 e	0.001 e	0.007 a	0.004 c	0.002 d
41	limonene	0.070 d	0.130 b	0.036 f	0.061 de	0.107 c	0.142 a	0.053 e
47	γ-terpinene	0.063 d	0.105 c	0.096 c	0.074 d	0.147 b	0.280 a	0.060 d
53	terpinolene	0.643 d	0.851 c	0.309 f	0.445 e	1.515 b	1.814 a	0.599 d
293	β-ionone	0.00025 c	tr	0.00027 c	nd	tr	0.00167 a	0.00102 b

* Means with same letters in a line are not significantly different, Tukey-Test (p = 0.05)

nd not detected

tr trace, peak area not integrated

Myristicin was not detected in essential oils of 'Napoli' and 'White Satin' in both years. But relative high amounts were found in the oil of 'Nutri Red' (Tab. 3). The essential oil of 'bejo 01-0102' did not contain any β-ionone.

Results of external quantification of oil components are documented in Tab. 2. In both years the essential oil of 'Nutri Red' had the highest levels of terpinolene; also 'Mello Yello' had significantly higher amounts of terpinolene compared with the other cultivars. In comparison with orange, white and two-coloured cultivars 'Nutri Red' and 'Mello Yello' had significantly higher levels of γ-terpinene. On the other hand, 'Napoli' had the highest content of β-myrcene in the essential oil. White and yellow carrots had significantly higher levels of this monoterpene in the essential oils compared with the other cultivars. The entire full purple carrots had significantly higher amounts of β-myrcene in the essential oil than the two-coloured one. The limonene levels of the analysed cultivars ranged from 0,052 - 0,155 mg (in 2003) and 0,036 - 0,142 mg (in 2004) in the essential oil of 100 g fw. 'White Satin' and 'Nutri Red' had the highest amounts in both years, whereas 'Purple Haze' and 'Bolero' were the cultivars with the lowest levels. 'Mello Yello' and 'White Satin' were the cultivars with highest levels of α-terpinene in the essential root oils, whereas both purple coloured carrots had the lowest amounts of this monoterpene.

Results of relative quantification of oil components are documented in Tab. 3. In both years the highest relative amounts of α-pinene and β-pinene were detected in the essential oil of 'Nutri Red'. Also, 'White Satin' and 'Purple Haze' had significantly higher relative amounts of α-pinene compared with the other cultivars. The purple coloured carrots had similar to 'Bolero' significantly low relative amounts of β-phellandrene in the essential root oils. The highest relative amounts of p-cymene were found in the essential oils of 'Mello Yello' and 'Nutri Red', followed by 'White Satin'.

Terpinene-4-ol could not be separated from β-caryophyllene by GC-FID, but detected by GC-MS, it was only a small shoulder of the β-caryophyllene peak. Therefore, calculations and statistical procedures were carried out for the sum of these two components. But the

following interpretations were valid only for β-caryophyllene. The significantly highest amount was analysed in the essential oil of 'White Satin'. The other new coloured cultivars had the lowest levels of this sesquiterpene. 'Purple Haze' had higher levels compared with 'bejo 01-0102'.

The relative amounts of β-Z-farnesene were significantly the highest in essential oil of 'Nutri Red'. Compared with the purple coloured cultivars, the levels of this compound was significantly higher in essential oil of 'White Satin'. The α-humulene and another sesquiterpene (K229, not identified) were in significantly highest amounts in the essential oil of 'White Satin', whereas 'Nutri Red' and 'bejo 01-0102' had the lowest levels. The highest relative amounts of D-germacrene were analysed in the essential oils of 'White Satin' and 'Mello Yello'. The relative amounts of zingiberene were significantly higher in the essential oils of 'Mello Yello' and 'Nutri Red' than in the other cultivars. In every year this sesquiterpene was significantly higher in the oil of 'Napoli' and 'Purple Haze' than in that of 'White Satin', 'bejo 01-0102' and 'Bolero'. In the essential oil of 'Nutri Red' there was the highest relative amount of β-bisabolene and trans-γ-bisabolene.

Sugar content

Tab. 4 shows the content of the three sugar fractions. Sucrose was the predominant sugar in carrots. 'Purple Haze', 'Nutri Red' and 'Bolero' had the highest amount of sucrose, independent of season. On the other hand, the levels of glucose and fructose of these cultivars and the purple 'bejo 01-0102' were significantly lower compared with the other cultivars.

Discussion

The purpose of this study was to analyse the most important aroma relevant components, essential oils and sugars, of new coloured carrot cultivars. For orange cultivars it is well known that these substances

Tab. 3: Relative amounts of compounds in essential oil of different carrot cultivars (rsm)

2003

peak	compound	Napoli F ₁	White Satin F ₁	Purple Haze F ₁	bejo 01-0102	Mello Yello F ₁	Nutri Red	Bolero F ₁
19	α -pinene	60.4 c*	161.4 b	209.7 b	9.9 c	28.4 c	304.0 a	21.6 c
29	β -pinene	47.9 cd	115.8 b	49.3 cd	16.7 cd	64.2 c	265.9 a	7.34 d
36	α -phellandrene	4.59 cd	7.23 bc	3.64 d	2.49 d	9.50 b	16.25 a	3.24 d
42	β -phellandrene	5.06 b	7.83 a	2.29 c	1.65 c	5.35 b	8.23 a	1.25 c
52	p-cymene	8.10 c	21.93 b	7.73 c	11.39 c	33.51 a	38.20 a	6.23 c
150	bornyl acetate	13.75 d	31.59 b	7.50 ef	22.20 c	9.56 de	52.93 a	2.97 f
158 + 157	β -caryophyllene + terpinene-4-ol	426.5 b	1451.2 a	275.5 c	83.5 d	129.6 d	103.4 d	343.1 bc
175	β -Z-farnesene	5.78 cd	14.47 b	2.55 d	9.64 c	4.46 d	42.93 a	3.00 d
184	α -humulene	29.47 b	96.44 a	18.62 cd	10.81 de	25.17 bc	7.51 e	22.86 bc
199	D-germacrene	7.17 b	24.59 a	4.22 bc	6.84 b	26.27 a	1.68 c	1.26 c
200	zingiberene	1.22 d	0.99 de	2.03 c	0.78 de	4.12 b	5.01 a	0.35 e
203	β -bisabolene	7.09 de	17.35 b	11.95 c	7.73 cde	11.60 cd	38.98 a	4.70 e
223	trans- γ -bisabolene (tentatively)	151.6 d	9.0 f	248.2 c	78.4 e	340.8 b	537.0 a	45.2 ef
229	sesquiterpene (not identified)	14.64 b	84.50 a	13.67 bcd	0.48 e	2.49 cde	2.15 de	14.37 bc
395	α -bisabolol	3.45 d	7.43 b	5.20 c	2.42 d	8.51 a	6.97 b	0.90 e
415	myristicin	nd	nd	3.97 c	5.28 c	17.97 b	93.84 a	5.59 c

* Means with same letters in a line are not significantly different, Tukey-Test (p = 0.05)

nd not detected

2004

peak	compound	Napoli F ₁	White Satin F ₁	Purple Haze F ₁	bejo 01-0102	Mello Yello F ₁	Nutri Red	Bolero F ₁
19	α -pinene	39.1 c	92.1 b	111.2 b	5.1 e	31.2 cd	273.1 a	8.9 de
29	β -pinene	61.5 c	86.2 b	30.8 d	5.4 e	70.9 c	148.7 a	8.2 e
36	α -phellandrene	5.92 d	10.97 c	1.95 e	2.42 e	14.36 b	17.53 a	3.02 e
42	β -phellandrene	6.60 b	7.29 b	2.28 c	1.51 c	6.59 b	8.46 a	1.66 c
52	p-cymene	11.09 c	23.26 b	4.46 d	7.08 d	37.02 a	36.35 a	5.89 d
150	bornyl acetate	14.55 b	36.76 a	6.67 cd	8.34 c	14.78 b	36.85 a	4.51 d
158 + 157	β -caryophyllene + terpinene-4-ol	807.8 b	1386.6 a	217.2 d	51.9 e	133.2 de	152.4 de	330.5 c
175	β -Z-farnesene	16.14 b	16.94 b	2.46 d	4.94 c	4.32 cd	29.27 a	3.43 cd
184	α -humulene	52.31 b	91.14 a	13.85 de	8.83 e	19.65 cd	10.51 e	21.42 c
199	D-germacrene	17.25 c	38.15 b	5.66 d	4.50 de	54.60 a	1.47 de	1.14 e
200	zingiberene	2.85 b	0.83 d	2.02 c	0.99 d	4.06 a	3.91 a	0.25 e
203	β -bisabolene	16.91 b	11.23 c	7.64 d	6.57 de	12.28 c	22.09 a	4.75 e
223	trans- γ -bisabolene (tentatively)	377.9 b	8.4 e	228.8 c	124.9 d	354.2 b	437.2 a	34.4 e
229	sesquiterpene (not identified)	32.76 b	68.50 a	6.41 d	0.40 e	1.65 de	1.91 de	14.43 c
395	α -bisabolol	5.54 b	5.73 b	3.55 d	2.12 e	6.73 a	4.34 c	0.70 f
415	myristicin	nd	nd	0.19 c	3.32 b	nd	56.32 a	0.19 c

* Means with same letters in a line are not significantly different, Tukey-Test (p = 0.05)

nd not detected

are influenced by genetic variation, to a lesser extent by climate and soil (SIMON et al., 1980; SIMON, 1982a; SIMON, 1982b; SIMON et al., 1982; HABEGGER et al., 1996; HABEGGER and SCHNITZLER, 2000). Therefore, two orange cultivars, 'Napoli' and 'Bolero', were chosen for comparison. The results showed significant differences in content of sugars, essential oils and quantitative composition of oils.

'White Satin' is most suitable for fresh consumption as attributed to the agreeable aroma (SURLLES et al., 2004). The high amount of essential oil was confirmed by static headspace analyses (ALASALVAR et al., 2001). In comparison to orange cultivars, essential oil of 'White Satin'

is characterized by higher levels of several mono- and sesquiterpenes. Fresh, fruity and carrot like attributes were described in GC-sniffing-analyses especially for α -terpinene, limonene, β -phellandrene, terpinolene, β -caryophyllene (HABEGGER et al., 1996).

The sensory attribute sweetness is influenced by sugar content, and sucrose is the predominant sugar in carrots, but high levels of terpenoids may mask the overall sweetness response (HOWARD et al. 1995; SIMON et al., 1980). 'Purple Haze' and 'Bolero' with lesser amounts of essential oil have higher sugar contents compared with 'Napoli'. Sensory evaluation by untrained panelists resulted in less

Tab. 4: Sugar content of different carrot cultivars (g/100 g fw)

2003

cultivar	sucrose	glucose	fructose
Napoli F ₁	2.126 d*	0.965 c	0.828 ab
White Satin F ₁	2.257 d	1.025 b	0.859 a
Purple Haze F ₁	3.666 b	0.249 f	0.230 d
bejo 01-0102	2.756 c	0.280 e	0.242 d
Mello Yello F ₁	1.748 e	1.138 a	0.808 b
Nutri Red	3.531 b	0.156 g	0.149 e
Bolero F ₁	4.416 a	0.364 d	0.317 c

*Means with same letters in a column are not significantly different, Tukey-Test (p = 0.05)

2004

cultivar	sucrose	glucose	fructose
Napoli F ₁	2.665 e*	0.512 c	0.399 c
White Satin F ₁	2.932 d	1.080 b	0.592 a
Purple Haze F ₁	4.153 b	0.121 e	0.059 g
bejo 01-0102	3.317 c	0.219 d	0.180 e
Mello Yello F ₁	2.110 f	1.298 a	0.526 b
Nutri Red	4.421 a	0.082 e	0.086 f
Bolero F ₁	3.909 b	0.540 c	0.323 d

*Means with same letters in a column are not significantly different, Tukey-Test (p = 0.05)

favoured purple-orange carrots than white and orange in the criteria sweetness (SURLES et al., 2004). But the sensory profile analysis of different coloured carrots showed, that the purple carrot with orange core was significantly sweeter than yellow, white and orange ones (ALASALVAR et al., 2001), which may be due to the higher sucrose level in the purple cultivar. As well, 'Bolero' is known as a sweet carrot (KÜHLING and BITTER, 2003; STEINER et al., 2004).

'Mello Yello' is a very appealing carrot because of the yellow colour. The total amount of essential oil was similar to 'Napoli'. In comparison to the orange varieties, the higher levels of sabinene, γ -terpinene, terpinolene, α -phellandrene, p-cymene, D-germacrene, zingiberene, trans- γ -bisabolene and myristicin are conspicuously. In sensory evaluation, the flavour and overall acceptance of yellow carrots were significantly worse than white and orange ones (SURLES et al., 2004).

'Nutri Red' is a new carrot cultivar rich in lycopene (GRASSMANN, 2005). Because of the aroma, consumption is recommended as cooked and not for fresh. This may be the reason for poor results in sensory evaluation (SURLES et al., 2004). 'Nutri Red' has the highest total amount of essential oil in our investigations. In comparison with the orange cultivars, the essential oil of 'Nutri Red' has extremely low levels of sabinene, β -caryophyllene, α -humulene, but is rich in limonene, γ -terpinene, terpinolene, α -pinene, β -pinene, α -phellandrene, β -phellandrene, p-cymene, bornyl acetate, β -Z-farnesene, zingiberene, β -bisabolene, trans- γ -bisabolene, α -bisabolol and myristicin.

The cultivar 'bejo 01-0102' is an entirely purple coloured carrot. It is known as 'black carrot' in carrot juice, because of the high anthocyanine level (GRASSMANN, 2005; KOST, 2003).

The essential oil of carrots has great potential for antioxidative capacity due to its composition. In the MDA-test, a model system for lipid peroxidation, following substances had antioxidative capacity: γ -terpinene, α -humulene, terpinolene, β -caryophyllene, α -terpinene (VÖLKER, 2004) and furthermore β -myrcene, p-cymene, α -phellandrene and myristicin (GRÜNZWEIG, 2004).

The amount of volatile aroma substances is influenced by various exogenous parameters. PAILLAN-LEGUE (1987) showed that the level of essential oil in parsley decreased by reduced global radiation.

The same correlation was proved in other leafy vegetables and spices (HE, 1999; SHU and PARK, 1999a; MICHALSKY et al., 1997). Although during growth, carrot roots are not directly exposed to radiation, the amount of essential oil increased during season of high global solar radiation.

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