

Effects of Cold Storage on Essential Oils of Peel of Thompson Navel Oranges

Marianna Usai,*† Giovanni Arras, and Franco Fronteddu

CNR Istituto per lo Studio dei Problemi Bioagronomici delle Colture Arboree Mediterranee, Via De Nicola 1, 07100 Sassari, Italy

Thirty-three constituents accounting for 96.64% of total volatiles of Thompson navel orange peel oils have been identified and quantified in a single GC capillary run. The quantitation was performed using appropriate response factors and identification using pure samples and GC-mass spectrometry. After identification, experiments were carried out to test qualitative and quantitative differences on essential oils of peel of Thompson navel oranges stored under different cold-storage conditions. During storage at a constant temperature of 6 °C and at a cyclic temperature of 6 days at 2 °C plus 1 day at 14 °C, an increase of volatile compounds (acetaldehyde, formic acid, formaldehyde, and acetic acid) and a decrease of limonene content were observed. The cold-storage trials with Thompson navel oranges showed that the minor variations in the content of essential oils were obtained using cyclic temperature storage with short cycles: 6 days at 6 °C plus 1 day at 14 °C and 18 days at 6 °C plus 7 days at 14 °C.

INTRODUCTION

Citrus oils of very complex composition are contained in oval, balloon-shaped oil sacs or vesicles located in the outer rind or flavedo of the fruit. Winton and Winton (1935) described the exact location of these oil sacs in their discussion on the microscopic structure of the flavedo of oranges. All essential oils, in particular those of citrus fruits, have been studied either for their economical importance or for scientific purposes. Many investigators have shown that the quality of citrus oils is dependent on several factors, such as soil, climate, method of extraction of the oil, weather, and maturity and variety of the fruit (Wolford et al., 1971). Hood (1916) stated that the oil content did not reach its maximum until the oranges were fully mature, but the quantities present before ripening were feasible for extraction (By Scora et al., 1969).

The problems connected with the storage of essential oils received major attention from producers and consumers of oils for their economic and technologic effects. Flavors of essential oil are lost during storage when its typical organoleptic character evolves negatively and gives undesirable odors and the loss of original freshness. These modifications are not easily controlled, and sometimes it is not possible to avoid the deterioration of the flavors. This phenomenon is very evident in citrus oils because the technology used influences the stability of the oils.

The reasons for essential oil chemical changes are various, but one of the most important reactions involved is certainly the oxidation reaction. It is known, for example, that from limonene oxidation it is possible to obtain ca. 17 compounds and that *p*-cymene is the principal oxidation product of γ -terpinene and that its increase indicates that the oil lost its freshness (Mazza, 1987). Furthermore, the α - and β -pinene concentrations decrease constantly during the time giving myrtenol, myrtenal, and *trans*-pinocarveol; it is also known that when oranges were kept in cold storage for periods longer than 6 weeks prior to extraction, an increase in specific gravity, optical rotation, iodine number, and saponification value of the oil was found, accompanied by a decrease in the aldehyde content (Wolford et al., 1971).

Commercial considerations often require fruit from plant species of tropical and subtropical origins to be stored for long periods at low temperature. Susceptibility to chilling injury varies according to genetic and environmental factors, which characterize each individual fruit while growing on the tree; after harvesting, the process parameters adopted during storage acquire particular importance. As an example, researchers working on the orange, lemon, and grapefruit have shown that citrus fruits can benefit considerably from the application of cyclic temperature routines during cold storage (Chalutz et al., 1978; Hatton and Cubbedge, 1982; Chohen et al., 1983). Furthermore, researchers of our group (Poma Treccani et al., 1988; Arras and Usai, 1991) observed that using short cycles of temperatures gave good results in citrus storage. Actually, in Italy, for citrus storage are used only constant temperatures, but the results of various studies certainly encourage the introduction of cyclic temperatures also in commercial practices; at least it is observed that when cyclic temperature cold storage is used, a savings of 8–10% could be realized.

In this view we have investigated the composition of the essential oils of Thompson navel oranges at harvest time and during a cold storage of 12 weeks plus 2 weeks of shelf life. We used only total oils to avoid changes due to the use of silica gel; this possibility is confirmed also in the literature (Chamblee et al., 1991).

EXPERIMENTAL PROCEDURES

Storage. The trials were carried out on fruits from Thompson navel orange trees growing in Muravera (southeastern Sardinia). Harvesting took place on March 14, 1989, when the fruits were fully ripe (when the peel was fully colored and the TSS/acid ratio had reached 10.9, the optimum for cultivar and zone).

The harvested oranges were divided into five lots (900 fruits/lot, subdivided into three replications of 300), which were tested according to the following trials: lot A was stored at a constant temperature of 6 °C; lot B was stored at repeating cycles of 6 °C for 18 days plus 14 °C for 7 days; lot C was stored at repeating cycles of 6 °C for 6 days plus 14 °C for 1 day; lot D was stored at repeating cycles of 2 °C for 18 days plus 14 °C for 7 days; lot E was stored at repeating cycles of 2 °C for 6 days plus 14 °C for 1 day. After a storage of 12 weeks (RH = 90%), the lots were transferred to shelf-life conditions (20 °C, RH = 70%) for 2 more weeks.

† Present address: Istituto di Chimica Agraria, Università di Sassari, Via E. De Nicola 1, 07100 Sassari, Italy.

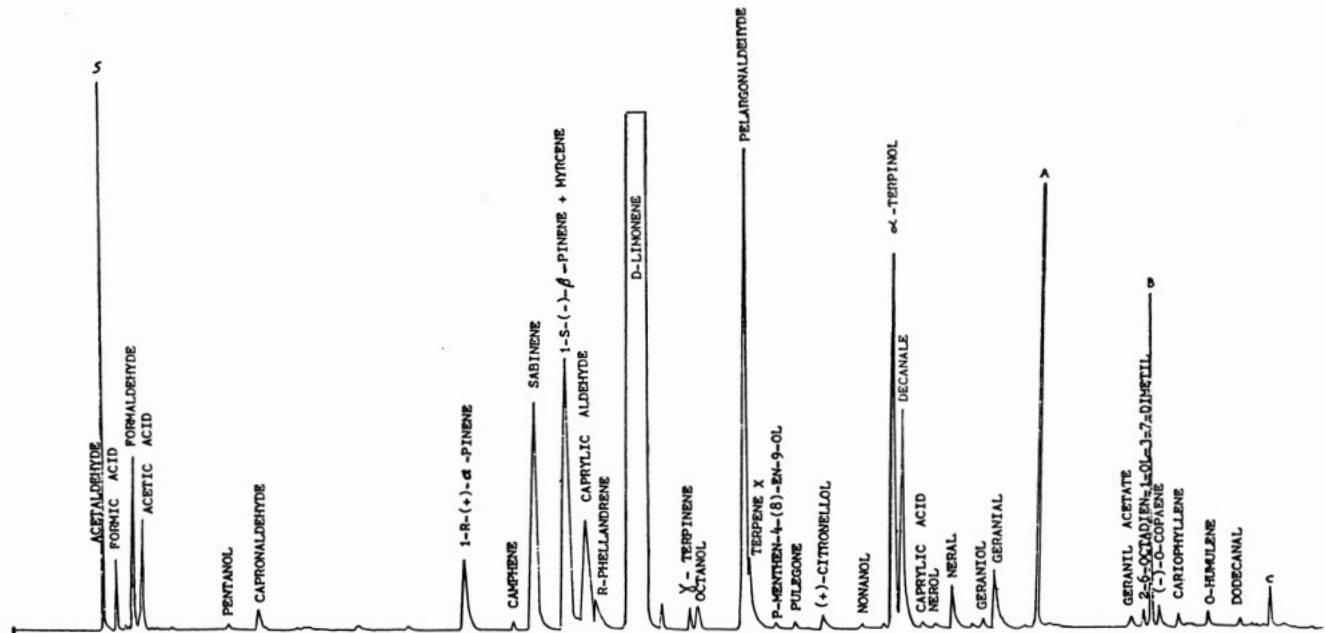


Figure 1. Gas chromatogram of essential oil of Thompson navel orange. S, A, B, C, deriving solvent's peaks.

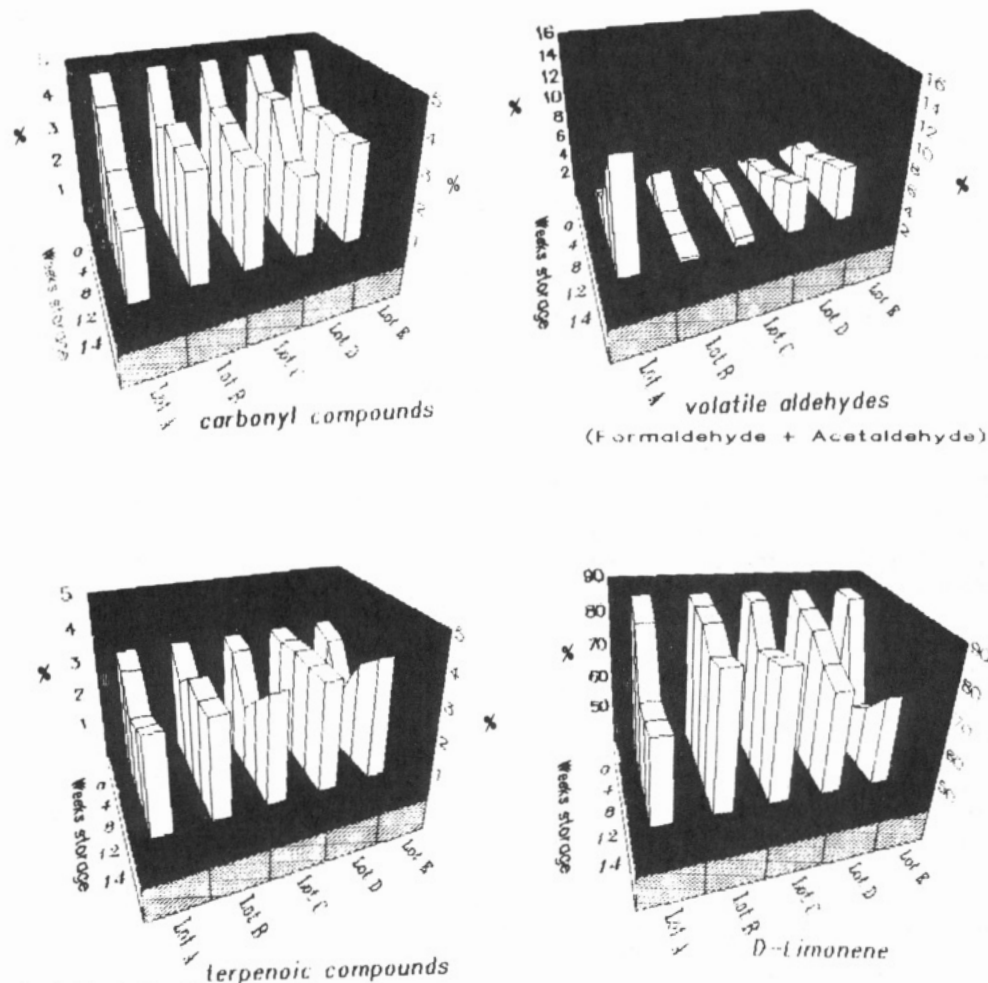


Figure 2. Variations of volatile aldehydes, *d*-limonene, and carbonylic and terpenic compounds in essential oil of Thompson navel orange.

Composition of essential oils was recorded at harvest time, at 4, 8, and 12 weeks of storage, and at the end of shelf life.

Extraction. For every control we prepared three samples of 100 g of flavedo of sound fruits; flavedo was homogenized for 15 min with petroleum ether (Germana et al., 1986), using low speed, room temperature, and a 1:3 ratio; the crude extract was filtered and the residual extracted again twice. Extracts were taken to

dryness in a rotavapor using a water temperature of below 40 °C and atmospheric pressure. For each sample we made four GC injections.

To be sure that the extraction with petroleum ether did not change the essential oil composition, we prepared one sample of each control extracted by pressing the oil sacs. The GC analyses

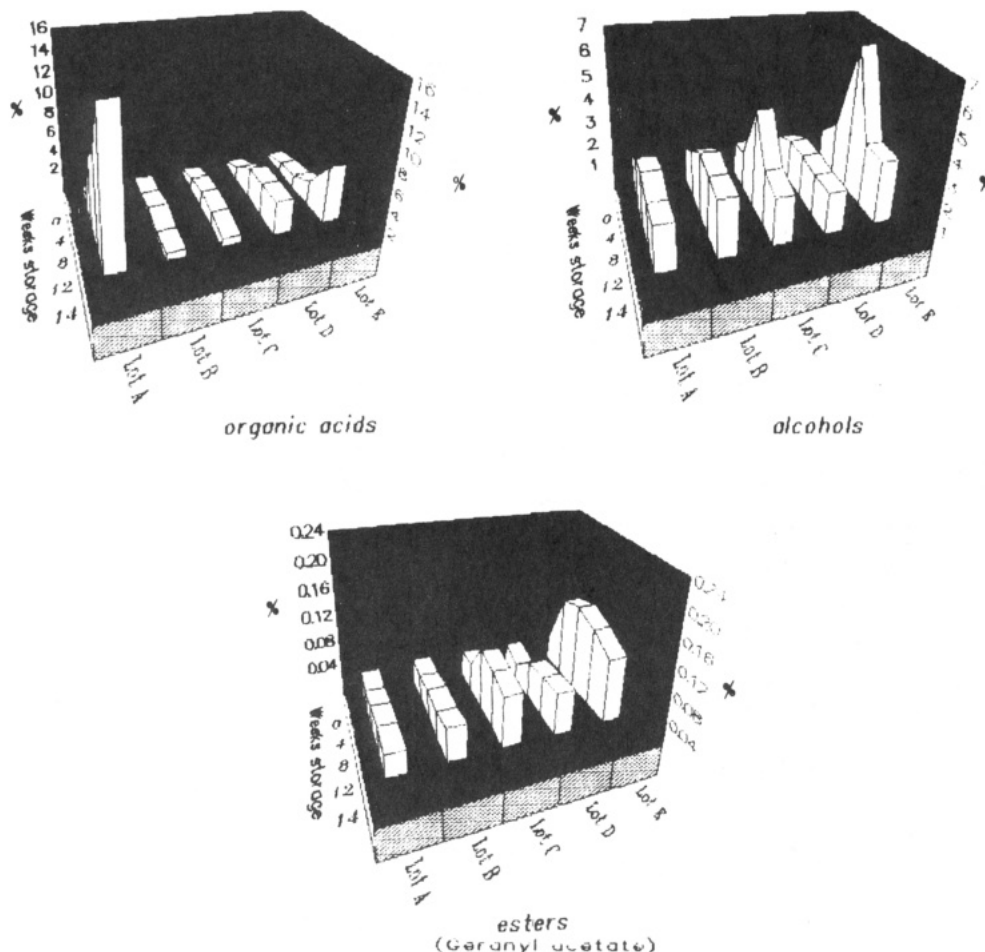


Figure 3. Variations of acids, alcohols, and esters in essential oil of Thompson navel orange.

showed that there were no appreciable changes between the two extraction methods.

To identify hydrocarbons deriving from petroleum ether, we evaporated 900 mL of solvent (using the same conditions) and the residual taken with a small amount of pentane was injected in the GC. The chromatogram showed three peaks: (a) $R_t = 37.30$, identified as $C_{15}H_{32}$; (b) $R_t = 41.60$, identified as $C_{19}H_{40}$; (c) $R_t = 46.50$, identified as $C_{26}H_{54}$ (chromatograms are available); identification of peaks was performed via GC-MS.

Gas Chromatography. For separations and quantitations a Varian 3300 gas chromatography was used; $0.2 \mu\text{L}$ was injected (split 1/50) into a fused-silica capillary column (length 50 m, i.d. 0.20 mm; bonded stationary phase NS-54, Supelco) and chromatographed under the following conditions: carrier gas, helium; oven, 50°C (8 min), increasing by $3^\circ\text{C}/\text{min}$ to 130°C (1 min) and by $5^\circ\text{C}/\text{min}$ to 205°C (20 min), and then by $20^\circ\text{C}/\text{min}$ to 225°C (5 min); detector and injector, 240°C .

The oils were analyzed without dilution, and the data reported in Table I are the average of four GC injections. Measurements of peak areas were performed with an electronic integrator; quantitation of each compound was expressed as a percentage of total peak area. Since it is known that oxygenated compounds have a lower detectability by FID than hydrocarbons (Dugo et al., 1983), we calculated response factors using a standard mixture composed of α -pinene, α -terpineol, neral, geranial, geranyl acetate, and caryophyllene, where terpene was 92%, aldehydes 5%, and alcohol, ester, and sesquiterpene 1% each. We found that hydrocarbons R_f is 1; aldehydes and ketones present in peel essential oils of oranges have a $R_f = 0.80$, alcohols 0.78, and esters 0.71. For this reason the experimental values were multiplied for the following correction factors: hydrocarbons 1; aldehydes and ketones 1.24; alcohols 1.28; and esters 1.408.

Reference Compounds. All standards for GC comparison of R_t were from Fluka and were all injected in GC to control purity.

Gas Chromatography-Mass Spectrometry. The GC-MS analyses were performed with a Perkin-Elmer ITD (ion trap

detector) coupled to a Perkin-Elmer Model 8321 gas chromatograph equipped with a Supelco NS-54 fused-silica capillary column (length 50 m, i.d. 0.20 mm) connected to the ion source of the mass spectrometer. The split/splitless injection port was maintained at 240°C , and the oven temperature was programmed as follows: 50°C (8 min), increasing by $3^\circ\text{C}/\text{min}$ to 130°C (1 min) and by $5^\circ\text{C}/\text{min}$ to 205°C (20 min) and then by $20^\circ\text{C}/\text{min}$ to 225°C (5 min).

RESULTS AND DISCUSSION

As shown in the gas chromatogram of the volatile essential oils of Thompson navel oranges at harvest conditions, reported in Figure 1, it was possible to identify 33 constituents by comparison of retention time to that of an authentic sample confirmed by GC-MS; for *p*-menthen-4(8)-en-9-ol, pulegone, and 3,7-dimethyl-2,6-octadien-1-ol we have only the GC-MS identification. The identification GC-MS was based on the match of the most abundant peaks of the mass spectrum with published data (*Eight Peak Index of Mass Spectra*, 1974; Heller and Milne, 1978). In Table I are reported the variations of percentages of every component during cold storage and shelf life; the compounds identified (at harvest conditions) constitute 96.64% of the total.

The components of the essential oils were divided into six groups: carbonylic compounds, volatile aldehydes, acids, esters, and terpenic compounds, and limonene.

As reported in Figures 2 and 3, all groups are sensitive to cold-storage conditions since the first month of conservation. The increase of alcohols in lots C and E and the corresponding decrease of terpenic compounds are noteworthy. This effect could be explained with formation of α -terpineol by oxidation of terpenes. In lots A, D, and

Table I. Variation of Chemical Content in Essential Oil of Thompson Navel Orange

compound ^a	lot A				lot B				lot C				lot D				lot E				
	HC ^b	4 ^c	8 ^c	12 ^c	SL ^c	4	8	12	SL	4	8	12	SL	4	8	12	SL	4	8	12	SL
	volatile aldehydes	0.442	2.042	3.098	7.167	9.820	2.773	0.643	0.396	0.357	2.060	2.338	1.894	0.851	2.125	2.498	3.698	4.832	3.250	3.407	4.316
formaldehyde	0.000	0.000	0.270	0.632	1.365	0.156	0.047	0.039	0.037	0.000	0.040	0.049	0.065	0.000	0.186	0.246	0.333	0.000	0.059	0.214	0.489
acetaldehyde	0.442	2.046	3.368	7.799	11.185	2.929	0.690	0.435	0.394	1.060	2.378	1.943	0.916	2.125	2.684	3.944	5.165	3.250	3.466	4.530	5.524
carbonylic compounds	0.085	0.100	0.021	0.110	0.162	0.229	0.359	0.369	0.386	0.060	0.060	0.068	0.075	0.085	0.080	0.101	0.107	0.068	0.044	0.110	0.125
capronaldehyde	0.768	0.410	0.277	0.249	0.230	0.398	0.234	0.256	0.266	0.353	0.205	0.358	0.403	0.419	0.369	0.334	0.231	0.387	0.339	0.332	0.329
caprylaldehyde	2.455	2.419	1.795	1.202	1.277	1.767	2.022	2.008	1.926	1.698	1.601	1.500	1.686	1.946	2.266	1.238	1.474	1.686	1.602	1.636	1.929
pelargonaldehyde	0.019	0.022	0.021	0.023	0.023	0.019	0.021	0.024	0.023	0.024	0.023	0.025	0.024	0.024	0.022	0.021	0.023	0.024	0.019	0.024	0.025
pulegone	0.886	0.757	0.431	0.434	0.431	0.638	0.683	0.622	0.559	1.205	0.978	0.768	0.628	1.006	0.899	5.100	0.425	0.686	0.655	0.524	0.544
decanal	0.152	0.104	0.037	0.031	0.024	0.141	0.071	0.052	0.048	0.151	0.111	0.079	0.064	0.081	0.074	0.071	0.066	0.150	0.110	0.063	0.047
neral	0.271	0.208	0.086	0.018	0.012	0.250	0.183	0.124	0.100	0.269	0.186	0.161	0.145	0.147	0.142	0.124	0.088	0.274	0.266	0.207	0.126
geranial	0.024	0.023	0.029	0.023	0.028	0.029	0.018	0.034	0.045	0.009	0.140	0.110	0.110	0.096	0.084	0.095	0.106	0.022	0.038	0.054	0.063
dodecanal	4.663	4.043	2.687	2.090	2.131	3.471	3.591	3.489	3.353	3.469	3.300	3.069	3.136	3.804	3.944	2.494	2.520	3.297	3.073	2.950	3.188
total																					
terpenes	0.304	0.294	0.153	0.250	0.348	0.185	0.290	0.298	0.312	0.322	0.160	0.340	0.359	0.316	0.320	0.330	0.373	0.328	0.137	0.228	0.397
1(R)-(+)- α -pinene	0.002	0.003	0.002	0.004	0.003	0.002	0.002	0.003	0.005	0.003	0.004	0.002	0.004	0.003	0.002	0.005	0.004	0.005	0.002	0.003	0.004
camphene	1.122	1.216	0.850	1.028	1.117	0.844	1.155	0.999	0.929	1.229	0.555	0.899	1.198	1.410	1.350	1.320	1.306	1.014	0.518	1.620	1.804
sabinene	1.533	1.377	1.075	1.112	1.278	1.359	1.478	1.402	1.477	1.488	0.937	1.121	1.520	1.363	1.398	1.401	1.417	1.475	1.836	1.028	1.322
1(S)-(-)- β -pinene + miricene	0.270	0.170	0.062	0.061	0.066	0.130	0.067	0.089	0.098	0.105	0.068	0.098	0.118	0.178	0.173	0.150	0.094	0.178	0.066	0.061	0.053
(R)-phellandrene	0.034	0.028	0.052	0.028	0.031	0.030	0.040	0.035	0.025	0.021	0.025	0.037	0.046	0.015	0.030	0.031	0.033	0.032	0.011	0.019	0.027
γ -terpinene	0.060	0.061	0.065	0.063	0.068	0.029	0.073	0.084	0.093	0.033	0.079	0.099	0.096	0.026	0.070	0.070	0.072	0.027	0.044	0.095	0.073
(-)- α -copaene	0.028	0.026	0.015	0.025	0.038	0.023	0.032	0.039	0.055	0.033	0.100	0.077	0.045	0.025	0.048	0.049	0.051	0.028	0.065	0.055	0.045
carophyllene	0.031	0.025	0.015	0.015	0.012	0.019	0.033	0.051	0.054	0.035	0.047	0.037	0.043	0.012	0.032	0.032	0.042	0.024	0.038	0.078	0.083
α -humulene	86.179	81.934	63.921	64.000	65.621	85.772	84.961	80.000	81.885	86.564	76.398	78.520	80.710	83.497	80.978	75.000	72.023	85.940	55.125	60.000	68.558
limonene	89.563	85.134	66.210	66.586	68.582	88.392	88.131	83.000	84.933	89.833	78.373	81.225	84.104	86.845	84.401	78.393	75.415	89.057	56.842	63.187	72.366
total																					
organic acids	0.129	0.383	1.235	3.628	8.791	0.178	0.865	0.428	0.503	0.098	0.267	0.418	0.685	0.175	0.228	0.267	0.321	0.203	0.564	1.781	4.936
formic acid	0.263	1.159	5.908	5.990	6.492	0.399	1.777	2.005	2.243	1.073	1.412	1.071	2.246	1.281	2.891	3.070	3.132	0.867	0.834	0.898	1.029
acetic acid	0.012	0.040	0.007	0.025	0.007	0.031	0.056	0.048	0.018	0.008	0.004	0.004	0.003	0.048	0.043	0.035	0.020	0.028	0.021	0.017	0.012
caprylic acid	0.404	1.562	7.122	9.643	15.290	0.608	1.098	0.681	0.764	1.179	1.683	1.493	0.934	1.504	3.162	3.372	3.463	1.098	1.419	2.696	5.977
total																					
alcohols	0.014	0.017	0.026	0.067	0.071	0.020	0.008	0.012	0.011	0.019	0.015	0.019	0.017	0.016	0.023	0.026	0.029	0.015	0.020	0.035	0.055
pentanol	0.171	0.341	0.490	0.295	0.026	0.294	0.561	0.403	0.056	0.147	0.497	0.131	0.147	0.152	0.149	0.110	0.092	0.108	0.686	0.730	0.814
octanol	0.008	0.008	0.010	0.009	0.010	0.010	0.010	0.009	0.011	0.007	0.009	0.008	0.010	0.007	0.009	0.011	0.011	0.008	0.008	0.010	0.012
<i>p</i> -methen-4(8)- en-9-ol	0.049	0.056	0.057	0.056	0.058	0.048	0.048	0.055	0.057	0.049	0.053	0.055	0.059	0.048	0.053	0.063	0.057	0.049	0.054	0.059	0.062
(+)-citronellol	0.008	0.010	0.012	0.012	0.014	0.008	0.009	0.009	0.011	0.008	0.010	0.009	0.011	0.008	0.010	0.012	0.012	0.009	0.009	0.011	0.014
nonanol	1.411	1.698	1.708	1.434	1.708	1.743	2.090	2.030	2.243	1.346	3.694	2.147	1.811	1.605	1.597	1.537	1.564	2.202	5.619	1.917	1.777
α -terpineol	0.056	0.052	0.058	0.057	0.058	0.048	0.039	0.065	0.081	0.067	0.051	0.048	0.025	0.084	0.076	0.074	0.069	0.048	0.206	0.113	0.065
nerol	0.010	0.008	0.011	0.010	0.005	0.017	0.010	0.015	0.021	0.010	0.009	0.011	0.010	0.011	0.012	0.010	0.008	0.012	0.011	0.016	0.014
geraniol	0.043	0.047	0.057	0.056	0.058	0.047	0.049	0.053	0.059	0.045	0.050	0.050	0.057	0.044	0.048	0.053	0.055	0.049	0.051	0.058	0.064
3,7-dimethyl-2,6- octadien-1-ol	1.528	2.237	2.429	1.996	2.026	2.235	2.816	2.651	2.550	1.698	4.388	2.478	2.147	1.982	1.977	1.886	1.897	2.500	6.664	2.949	2.877
total																					
esters	0.035	0.033	0.039	0.04	0.035	0.04	0.047	0.043	0.051	0.043	0.093	0.086	0.078	0.028	0.057	0.061	0.065	0.126	0.135	0.123	0.099
geranyl acetate																					

^a Total identified components of essential peel oils of Thompson navel oranges at the harvest time = 96.635%; absolute weight percent using response factors, average of four GC runs. ^b Harvest conditions. 4, 8, and 12 represent the weeks of storage in which analytical parameters were recorded; SL refers to analytical parameters recorded at the end of shelf life.

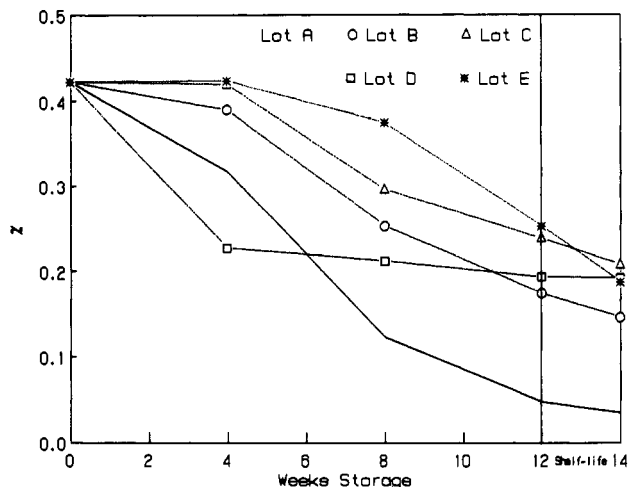


Figure 4. Variations of citral in essential oil of Thompson navel orange.

E a decrease of aldehydes (Wolford et al., 1971) and a large increase of volatile aldehydes and acids are noticed. In addition, noteworthy, are also the variations of limonene content during cold storage. In fact, the Thompson navel cultivar has 86.17% limonene at harvest time; this percentage is reduced to 65.6% in trial A, to 81.2% in trial B, to 80.7% in trial C, to 72% in trial D, and to 68.5% in trial E. The complete trend is graphed in Figure 2.

Oxygenate compounds are such important contributors to citrus flavor that one of the standards of identity for various citrus peel oils used in flavoring citrus and other products is the total aldehyde content. In citrus oils, the primary flavoring components are the two isomeric monoterpene aldehydes, neral and geranial, together called citral. The stability of concentration of these two compounds is therefore indicative that the storage used is useful to preserve the composition of peel oils. In Figure 4 is graphed the trend of citral during storage. The differences between constant temperature and repeating cyclic temperatures are evident; in fact, in the last case the content of citral is always much more preserved.

CONCLUSIONS

Examination of the chemical composition of the essential oils of peel derived from cold storage has revealed that the least variations were obtained under cyclic temperature, in particular when the temperature was never under 6 °C (lots C and B). Under these conditions it is possible to have little degradation of the essential oils until 3 months from harvest. In particular, lot C gave the best results also for citral content.

In the other three lots examined the essential oils of stored oranges show significant variations in their components. These data are in accordance with those reported in a previous paper in which we discussed the variations of juice metabolites and physiological and mycological damages from cold storage (Arras and Usai, 1990).

The variation of content in volatile aldehydes and in acids might be taken as a degradation parameter of Thompson navel oranges, as well as the variation in the content of limonene and in the content of citral.

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Registry No. Formaldehyde, 50-00-0; acetaldehyde, 75-07-0; capronaldehyde, 66-25-1; caprylaldehyde, 124-13-0; pelargonaldehyde, 124-19-6; pulegone, 89-82-7; decanal, 112-31-2; neral, 106-26-3; geranial, 141-27-5; dodecanal, 112-54-9; (1R)-(+)- α -pinene, 7785-70-8; camphene, 79-92-5; sabinene, 3387-41-5; β -pinene, 127-91-3; (R)-phellandrene, 4221-98-1; γ -terpinene, 99-85-4; (-)- α -copaene, 3856-25-5; caryophyllene, 87-44-5; α -humulene, 6753-98-6; limonene, 138-86-3; formic acid, 64-18-6; acetic acid, 64-19-7; caprylic acid, 124-07-2; pentanol, 71-41-0; octanol, 111-87-5; *p*-menth-4(8)-en-9-ol, 15714-11-1; (+)-citronellol, 1117-61-9; nonanol, 143-08-8; α -terpineol, 98-55-5; nerol, 106-25-2; geraniol, 106-24-1; 2,6-octadien-1-ol, 24532-11-4; geranyl acetate, 105-87-3; myrcene, 123-35-3.