Influence of Ethylene Removal on the Volatile Development in Passa Crassana Pears Stored in a Controlled Atmosphere

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ABSTRACT

The influence of ethylene removal by a catalytic converter on the quality of Passa Crassana pears stored in a controlled atmosphere was studied sampling both cold atmospheres and fruit during a 25 week storage period.

The volatile cold room atmosphere analysis showed that there was a time delay in the ripening of the pears stored with ethylene removal; this fact was shown also by the other chemical and physical analyses that described the test fruit as riper than the others at the end of the storage period. The high-boiling volatile substances (decadienoate esters) gradually increased in the fruit pulp of both types of storage, reaching about half of the total production at the end of storage.

After the post-storage ripening period at room temperature, for both storage modes, the disappearance in the fruit flesh of pentyl acetate, ethyl propanoate and hexanal as well as the appearance of butyl acetate and hexyl acetate were ascertained. After maturation, the high-boiling compounds were present in a different proportion according to the mode of storage. A significant correlation was found between the ratio high-boiling/low-boiling compounds and the acceptance scores of sensory evaluations.

INTRODUCTION

Among the techniques used to prevent the internal browning of Passa Crassana pears, a characteristic chilling injury, the storage of fruit at 5–6°C

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(Leblond, 1972) coupled with a high CO_2 level controlled atmosphere (CA)—8% CO_2, 4% O_2—(Gorini *et al.*, 1982; Gorini, 1984), is sufficient to restrict the damage to a very low percentage, without the softening of the pulp; but, at this temperature a fast yellowing of fruit occurs.

Rizzolo *et al.* (1987) succeeded in delaying the de-greening of the fruit using ethylene removal (ER) by means of a catalytic converter. The analyses (pH, titratable acidity, dry matter, soluble sugars, colour and firmness) on fruit stored both with ER and without ER ('test') during a 25 week storage time, showed that the ER fruit were less ripened than the test ones; this fact, however, did not impair flesh softening when the fruit were on the market: in fact, both the sensory evaluation scores and colour analysis, carried out after having ripened the fruit at ambient temperature, showed that ER fruits were rated as being of a better quality than the 'test' ones. In the end, the ER fruit had an higher vitality, so allowing a longer storage period and delaying their market date.

Better quality means better flavour, too; therefore, it would be interesting to know the effect of the ER by means of a catalytic system on volatile development during the storage time.

According to Paillard (1975), the volatile metabolism in the Passa Crassana pear is influenced by the type of cold room atmosphere: the pears stored in CA at 0°C produced fewer volatiles than fruit stored in air, while the 10% CO_2 CA fruit produced a great deal of volatiles when kept at room temperature. During the ripening process after storage (Phan Chon Ton, 1965, 1968) the typical 'Passa Crassana' flavour was developed after about 15 days; moreover, immediately before complete maturation, Strandzhev (1974*a,b*; 1975*a,b*) ascertained the presence of *cis*-2,4-decadienoic acid esters, which had been previously recognized by Jennings & Sevenants (1964) as the character impact compounds for Bartlett pear; Strandzhev also identified the low-boiling compounds found by Paillard (1975) and Phan Chon Ton (1968).

MATERIALS AND METHODS

Fruit and cold storage

The research was carried out on Passa Crassana pears, cold-stored at 5°C in CA (4% O_2, 6–8% CO_2) in two 40-ton storage rooms; one of them was fitted with a Swingtherm catalytic converter (Woyciechowski *et al.*, 1985) to remove ethylene, which was continuously working during the whole storage time of 25 weeks. Details are reported in a previous paper (Rizzolo *et al.*, 1987). The two modes of storage are referred to as 'ER' for the one with ethylene removal, and 'test' for the CA alone.

Sampling and analysis of cold room atmospheres

The volatile compounds of 45 litres of refrigerated atmosphere were adsorbed on 100 mg of activated coconut charcoal (20–40 mesh) flowing the air through a tube connected to a personal air sampling pump preset at a flow rate of 1 litre/min.

Then, the desorption of the sample from the sorbent was achieved using the thermal desorber TD 120b (Dani) fitted onto the injector port of the gas chromatograph (170°C for 20 min; injection time 5 s).

Sampling and analysis of fruit

Fruit were sampled from the two storage systems after 4, 6, 8, 14, 17 and 25 weeks of storage and analysed as soon as possible (unripened fruit). After 14, 17 and 25 weeks of storage, two boxes of pears were taken out of the two cold rooms and kept at ambient temperature (20°C) for ten days to achieve maturation (ripened fruit).

The headspace GC analysis of total volatile substances was carried out on sliced flesh according to a procedure previously described (Rizzolo, 1988).

GC analysis of volatile substances

A Dani 6800 HR gas chromatograph equipped with a FID detector was used. Volatiles separation was performed using a 4 m stainless steel column packed with 10% Carbowax 20M on 80/100 mesh Carbopack P-AW. Gas flow pressures were: nitrogen, 1·9 bar; hydrogen, 0·9 bar; air, 1·5 bar (1 bar = 10^5 Pa). Instrument temperatures were: injector and detector, 250°C; oven programme, 50°C for 8 min, to 180°C at 4°C/min and held for 30 min. The peaks were recorded, stored and reprocessed using the Chromatopack CR3A Data Processor (Shimadzu). The GC/MS analysis was performed according to the conditions reported in a previous paper (Di Cesare *et al.*, 1988).

The identified low-boiling compounds were estimated by relating the peak area of each compound to that of the corresponding standard, and were expressed as μmol of each compound per g of fruit flesh.

The high-boiling compounds were each estimated as μmol of hexyl acetate per g of fruit flesh. The analysis of variance of data was performed by using the BMD package.

RESULTS AND DISCUSSION

Figure 1 shows the trends of the total volatiles contained in the two cold room atmospheres for the first four sampling dates. The volatile emanation
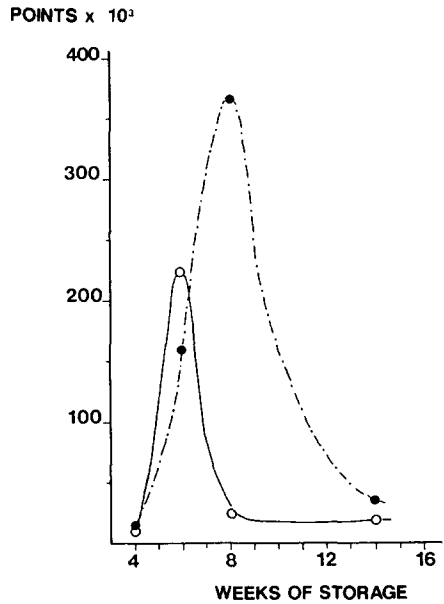
POINTS x 10^3

Fig. 1. Total volatile substances (points $\times$ 10^3) in 45 litres of cold room atmosphere ($\bigcirc$ = test; $\bullet$ = ER).

was affected by the ER process; in fact there was a time shift of the maximum volatile production in the ER atmosphere. The list of the identified compounds in the pulp of fruits is reported in Table 1. All the identified compounds had already been found in pears (Polesello, 1980), and specifically in Italian Passa Crassana cultivar (Giannone and Baldrati, 1967).

With the delay of the storage time, there was an accumulation of volatiles in the flesh; higher amounts were observed for the 'test' fruit, as shown in Fig. 2.

Table 2 lists the amounts of volatiles developed by 'test' and ER unripened fruit: a difference between the two treatments was found and it was
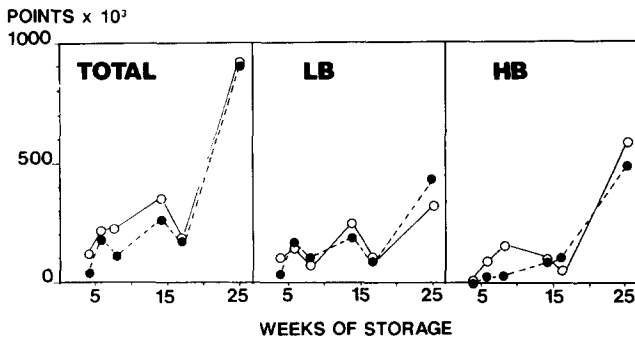

Fig. 2. Sums of total, low-boiling (LB), and high-boiling (HB) areas for unripened fruit coming from ($\bigcirc$) test and ($\bullet$) ER storage rooms during the whole storage time.

TABLE 1
Retention Times amd Identified Compounds in Passa Crassana Pears

Peak number	Retention time (min)	Compounds	Identification[a]		
1	2	ethylene	RT,	St	
2	2·3	unknown			
3	3·3	unknown			
4	5·1	acetaldehyde	RT,	St	
5	8·6	methyl acetate	RT,	St	
6	10·0	acetone	RT,	St,	MS
7	12·1	ethyl acetate	RT,	St,	MS
8	14·5	ethylmethylketone	RT,	St	
9	15·3	ethanol	RT,	St,	MS
10	18·4	ethyl propanoate	RT,	St	
11	19·1	unknown			
12	19·8	unknown			
13	21·7	2-methylpropyl acetate	RT,	St	
14	22·5	unknown			
15	24·8	butyl acetate	RT,	St,	MS
16	25·3	hexanal	RT,	St	
17	25·5	1-butanol	RT,	St,	MS
18	29·9	pentyl acetate	RT,	St,	MS
19	30·4	3-methyl-1-butanol	RT,	St,	MS
20	31·5	unknown			
21	32·6	1-pentanol	RT,	St	
22	34·3	hexyl acetate	RT,	St,	MS
23	35·5	1-hexanol	RT,	St,	MS
24	41·1	1-octanol	RT,	St,	MS
25	42·4	methyl-(Z)-dec-4-enoate	RT,	MS	
26	43·5	ethyl-(Z)-dec-4-enoate	RT,	MS	
27	45·5	methyl-(E),(Z)-deca-2,4-dienoate[b]	RT,	MS	
28	46·0	methyl-(E),(E)-deca-2,4-dienoate[b]	RT,	MS	
29	48·0	unknown			
30	51·0	ethyl-(E),(Z)-deca-2,4-dienoate[b]	RT,	MS	
31	55·0	unknown			
32	64·0	ethyl (E),(E)-deca-2,4-dienoate[b]	RT,	MS	

[a] RT is retention time, St is standard, and MS is GC/MS.
[b] Stereoisomery tentatively assigned according to the findings of Shiota (1990).

statistically significant for ethanol, 2-methylpropyl acetate, butyl acetate, hexanal, 3-methyl-1-butanol, 1-pentanol, hexyl acetate and methyl(E), (Z)-deca-2,4-dienoate.

Volatile development showed similar trends in both the systems: methyl acetate, ethyl acetate, 1-butanol, 1-hexanol and ethylmethylketone increased, while butyl acetate and pentyl acetate decreased to very low levels.

TABLE 2

Volatiles (μmol $\times$ 10^{-4}/g of Sliced Flesh) Produced by Unripened Passa Crassana Pears Stored in (A) Test and (B) ER Rooms[a]

Compound number		Weeks of storage					
		4	6	8	14	17	25
4	A	25·2	43·6	5·8	19·3	37·9	83·8
	B	21·5	43·4	5·3	48·8	9·5	97·0
5	A	2·8	22·2	2·4	7·9	11·0	15·8
	B	0·02	6·8	3·1	15·8	2·5	52·6
6	A	7·0	4·7	2·9	3·0	4·5	5·4
	B	3·4	3·8	4·7	15·4	3·0	4·1
7	A	1·1	1·0	2·5	6·6	6·2	21·8
	B	1·2	12·7	13·0	15·2	3·4	10·0
8	A	0·9	1·5	3·1	12·5	15·8	33·4
	B	1·0	1·3	1·4	25·7	21·2	59·2
9	A	37·0	47·8	15·4	105·2	25·0	40·4
	B	7·7	236·2	148·0	78·8	27·2	41·5[b]
10	A	0·5	1·6	0·2	0·7	1·8	1·3
	B	0·2	0·5	4·7	1·4	0·9	1·1
13	A	2·4	1·0	1·9	0·8	0·5	0·0
	B	0·01	0·3	1·3	0·3	0·02	0·0[b]
15	A	3·3	4·4	1·5	7·1	9·6	0·0
	B	1·0	0·2	1·2	5·0	3·8	0·0[b]
16	A	0·5	0·6	0·9	0·6	0·5	1·3
	B	0·1	0·2	0·1	0·4	0·2	0·8[b]
17	A	11·2	16·4	4·9	7·5	16·2	88·4
	B	4·7	13·0	6·3	12·0	20·2	122·6
18	A	0·5	0·4	2·2	1·2	0·5	0·01
	B	1·0	0·5	1·3	0·8	0·3	0·01
19	A	0·2	0·0	1·8	0·2	0·07	0·0[b]
	B	tr	tr	tr	0·01	tr	tr
21	A	0·05	0·0	1·2	0·8	1·8	0·8
	B	0·0	0·0	0·0	1·6	0·02	0·1[b]
22	A	1·6	0·8	0·3	0·6	2·0	1·3
	B	0·2	0·3	0·2	0·5	1·5	0·1[b]
23	A	38·6	15·4	5·0	13·0	12·9	63·2
	B	7·5	10·1	14·8	29·0	12·8	60·0
24	A	8·4	1·4	9·7	2·4	3·4	12·6
	B	0·2	1·3	5·4	14·4	3·6	14·1
26	A	1·1	2·6	20·0	2·4	7·5	9·8
	B	0·0	36·64	3·1	14·1	0·9	8·3
27	A	0·0	6·1	16·1	14·9	2·4	137·2
	B	0·0	12·2	2·2	4·6	4·0	43·5[b]
30	A	0·0	6·1	8·9	46·0	2·0	14·8
	B	0·0	0·1	0·0	20·1	1·7	25·9
32	A	0·0	0·0	0·2	0·0	5·3	6·2
	B	0·0	0·0	0·0	0·0	0·0	17·7

[a] All figures are the average of five replications.
[b] Statistically significant differences between the two treatments ($P > 90\%$).

TABLE 3

Percent distribution of Low-Boiling (LB) and High-Boiling (HB) Compounds Before and After Ripening

Weeks of storage	ER		Test	
	LB	HB	LB	HB
Unripened fruit				
4	97·0	3·0	88·4	11·6
6	91·9	8·1	59·6	40·4
8	81·7	18·3	33·3	66·7
14	68·6	31·4	69·7	30·3
17	49·9	51·1	69·4	30·6
25	46·5	53·5	35·3	64·7
Ripened fruit				
14	85·4	14·6	93·8	6·2
17	97·8	2·2	95·8	4·2
25	52·2	47·8	61·0	39·0

Furthermore, hexyl acetate and hexanal showed a different behaviour according to the storage mode: hexyl acetate decreased till the eighth week of storage and, afterwards, increased in the test room, while for the ER one, its amount gradually increased, reaching the maximum at the seventeenth week, and then decreased at the end of storage. Hexanal was almost constant in the test fruit, while it increased in the ER ones.

Some high-boiling compounds developed at the first sampling time only in the 'test' fruit; the formation of these compounds in ER unripened fruit was delayed as displayed by their increasing percentages of total volatiles (Table 3), and it reached about half of the total volatile production at the end of the storage; the amounts were slightly higher in 'test' pears and this fact agreed with the results of the other analyses (Rizzolo *et al.*, 1987), showing that 'test' fruits were riper than ER ones. Making the comparison between the volatile substances formed in fruit flesh and those given off in the cold room atmosphere during storage, it is evident that there was a delay in the ripening of ER pears. On the same sampling date there was a great difference in the amount of volatiles for the two modes of storage, but if the 'test' atmosphere taken at one sampling date is compared with the ER one at the following date, we find that the amount of volatiles produced is quite the same. This could be an index of the 1-month delay of maturation in ER fruit, confirming the findings reported in previous work (Rizzolo *et al.*, 1987).

After post-storage ripening at ambient temperature, ER fruit produced higher amounts of volatiles than the others (Fig. 3), even if there were no significant differences. The amount of the developed compounds depended
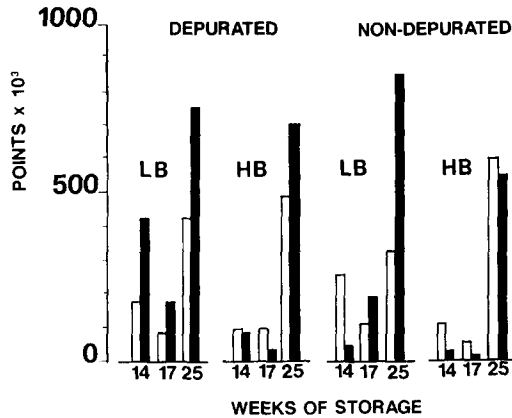
Fig. 3.   Amounts of low-boiling (LB) and high-boiling (HB) compounds in both the storage
modes in (☐) unripened and (■) ripened pears.

on the storage time and mainly on its mode. In both the storage conditions, fruit after 17 weeks of cold storage, produced the lowest amounts of volatiles when ripened, showing the least vitality; conversely, those ripened after a 25 week storage time, produced the highest amount of volatiles, especially of ethyl acetate, butyl acetate, hexyl acetate, ethanol and acetone (Table 4). Moreover, pentyl acetate, ethyl propanoate and hexanal were not found whatever the time and type of storage applied before maturation. The disappearance in the fruit flesh of pentyl acetate, ethyl propanoate and hexanal as well as the appearance of butyl acetate and hexyl acetate were in agreement with the finding on Passa Crassana pears reported by Phan Chon Ton (1968) and Paillard (1975); these authors related this condition to the best organoleptic qualities of this cultivar achieved with ripening.

It should be noted that after post-storage maturation, the high-boiling compounds were present in a different proportion according to the mode of storage (Table 3). Furthermore, a correlation (Fig. 4) was found between the
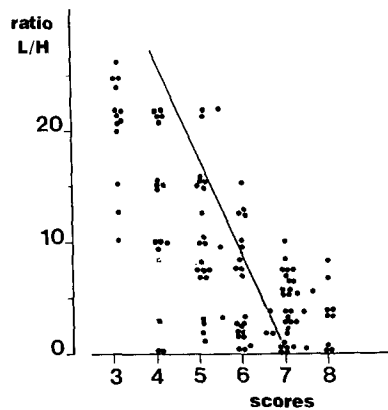

Fig. 4.   Regression curve of acceptance scores versus ratio low-boiling/high-boiling compound areas (L/H); $r = -0.82$.

TABLE 4

Low-Boiling Volatile Substances (μmol $\times 10^{-4}$/g of Sliced Flesh) in Ripened Fruit[a] for (A) ER and (B) Test

Peak number		Weeks of storage		
		14	17	25
4	A	97·2	29·0	687·6
	B	65·8	18·4	68·6
5	A	33·6	3·0	122·0
	B	23·1	2·0	29·4
6	A	8·8	1·9	20·8
	B	9·6	1·9	27·9
7	A	50·8	4·2	73·4
	B	31·8	17·0	124·2
8	A	34·3	3·8	93·5
	B	21·4	6·9	127·0
9	A	133·6	38·2	647·2
	B	146·2	81·0	686·3
10	A	4·1	1·1	0·2
	B	6·1	0·8	8·7
13	A	8·8	1·3	5·7
	B	1·0	1·8	9·7
15	A	1·3	0·1	0·2
	B	0·8	1·8	3·8
16	A	0·6	0·0	0·1
	B	1·0	0·1	0·4
17	A	24·1	0·0	15·4
	B	3·3	5·8	29·4
18	A	0·9	0·0	12·3
	B	0·4	0·0	4·0
22	A	2·1	0·8	2·0
	B	1·9	0·1	3·1
23	A	15·1	47·7	8·4
	B	15·2	46·2	50·5
24	A	8·7	1·2	47·6
	B	2·3	2·2	11·4
26	A	2·2	0·0	39·1
	B	1·4	0·5	3·8
27	A	1·6	0·0	16·9
	B	0·0	0·0	12·8
28	A	1·6	0·0	15·6
	B	0·1	0·0	22·3
32	A	0·4	0·0	12·86
	B	0·0	0·0	12·24

[a] All figures are averages of five replications.

ratio low-boiling/high-boiling compounds (L/H) and the acceptance scores of sensory evaluations (Rizzolo *et al.*, 1987) ($r = -0.82$, 29 dof): fruit with a low ratio L/H got higher scores, suggesting that a high amount of high-boiling compounds (i.e. 2,4-decadienoates) in the pear flesh might give a more accepted product. The decreased content of high boiling compounds found in the 'test' fruit might suggest its over-ripening, as the decadienoates reach a maximum at the optimal ripening stage and decrease with over-ripening, as pointed out by Jennings *et al.* (1964); this decay reduces the fruit acceptance.

Thus, the Passa Crassana pears which underwent post-storage ripening, had a better quality aroma as a result of the ER from cold room atmosphere by using the catalytic converter.

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